

A SIMPLE FORMULA FOR CALCULATING RESONANCE ENERGY OF BENZENOID HYDROCARBONS

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The topological resonance energy (*TRE*) of a catacondensed benzenoid hydrocarbon with *h* six-membered rings and *K* Kekulé structures can be calculated by the (approximate) formula $TRE = Ah + B + CK e^{-Dh}$, where $A = 0.136$, $B = -0.223$, $C = 0.281$, and $D = 0.454$. Thus, within classes of benzenoid isomers, *TRE* is an increasing linear function of *K*. The greater is *h*, the smaller the effect of the number of Kekulé structures on *TRE*.

Key words: benzenoid hydrocarbons; resonance energy; topological resonance energy; Kekulé structures

ЕДНОСТАВНА ФОРМУЛА ЗА ПРЕСМЕТУВАЊЕ НА ЕНЕРГИЈАТА НА РЕЗОНАНЦИЈА НА БЕНЗЕНОИДНИТЕ ЈАГЛЕВОДОРОДИ

Тополошката енергија на резонанција (*TRE*) на катакондензиран бензеноиден јагледород со *h* шесточлени прстени и *K* структури на Кекулé може да се пресмета со помош на (апроксимативната) формула $TRE = Ah + B + CK e^{-Dh}$, каде што: $A = 0,136$, $B = -0,223$, $C = 0,281$ и $D = 0,454$. Тоа значи дека во класата на бензеноидните изомери *TRE* е растечка линеарна функција од *K*. Колку е поголем *h* толку помало е влијанието на бројот на Кекулéовите структури врз *TRE*.

Клучни зборови: бензеноидни јагледороди; енергија на резонанција; тополошка енергија на резонанција; Кекулéови структури

INTRODUCTION

Resonance energy is a standard concept in the theoretical chemistry of conjugated molecules [1–4]. After the publication of the seminal work by Dewar and de Llano [5], a large number of different *TRE* resonance energies were put forward in the chemical literature, and their properties examined in detail [6–19]. Most of this work was done in the 1970s [6–19], and (with a few noteworthy exceptions [20–24]) research along these lines significantly attenuated in the 1980s and the later years. Recently the interest towards resonance energy has again increased, as seen from the review articles [25–28] and some most *TRE* cent papers [29–32].

In this paper we report results obtained within our studies [30–32] of the structure–dependence of resonance energy. Of the several (mutually related) variants of resonance energy, we examined here the so-called “topological resonance energy”, *TRE*. This resonance energy was put forward independently by Gutman, Milun and Trinajstić [14, 17] and Aihara [16, 18]. Its numerous chemical applications are described elsewhere [4, 16–18, 33–36]. We have decided to investigate *TRE* (and not some other resonance energy) because, in contrast to the similar resonance energies proposed by Dewar and de Llano [5, 7], Balaban [6], Hess and Schaad [8, 9], Milun et al. [10], Herndon et al. [11, 12], Wilcox [13], Randić [15, 19], and Jiang et al. [20], *TRE* is defined without introducing any new ad-

justable parameters. Note that because the TRE -value of acyclic conjugated systems is exactly zero, the TRE measures the energy-effect of the π -electron conjugation along all cycles present in the considered molecule.

TRE is defined as the difference between total π -electron energy (E) and a suitably constructed reference energy (E^{ref}):

$$TRE = E - E^{ref}. \quad (1)$$

In Eq. (1) E is the total π -electron energy, computed by means of the HMO approximation, and expressed in the units of the carbon-carbon resonance energy β ; for details on E see the recent TRE view [37] and the references quoted therein. If g_i is the occupation number of the i -th π -electron molecular orbital, then

$$E = \sum_{i=1}^n g_i x_i \quad (2)$$

where x_i , $i = 1, 2, \dots, n$, are the eigenvalues of the molecular graph representing the π -electron system under consideration [3, 4], labelled so that

$$x_1 \geq x_2 \geq \dots \geq x_n.$$

The quantity E^{ref} is defined in full analogy with Eq. (2), as:

$$E^{ref} = \sum_{i=1}^n g_i y_i$$

where y_i , $i = 1, 2, \dots, n$, are the zeros of the matching polynomial of the molecular graph, and

$$y_1 \geq y_2 \geq \dots \geq y_n.$$

Details on the matching polynomial can be found in the books [4, 38] and elsewhere [16, 17].

