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Some Observations on the Topological Resonance Energy of Benzenoid Hydrocarbons*

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Two empirical rules are formulated for the topological resonance energy (TRE) of benzenoid hydrocarbons: (*a*) TRE is roughly linear function of the number of Kekulé structures, and (*b*) in a homologous series containing a linear polyacene fragment, TRE is a linear function of the length of this fragment.

In certain cases, however, the TRE model leads to incorrect predictions. There exist pairs of isomeric benzenoid hydrocarbons, in which the isomer with a greater number of Kekulé structures has smaller TRE.

The present study indicates that the TRE model needs to be critically revised.

INTRODUCTION

A new theoretical approach to the problem of aromaticity was proposed a few years ago[1,2]. This approach was essentially an algebraic reformulation of the Dewar resonance energy concept. The new resonance energy was named[2] »topological« (TRE), since it has been discovered using graph-theoretical considerations. The basic assumption of the TRE model is that the larger the topological resonance energy, the larger the aromaticity of the conjugated system considered. Compounds having positive TRE values are classified as aromatic whereas compounds with negative TRE's are said to be antiaromatic.

In a series of papers Aihara[3,4] and Trinajstić with coworkers[5] examined the topological resonance energy of various classes of conjugated molecules. Their conclusion was that TRE reproduces the aromaticity of every class of compounds considered. Although the fact that the TRE model gives acceptable results in very many cases cannot be denied, a deeper analysis showed that neither were the chemical predictions based on the TRE model always correct[6] nor were the ideas behind the TRE concept free of difficulties[7].

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* Part XV of the series »Topological Properties of Benzenoid Systems«

In order to clarify the controversy between the apparent success[3,4,5] of the model in many cases and the failures of the same model in other cases[6,7] we made a critical reexamination of the topological resonance energies of benzenoid hydrocarbons[8]. These conjugated systems have been chosen because they are well defined substances and their physico-chemical behaviour is known in details. In addition, the topological properties of benzenoid systems are nowadays relatively well understood.

It is, however, not easy to find precise criteria for the validity of the TRE model because of the confusing situation that TRE, being a *quantitative* measure of aromaticity, has (to the authors' knowledge) not yet been related to any experimentally measured quantitative physical property of the respective conjugated compound. The actual connection between TRE and the (experimental) thermodynamic stability of conjugated compounds remains still to be clarified and verified in the future.

In the present study we tried to overcome this ambiguity by examining whether the TRE model correctly reproduces the following two general properties of benzenoid hydrocarbons, which are well known and beyond dispute in organic chemistry.

1^0 Benzenoid hydrocarbons for which no Kekulé valence structures can be drawn have an open-shell electron configuration[11] and thus behave like unstable, highly reactive polyradical species[12]. Such systems always have greater total π-electron energies than their isomers for which Kekulé structures do exist. Thus (at least within the framework of the HMO model) these polyradicals are always predicted to be thermodynamically less stable.

Conjugated systems having a high chemical reactivity and a low thermodynamical stability are usually regarded as possesing a low degree of aromaticity. Therefore benzenoid hydrocarbons for which Kekulé structures cannot be drawn should have considerably smaller TRE values than their closed--shell isomers.

2^0 Aromaticity of benzenoid hydrocarbons is proportional to the number of Kekulé structures[13,14]. Therefore, in a series of isomeric benzenoid hydrocarbons, TRE should increase with the increasing number of Kekulé structures.

Let K denote the number of Kekulé structures of the conjugated molecule under consideration. Then the Dewar resonance energy of benzenoid hydrocarbons was shown[14] to be satisfactorily reproduced by the simple formula $A \log K$, where A is a constant.

