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On the Topological Resonance Energy of Porphins and Related Structures^{1*}

P. Ilić** and N. Trinajstić

The »Rugjer Bošković« Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

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Porphinoid, both existing and hypothetical systems, are represented by graphs at the nearest-neighbour level of approximation. By dimer covering of these graphs characteristic and reference polynomials are obtained and the topological resonance energy is calculated. It has been found that aromatic stabilization of porphins is mainly due to the high topological resonance energy value of pyrrole-type rings, while aromatic stabilization of phthalocyanins is due mainly to high resonance stabilization of i-indole-type rings.

The many facets of the chemistry and the physics of porphins have given them a significance beyond their biological rôle². The physics of porphins, established upon massive experimental work³⁻¹³ has been used in many instances to back up the model of the porphin chemistry. The chemistry, either experimental¹⁴⁻²³ or theoretical²⁴⁻³⁵ has been commonly considered in terms of the aromatic character of the porphin nucleus^{2,36-39}. Not quite sharing the euphoric view⁴⁰ that aromaticity is an essential prerequisite for biologically active chemical compounds, we used the newly developed⁴¹⁻⁴³ topological resonance energy concept as a theoretical probe into the aromaticity of porphin and related structures. By straightforward use of this method we bypassed the early-stage dilemma of a choice of a method to be used. We have had, however, to face the consequences of such a choice, (vide infra). The topological resonance energy, *TRE*, concept, was developed as the algebraic formalism expressing the ideas of Breslow⁴⁴, Dewar⁴⁵, and Hess and Schaad⁴⁶. The essential part of the idea is quantification of the resonance energy of a conjugated cyclic structure with respect to a linear, reference structure. Our approach to this quantification is based on graph representation and the ensuing algebra is graph-theory algebra.

OUTLINE OF THE THEORY

Molecules may be represented by graphs; that is, by the set of vertices, $v_i \in V$, connected by lines defined as the set of unordered pairs of vertices, $v_i, v_j \in O$ ⁴⁷. The set Q is also known as the set of edges. Graphs are mathematical

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** Permanent address: Faculty of Sciences and Mathematics, University in Sarajevo, P.O.B. 207, 71001 Sarajevo, Bosnia and Herzegovina, Yugoslavia.

objects and any meaning they could be given beyond that has been done through an association of graph elements with physical quantities. At the present stage graphs have been used within the formalism based on the idea of tight-binding interactions⁴⁸, that is, priority has been conferred upon the topology rather than the geometry of a system under consideration. Since connectivity of nearest-neighbours plays a crucial rôle in this physical representation, the adjacency, defined for homonuclear conjugated systems in Galois Field 2, is used for constructing the characteristic polynomial of a graph. This step is accomplished by a combinatorial procedure. By covering a graph by a dimer⁴⁹ one gets the characteristic polynomial in the form^{43,52},

$$P(G; x) = \sum_{i,j(i)}^{i \max} \sum_{d=0}^m (-2)^{2d+n_{i,j(i)}} D(G-R_{i,j(i)}; d) x^{N-2d-n_{i,j(i)}} \quad (1)$$

The meaning of the symbols is as follows:

- d the number of dimers; a dimer is defined as two vertices connected by an edge: $\circ \text{---} \circ$
- D the number of arrangements of d dimers on a graph G ,
- N the number of vertices of a graph G ,
- R rings that are to be excised from a graph G ,
- m the maximal d number in a subgraph $G-R$,
- n the number of vertices in a subgraph $G-R$,
- $i, j(i)$ index for counting of disjoint elements; $i = 1, 2, \dots, r$
- r the number of principal rings in a G .

Linearly related structures in the formula (1) have interesting combinatorial properties; since they are obtained by covering a graph G with monovalent, dimer subgraphs, we have called them »acyclic«. Thus, the acyclic polynomial of a complete graph, G , reads,

$$P^{ac}(G; x) = \sum_d (-1)^d D(G; d) x^{N-2d} \quad (2)$$

This polynomial was given a meaning of a reference polynomial^{42,50}. Associating to the zeros of both polynomials, i. e. characteristic and acyclic, respectively, the common quantity β ($\sim 2.3 \times 10^5$ J/mol)⁴² one can speak of the energy of a conjugated molecule and its reference structure. A simple linear relation,

$$\begin{aligned} \Delta &= a_1 x_1 + a_2 x_2 + \dots + a_k x_k - b_1 y_1 - b_2 y_2 - \dots - b_m y_m = \\ &= (a_1 x_1 - b_1 y_1) + (a_2 x_2 - b_2 y_2) + \dots + (a_k x_k - b_m y_m) \end{aligned} \quad (3)$$

where,

x_k, y_m are the zeros of the characteristic and the acyclic polynomial, respectively, and

a_k, b_m are the corresponding »orbital« occupancy numbers,

quantifies the pi-electron energy difference between the conjugated cyclic system and its reference structure. This difference was named the topological resonance energy, *TRE*, and has been shown^{41-43, 50-52} to correlate with the general properties of conjugated hydrocarbons⁵³.