From the very beginning [16, 17] it was recognized that in the case of polycyclic conjugated hydrocarbons, molecular size (or more precisely: the number of carbon atoms and carbon-carbon bonds) is the main factor influencing the numerical value of TRE . Therefore, in order to eliminate the (large) size-dependent effects, and make the (smaller) effects of other structural details visible, it is necessary to restrict the examination of TRE to isomers, possibly to sets consisting of large number of isomers. In the 1970s and 1980s, when such studies were actual, the power of available computing machines did not permit the calculation of

TRE -values for a large number of large conjugated molecules. Later, when sufficiently powerful computers became available, the interest of scholars was shifted to other topics. Thus, it happened that until quite recently [32] it was not noticed that within sets of isomeric benzenoid hydrocarbons, the main factor determining TRE is the number K of Kekulé structures, and that the form of the relation between TRE and K is the simplest possible – linear:

$$TRE \approx aK + b. \quad (3)$$

An example illustrating Eq. (3) is given in Fig. 1.

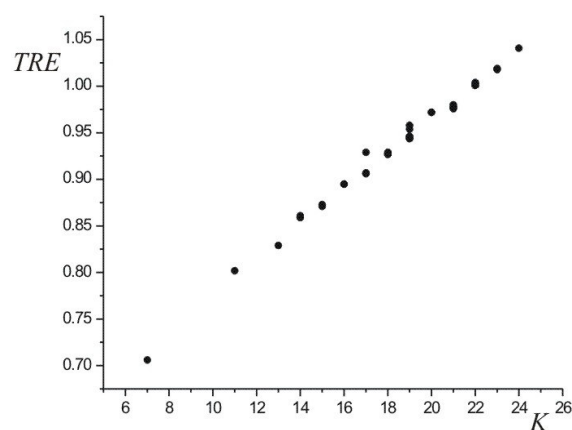


Fig. 1. Topological resonance energy (TRE) of a set consisting of 36 (= all possible) isomeric hexacyclic catacondensed benzenoid hydrocarbons $C_{26}H_{16}$ vs. the respective Kekulé structure count (K)

In this paper we report the results of a more detailed examination of Eq. (3), which revealed that the coefficients a and b depend on the number h of hexagons, so that b is a linear function of h , whereas a is an exponentially decreasing function of h . Our main finding is that the TRE -value of a h -cyclic catacondensed benzenoid hydrocarbon with K Kekulé structures is well reproduced by the formula

$$TRE \approx A h + B + C K e^{-Dh} \quad (4)$$

where $A = 0.136 \pm 0.001$, $B = -0.223 \pm 0.006$, $C = 0.281 \pm 0.005$, and $D = 0.454 \pm 0.003$.

NUMERICAL WORK

Our investigations of Eq. (3) were performed on sets of isomeric catacondensed benzenoid hydrocarbons containing h six-membered rings, for

$h = 3, 4, 5, 6, 7, 8$. For a given value of h , each catacondensed benzenoid species has $4h + 2$ carbon-atoms, $5h + 1$ carbon-carbon bonds, and its formula is $C_{4h+2}H_{2h+4}$.

The sets with $h \leq 7$ consisted of all possible isomers, whereas the set for $h = 8$ contained only 25% of the possible number of isomers; for details see Table 1. The benzenoid isomers were taken from the book [39]; in the case $h = 8$, of the 441 possible isomers, each fourth (in the order given in [39]) has been selected.

Table 1 shows the values of the coefficients a and b in Eq. (3), for the six sets of isomers considered.

Table 1

The coefficients a and b in Eq. (3), obtained by least-squares fitting, for sets of catacondensed benzenoid hydrocarbons with h six-membered rings

h	#	a	b	R	SD
3	2	0.0710	0.191	1.000	0.0000
4	5	0.0460	0.322	0.994	0.0028
5	12	0.0293	0.456	0.998	0.0041
6	36	0.0187	0.592	0.996	0.0064
7	118	0.0117	0.732	0.993	0.0081
8	103	0.0074	0.873	0.994	0.0082

= number of isomers in the respective set; R = correlation coefficient; SD = standard deviation

The dependence of the logarithm of the coefficient a on h is almost perfectly linear (see Fig. 2). Also linear is the dependence of the coefficient b on h (see Fig. 3).