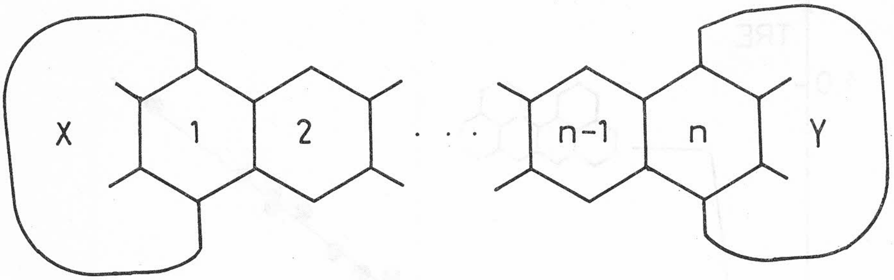
SOME OBSERVED REGULARITIES

Analysing the topological resonance energies of nearly 130 benzenoid hydrocarbons[8], we came to the following two rules, which have (to the authors' knowledge) not yet been reported in the literature.

Rule 1. — In a series of isomeric benzenoid hydrocarbons, TRE is approximately a linear function of the number of Kekulé structures.

This rule applies only to isomers for which the number of Kekulé structures is non-zero.

Let L_n denote a benzenoid system containing a linear polyacene fragment of length n, where X and Y symbolize arbitrary terminal groups.



L_n

Rule 2. — The topological resonance energy of L_n is in a good approximation, a linear function of n. Furthermore, $\mathrm{TRE}(L_{n+1}) - \mathrm{TRE}(L_n)$ is independent of the terminal groups X and Y.

As an illustration of Rule 1 we present a plot of the TRE values of various cata-condensed benzenoid systems with 5 and 7 six-membered rings versus the number of Kekulé structures (Figure 1). The points in Figure 1 lie near to a continuous line which is almost straight (correlation coefficients 0.998 and 0.995 for the 5- and 7-cyclic isomers, respectively). The larger the size of the isomers considered, the smaller the slope of the corresponding line. Another illustration of Rule 1 can be found on Figure 2.

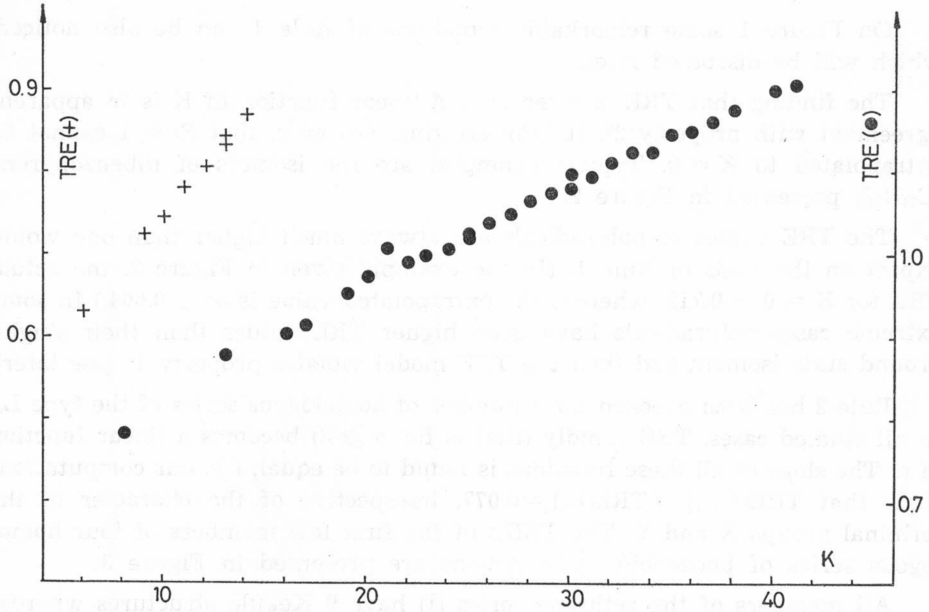


Figure 1. Topological resonance energies of 5-cyclic (+) and 7-cyclic (·) cata-condensed benzenoid systems as a function of the number of Kekulé structures (K). Note that all h-cyclic cata-condensed benzenoid hydrocarbons have the formula $C_{4h+2}H_{2h+4}$.