RESULTS AND DISCUSSION

Heterocycles in the porphin structure are represented graphically by introducing,

- i) weighted edges,
- ii) weighted self-loops⁵⁴⁻⁵⁶.

The first property, (i), means generalization of adjacency relations to the field of real numbers, R . The second property, (ii), is a more formal way of defining a weighted vertex*. We redefine the dimer covering formula as,

$$D_d = \prod_{i,j} W(i, j) \quad (4)$$

$W(i, j)$ being the weight of the edge connecting vertices i and j ,

$W(i, i)$ being the weight of the self-loop on a vertex i , obtained by a degraded dimer covering.

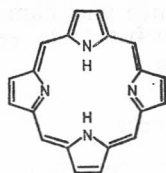
In order to conform the MO formalism that is isometric to the graph representation we use the heteroparameters for the heteroatoms and the heterobonds, (in this particular case for the nitrogens and the nitrogen-carbon bonds), as the appropriate edge weights. The most convenient set to be used seems to be that of Hess and Schaad⁵⁸. The topological resonance energy values for some of the structures of porphinoid topology are given in the Table I.

When discussing the meaning of *TRE* values an immediate problem arises; the question of whether the *TRE* quantity is size-dependent or not. In other words, a dilemma occurs as to whether *TRE* is an extensive or an intensive property. This question is not easily answered, however, it could be shown^{52,59} that *TRE* is essentially an intrinsic property. There are some extrinsic contributions as well, and one way to avoid them has been to divide the *TRE* by the number of pi-electrons present in a system, thus obtaining the topological resonance energy per electron, *TRE* (PE), index. Since most systems studied here are of similar size and molecular topology we shall use mostly *TRE* quantity as such.

By any reasonable criterion the *TRE* values of the systems in Table I are large enough for all those structures to be considered aromatic. The exception is the hypothetical all-pyrolenine-type species (2) which might better be classified as a nonaromatic species. The negligible contribution of the pyridin-type nitrogen to the *TRE* of the porphin system is well illustrated by the *TRE* values of the diaza- and tetraazaporphin (4 and 5). The fusion of the benzene rings results in a significant gain in the *TRE* value, as could be seen

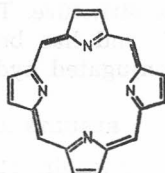
* Structures defined by sets V and Q , with weighted edges, that is, $W(i, j) \in R$; and self-loops, that is, $(v_i, v_i) \in Q$, are not graphs in strict terms⁵⁷.

TABLE I



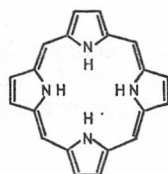
1

$$TRE = 0.39248$$



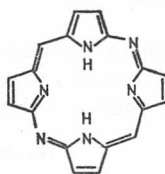
2

$$TRE = 0.02963$$



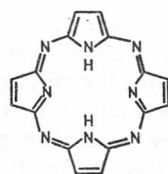
3

$$TRE = 0.47187$$



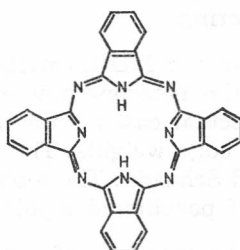
4

$$TRE = 0.29745$$



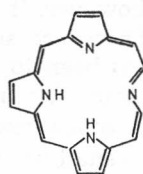
5

$$TRE = 0.37684$$



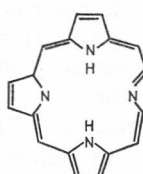
6

$$TRE = 0.70929$$



7

$$TRE = 0.35382$$



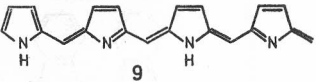
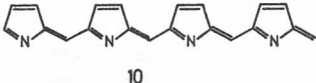
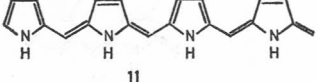
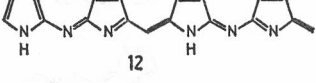
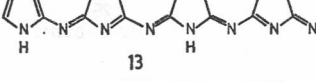
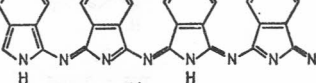
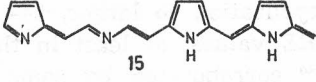
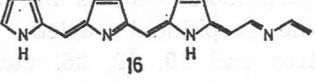
8

$$TRE = 0.26321$$

in the case of the phthalocyanin (6). This significant increment, however, may well be due to a probable extrinsic contribution to the overall TRE value of the phthalocyanin system. Thus, $TRE(PE)$ of the tetraazaporphin (5) is 0.01449, while $TRE(PE)$ of the phthalocyanin is 0.01689, indicating only a moderate increase in resonance stabilization with respect to the former. The appearance of the porphyrin molecular topology as a tied necklace provokes a question as to whether the TRE of porphyrinoid systems originates from the complete graph as

such or some specific parts of it. A straightforward way to check this assumption is to calculate the topological resonance energy values for the corresponding united necklaces. Table II contains the *TRE* values of graphs constructed by opening the previously closed necklaces.