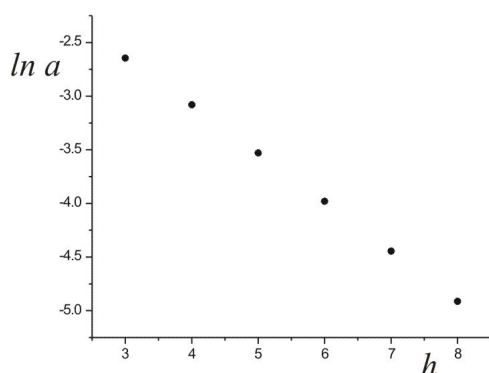


Fig. 2. Dependence of the coefficient a in Eq. (3) on the number of six-membered rings h ; for details see Table 1 and Eq. (5)

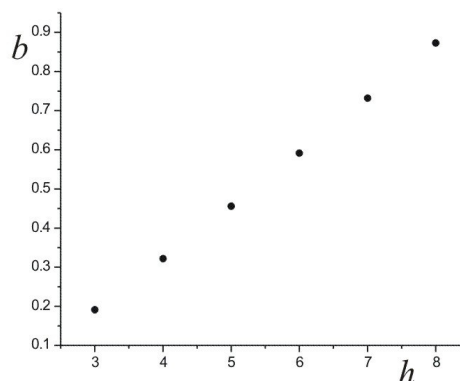


Fig. 3. Dependence of the coefficient b in Eq. (3) on the number of six-membered rings h ; for details see Table 1 and Eq. (6)

The respective regression lines are:

$$\ln a = (-0.453 \pm 0.003) h - (1.270 \pm 0.017) \quad (5)$$

$$b = (0.136 \pm 0.001) h - (0.223 \pm 0.006) \quad (6)$$

with correlation coefficients 0.99992 and 0.99989, respectively. Substituting the right-hand sides of Eqs. (5) and (6) back into (3), we arrive at formula (4).

DISCUSSION

By means of formula (4), the TRE -values of catacondensed benzenoid hydrocarbons can be computed with an error of less than 1%. (The average relative error for $h = 4, 5, 6, 7, 8$ is 0.41%, 0.41%, 0.57%, 0.59%, and 0.59%, respectively.) Such an accuracy is sufficient for all usual applications of the topological resonance energy.

Formula (3) shows that the number K of Kekulé structures is the main parameter determining the differences between the TRE -values of benzenoid isomers. Moreover, TRE is an increasing linear function of K . On the other hand, the effect of Kekulé structures exponentially decreases with the increasing size of the benzenoid systems.

Long time ago Hall [40, 41] studied the K -dependence of total π -electron energy of benzenoid molecules and obtained an approximate formula of the form fully analogous to Eq. (4):

$$E = A^* h + B^* + C^* K e^{-D^* h} \quad (7)$$

with $A^* = 5.708$, $B^* = 1.672$, $C^* = 0.538$, and $D^* = 0.459$.

Note that the numerical values of the constants D and D^* , occurring in the exponents of Eqs. (3) and (7) are practically equal. This detail leads to the conclusion that, within classes of isomeric benzenoid molecules, there must exist a good linear correlation between TRE and E . That this indeed is the case is illustrated in Fig. 4.

The linear correlation between TRE and E implies that (at least in the case of benzenoid systems) TRE and E depend on molecular structure in an analogous manner and that both can be used for reaching the same chemical inferences (about the degree of aromaticity and similar). Because the total π -electron energy can be calculated much easier than the topological resonance energy, from a practical point of view preference should be given to the former.

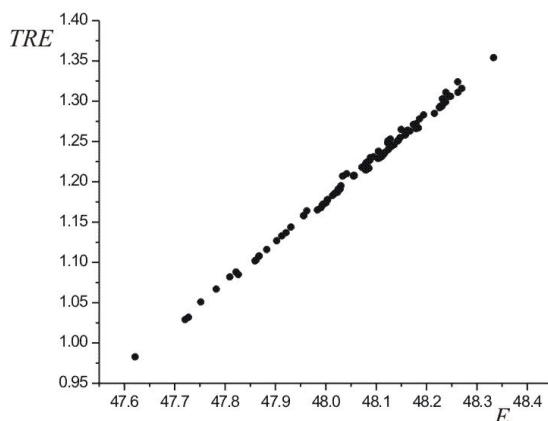


Fig. 4. Correlation between topological resonance energy (TRE) and total π -electron energy (E) in the case of catacondensed benzenoid hydrocarbons with $h = 8$ six membered rings; correlation coefficient = 0.998

To the authors' best knowledge, correlations of the kind shown in Fig. 4 are reported here for the first time. $ITRE$ remains a remarkable and difficult-to-understand fact that such correlations seem to have not been noticed already in the early days of the theory of topological resonance energy, e. g. in the papers [16–18].

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