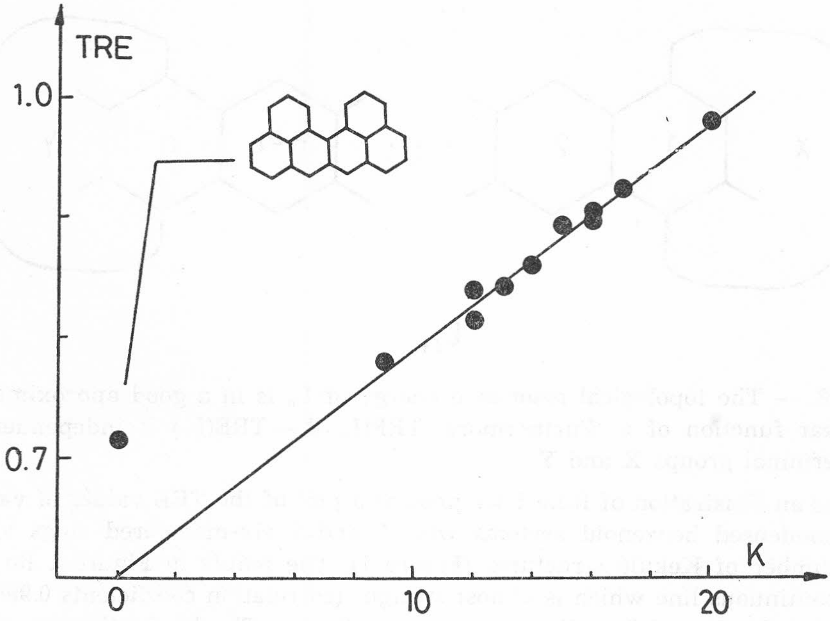


Figure 2. Topological resonance energies of 6-cyclic peri-condensed benzenoid hydrocarbons $C_{24}H_{14}$ as a function of the number of Kekulé structures (K). The straight line TRE = 0.0187 K + + 0.604 is obtained by least squares fitting of all data except the point for K = 0. Its correlation coefficient is 0.991.

On Figure 1 some remarkable violations of Rule 1 can be also noticed, which will be discussed later.

The finding that TRE is essentially a linear function of K is in apparent agreement with property 2^0. It is interesting, however, that Rule 1 cannot be extrapolated to $K = 0$. Typical examples are the isomers of dibenzopyrene ($C_{24}H_{14}$), presented in Figure 2.

The TRE values of polyradicals are always much higher than one would expect on the basis of Rule 1. (In the example given in Figure 2, the actual TRE for $K = 0$ is 0.715, whereas the extrapolated value is only 0.604.) In some extreme cases polyradicals have even higher TRE values than their singlet ground state isomers and then the TRE model violates property 1^0 (see later).

Rule 2 has been checked for a number of homologous series of the type L_n. In all studied cases, TRE rapidly (that is for $n \geqslant 3$) becomes a linear function of n. The slope of all these functions is found to be equal, i. e. our computations show that $\mathrm{TRE}(L_{n+1}) - \mathrm{TRE}(L_n) = 0.077$, irrespective of the character of the terminal groups X and Y. The TRE's of the first few members of four homologous series of benzenoid hydrocarbons are presented in Figure 3.

All members of the zethrene series (I) have 9 Kekulé structures whereas the number of Kekulé structures of the linear polyacene (II) with h six-membered rings is equal to $h + 1$. Then because of Rule 2, an h-cyclic homologue of zethrene will always have greater TRE than an h-cyclic linear polyacene. On the other hand, for $h > 8$ the number of Kekulé structures of the linear polyacene is greater than the number of Kekulé structures of the corresponding zethrene. Consequently, whenever the number of rings is