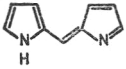
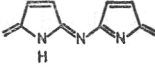
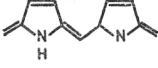
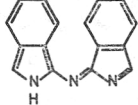
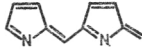
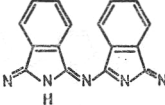
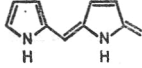
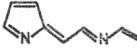
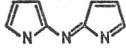
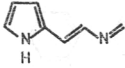
TABLE II

	<i>TRE</i> = 0.4467
9	
	<i>TRE</i> = 0.10559
10	
	<i>TRE</i> = 0.48275
11	
	<i>TRE</i> = 0.28209
12	
	<i>TRE</i> = 0.12026
13	
	<i>TRE</i> = 0.86525
14	
	<i>TRE</i> = 0.29026
15	
	<i>TRE</i> = 0.32607
16	

The results in the Table II are somewhat surprising in that in more than a half of the examples the linear variant seems to be more stabilized than the corresponding cyclic structure. This becomes clear after inspecting the *TRE* values of both the closed and the open necklaces of porphin, all-pyrrole-nine-type system, all-pyrrole-type system, phthalocyanin and chlorin, (1, 2, 3, 6, and 8, respectively). Going to the smaller constituent units, for example those of the pyrromethene-type, we get *TRE* results as given in Table III.

It is not possible to compare directly the *TRE* values from the Table III with those from the Tables I and II because of different sizes of systems but some conclusions can be drawn. The *TRE* values from the Table II suggest that most of the *TRE* contributions are due to the cyclization of the »small«,

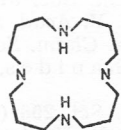
TABLE III

 17 $TRE = 0.28145$	 22 $TRE = 0.09060$
 18 $TRE = 0.08916$	 23 $TRE = 0.49623$
 19 $TRE = 0.06365$	 24 $TRE = 0.36533$
 20 $TRE = 0.25373$	 25 $TRE = -0.00293$
 21 $TRE = 0.19045$	 26 $TRE = 0.16195$

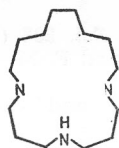
penta- and hexa-rings. Further cyclization to larger, 24- and 40-rings does not contribute significantly to TRE values, at least in the majority of the examples. The opinion exists,^{2,36,60} corroborated by some experimental findings,^{11,61,62} that pi-electrons of porphinoid systems are delocalized over a selected set of centres within the porphinoid nucleus. This set contains usually 16, 17, 18, 24, etc. centres and 18, 22, 26, etc. pi-electrons. We used the TRE approach to calculate the resonance energy of the most favourable, less favourable, and unfavourable, »large« rings that could offer a perimeter for pi-electron »circulation«. The results are given in the Table IV.

In accordance with some earlier theoretical results³⁹ it turns out that these rings do not show an appreciable resonance energy stabilization. In most of the cases they are nonaromatic systems while for some of them, (Table IV., 31, 32, and 34), the delocalization of pi-electrons would destabilize a system. These results are in accord with the suggestion of a dominant participation of small rings. Finally, if we compare the »elementary subunits« of the porphin nucleus, that is, pyrrole ring, (35), pyrroline ring, (36) and maleimide ring, (37), with the porphin itself, (Table I, 1.), it turns out that the average $TRE(PE)$ of the three subunits is 0.01789 while the $TRE(PE)$ of the porphin

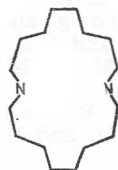
TABLE IV



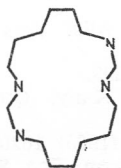
27
TRE = 0.06888



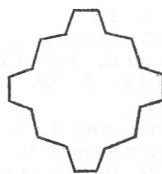
29
TRE = 0.05356



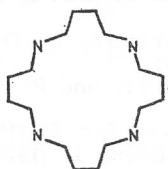
28
TRE = 0.07666



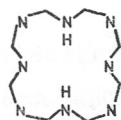
30
TRE = 0.06721



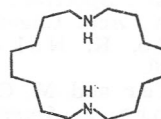
31
TRE = -0.23600



32
TRE = -0.18992

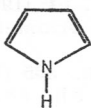


33
TRE = 0.05056

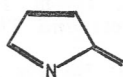


34
TRE = -0.05121

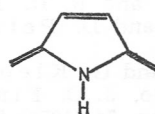
is 0.01510; that is, the resonance stabilization effect is approximately of the same significance to all of them.



35
TRE(PE) = 0.04038



36
TRE(PE) = 0.00794



37
TRE(PE) = 0.00537

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SAŽETAK

O topologijskoj resonancijskoj energiji porfina i srodnih struktura

P. Ilić i N. Trinajstić

Aromatičnost porfina i srodnih molekula studirana je s pomoću topologijske resonancijske energije. Nađeno je da je aromatička stabilizacija porfina uglavnom uzrokovana visokom vrijednošću topologijske resonancijske energije petočlanih prstenova s dušikom, dok je za ftalocijanine pokazano da su stabilizirani visokom resonancijskom energijom i-indolskih struktura.

INSTITUT »RUĐER BOŠKOVIĆ«,
ZAGREB, HRVATSKA

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