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Original Investigations

Failures of the Topological Resonance Energy Method*

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The topological resonance energy (TRE) is nowadays considered as one of the most reliable indices of stability and aromaticity of conjugated molecules. Seven groups of examples are constructed showing that the TRE concept leads sometimes to obviously false chemical conclusions.

Key words: Graph theory – Topological resonance energy.

A number of recent papers [1–8] deal with the application of topological resonance energy (TRE) for describing stability, aromaticity and related chemical properties of conjugated molecules. All authors [1–8] agree about the usefulness and predictive power of this new method. Therefore it seems to be important for the wide chemical community to point out some intrinsic ambiguities and failures of the TRE concept.

Topological resonance energy is a graph theoretical ("topological") reformulation of the formerly developed Dewar resonance energy (DRE) concept [9]. In contrast to DRE, TRE can be determined not only for classical conjugated molecules, but also for ions, radicals and excited states. This is usually assumed as an advantage of TRE over DRE. However, we shall demonstrate that in the case of non-classical conjugated systems, TRE leads to some rather obscure predictions. The failure of the TRE method when applied to conjugated radicals was first observed by Aihara [2].

The definition of topological resonance energy is [1, 4, 6]

$$\mathrm{TRE} = \sum_{j=1}^{n} g_j (x_j - x_j^R) \tag{1}$$

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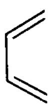
where x_j and x_j^R are the zeros of the characteristic and reference polynomial, respectively, of the molecular graph and g_j is the pertinent occupation number. All the applications of TRE are based on the expectation that

(a) TRE is proportional to the chemical stability of the conjugated molecule; among two isomers, the stabler one has greater TRE;

(b) conjugated systems with large positive, large negative or near-zero TRE can be classified as being aromatic, antiaromatic or non-aromatic, respectively.

These assumptions have been tested on numerous conjugated compounds and were found to agree with experimental findings in many cases [1–8]. Thus one was inclined to consider TRE as a universal measure of aromaticity of conjugated π-electron systems. We consider now several situations which show that neither the statement (a) nor (b) is generally valid and, furthermore, that the definition (1) is also not free of ambiguities. We shall restrict our attention to simple but convincing special cases, noting however that arbitrarily many examples of the same kind can be constructed if desired.

1° All acyclic conjugated hydrocarbons (in both ground and excited states, in neutral and ionic form) have zero TRE. Thus the stable non-aromatic conjugated polyene I and the hypothetic isoelectronic species II or III are predicted on the basis of the TRE criterion to have comparable stability and equal(!) aromaticity.



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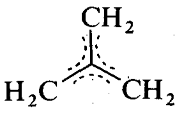

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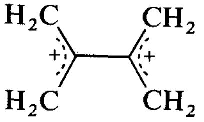

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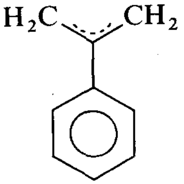
2° The TRE values of the systems IV and V (TRE = 0.260 in both cases) are similar to that of benzene (0.273). Hence, one must conclude that IV and V exhibit similar aromatic character as benzene. The mere fact that IV and V have equal TRE's is also a shortcoming of the method.



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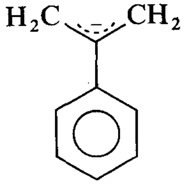

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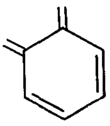

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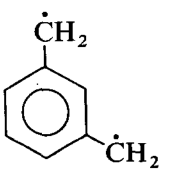

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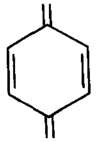

VIII

3° Among the three isomeric quinodimethanes (VI–VIII, TRE = 0.056, 0.096 and 0.061, respectively), the meta-isomer has the greatest TRE value, although it is a highly reactive biradical species.

4° In certain multiplet ground state systems the definition (1) is not unique. For example, the two highest bonding MO's of benzene are degenerate. Then in the benzene monocation one may set $g_1 = g_2 = 2$, $g_3 = 1$ (resulting in TRE = −0.210) or $g_1 = g_3 = 2$, $g_2 = 1$ (resulting in TRE = +0.687). A similar difficulty arises also in the case of benzene dication, monoanion, dianion etc.

5° The usually accepted TRE value (−1.226) of cyclobutadiene [6, 10] is obtained under the assumption that $g_1 = g_2 = 2$. However, according to Hund's rule one should take $g_1 = 2$, $g_2 = g_3 = 1$, which substituted back into Eq. (1) yields TRE = +0.304. Thus from a strict application of Eq. (1) we obtain the absurd conclusion that cyclobutadiene is more aromatic than benzene!

It is to be noted that Eq. (1) can be easily modified so that the contradictions 4° and 5° do not occur. Then, however, one has to abandon one of the crucial assumptions of the TRE method, namely that the occupation numbers for both the conjugated molecule and its reference structure are the same. This problem was recently analysed using a mapping argument [11], which however could not remove the ambiguities of Eq. (1).

In order to be able to compare the aromaticity of conjugated systems with inequal number of π-electrons, the TRE per electron (TREPE) index was proposed. The usefulness of TREPE in many cases is well documented [1, 2, 4, 5]. We point out here some cases where the TREPE criterion offers less satisfactory predictions. Aihara first noticed these difficulties with TREPE and proposed another index – TRE per conjugated bond [3].

6° Alternant hydrocarbon anions and cations have equal TRE. But then the TREPE of an anion is necessarily smaller than the TREPE of the corresponding cation. Therefore, the alternant cations are in all cases predicted to be more aromatic than the pertinent anions.

7° The fact that TREPE overestimates the aromaticity of cations is illustrated by the following example. The cyclopentadienyl anion $C_5H_5^-$, a commonly recognized aromatic system has TREPE = +0.05, while the hypothetic cations $C_5H_5^{3+}$ and $C_5H_5^{4+}$ have both a two times larger TREPE value (+0.10).

We hope that the above listed seven groups of examples are sufficient to demonstrate that the claim that TRE provides a reliable measure of aromaticity is not generally true. Certain evidently false predictions follow from imprudent use of topological resonance energy. Critical re-examination of the TRE concept and the scope of its applicability is therefore necessary, as well as caution when TRE is used for interpreting experimental findings.

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