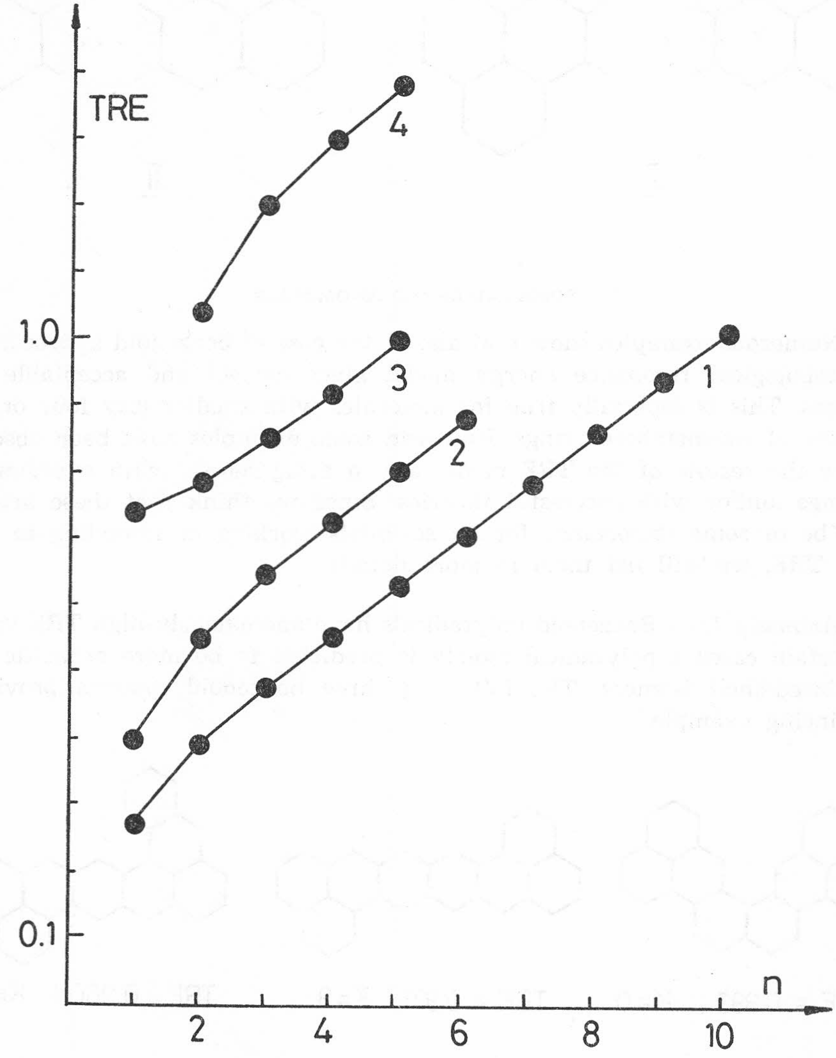
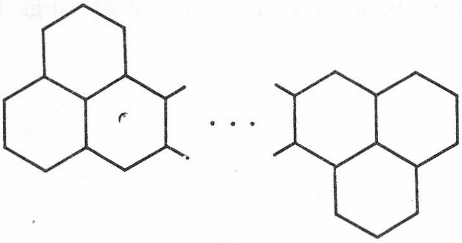


Figure 3. Topological resonance energies of benzenoid systems of the type L_n: linear polyacenes (1), 1.2-benzo-derivatives of linear polyacenes (2), the zethrene series (3) and tetrabenzo-derivatives of linear polyacenes (4).

greater than 8, the topological resonance energies of zenthrenes and of linear polyacenes violate property 2^0.

It is not difficult to see that arbitrarily many examples of this type can be constructed in the same manner.



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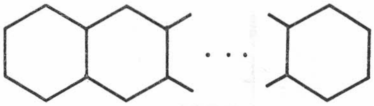
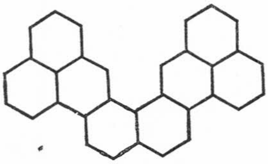


II

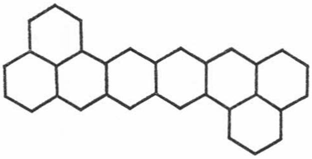
SOME OBSERVED ANOMALIES

Numerous examples show that also in the case of benzenoid hydrocarbons, the topological resonance energy model gives correct and acceptable predictions. This is especially true for molecules with smaller (say four or less) number of six-membered rings. However, some examples have been observed where the results of the TRE model are in disagreement with experimental findings and/or with successful theories. Since we think that these artifacts may be of some importance for all scientists working or intending to work with TRE, we will list them in more details.

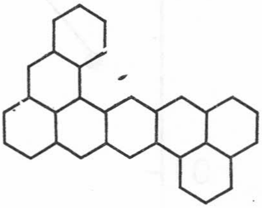
Anomaly 1. — Benzenoid polyradicals have anomalously high TRE values. In certain cases a polyradical moiety is predicted to be more aromatic than its closed-shell isomers. The following three benzenoid systems provide a convincing example.



TRE = 0.993 ; K=0



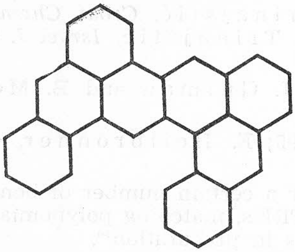
TRE = 0.921 ; K=9



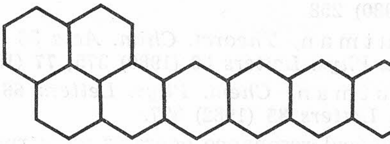
TRE = 0.960 ; K=12

It seems that this anomaly does not occur in benzenoid systems with less than 7 rings, but is not too rare in the case of larger molecules.

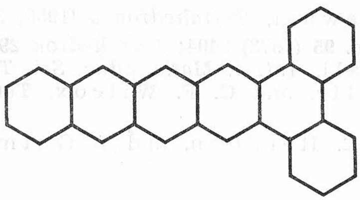
Anomaly 2. — Quite often among two benzenoid isomers, we find that the system with the greater number of Kekulé structures has a significantly smaller TRE. Two such examples will suffice.



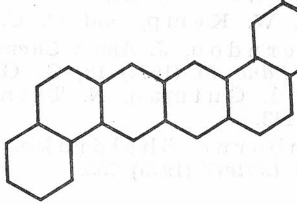
TRE = 1.011 ; K = 16



TRE = 0.971 ; K = 18



TRE = 1.006 ; K = 21



TRE = 0.998 ; K = 23

The above examples indicate that in the case of benzenoid hydrocarbons, the TRE model is much less successful than it was initially expected[1,2,3]. Whereas the model gives reliable results for smaller systems, the number of wrong predictions and artifacts increases considerably with increasing size of the molecules. Therefore, the TRE model should not be applied to benzenoid systems with 6 or more rings. Although the present study was restricted to benzenoid hydrocarbons only, we feel that similar or even greater difficulties could be observed in all other classes of conjugated molecules.

The conclusion of the present work is therefore that when dealing with large conjugated molecules, the chemical predictions based on the TRE model become quite uncertain (though correct in the majority of cases). The potential users of TRE should be rather cautious. The previous assertion about the great significance of TRE in theoretical organic chemistry needs revision.

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SAŽETAK

Neka zapažanja o topološkoj rezonancijskoj energiji benzenoidnih ugljikovodika

I. Gutman i B. Mohar

Formulirana su dva empirijska pravila za topološku rezonancijsku energiju (TRE) benzenoidnih ugljikovodika: (*a*) TRE je približno linearna funkcija broja Kekuléovih struktura, i (*b*) u homolognim nizovima TRE raste kao linearna funkcija duljine linearnog poliacenskog fragmenta.

U pojedinim slučajevima, međutim, model topološke rezonancijske energije dovodi do pogrešnih predviđanja. Postoje, naime, parovi izomernih benzenoidnih ugljikovodika kod kojih izomer s većim brojem Kekuléovih struktura ima manju vrijednost TRE. Ovakvih anomalija ima tim više što su promatrani konjugirani sustavi veći.

Rezultati ovog rada ukazuju da je potrebno kritički revidirati shvaćanje o primjenljivosti TRE modela u organskoj kemiji.