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On Some Further Classes of Isomers Which Exhibit Topological Effect on Molecular Orbitals*

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Some further classes of isomers exhibiting the Topological Effect on Molecular Orbitals (TEMO) are considered. They include two classes of hetero-substituted polyenes and three classes of substituted annulenes. The sixth class contains bridged annulenes where TEMO is exhibited only for the related matching spectra.

INTRODUCTION

The regularity of the molecular orbital (MO) energies arising form the different topologies of isomers is called the »Topological Effect on Molecular Orbitals (TEMO)«[1]. The effect has been confirmed by experimental findings[2], as well as by quantum-chemical computational procedures of various levels of sophistication[3,4]

The already existing classes of isomers which exhibit TEMO are extended in the present paper by a few further classes. They include two classes of hetero-substituted polyenes and three classes of substituted annulenes. The sixth class contains bridged annulenes where TEMO is exhibited only for the related matching spectra.

The mathematics of TEMO is relatively simple. Different topologies of the isomers M_A and M_B under consideration are appropriately described by the graphs A and B associated with the isomers[5]. The corresponding characteristic polynomials $\Phi(A; x)$ and $\Phi(B; x)$ are then compared. There are various classes of isomers[1-3] for which the difference function, $\Delta(B, A; x)$, satisfies:

$$\Delta(B, A; x) \equiv \Phi(B; x) - \Phi(A; x) \geq 0 \tag{1}$$

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The above inequality implies[1,6,7]

$$x_1(A) \geq x_1(B) \geq x_2(B) \geq x_2(A) \geq \dots$$

$$x_{2k-1}(A) \geq x_{2k-1}(B) \geq x_{2k}(B) \geq x_{2k}(A) \geq \dots \tag{2}$$

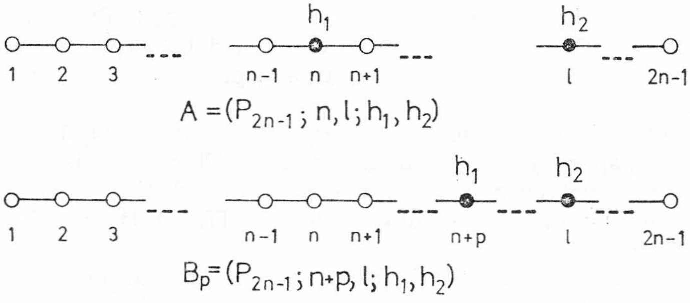
where $x_j(A)$ and $x_j(B)$, $j = 1, 2, \dots, N$, denote the roots of $\Phi(A; x)$ and $\Phi(B; x)$, respectively, i. e. the MO energies of the isomers M_A and M_B as calculated within the simple MO theory. N stands for the number of conjugated centers in the considered isomer and equals the number of vertices in the associated graph.

The interlacing rule (2) is called TEMO[1] and it enables predictions on the first absorption maxima, ionization potentials, etc., of the isomers M_A and M_B. In the case where the sign of $\Delta(B, A; x)$ generally changes along the energy parameter x-asis, TEMO with inversion[1] holds.

HETERO-SUBSTITUTED POLYENES

A linear polyene, $CH_2(CH)_{N-2}CH_2$, may be represented by the path graph, P_N, with N vertices. Let us introduce two heteroatoms into the polyene at the positions i and j. Let h_1 and h_2 stand for the values of the Coulomb integral of the first and the second heteroatom, respectively. The corresponding (weighted) graph is denoted by $(P_N; i, j; h_1, h_2)$.

Class 1. — Let N be an odd number, $N = 2n - 1$. Let consider the hetero-substituted polyene M_A with the first heteroatom at the position n in the middle of the polyene and with the second heteroatom at the position 1, $1 > n$. The related graph $A = (P_{2n-1}; n, 1; h_1, h_2)$ is shown in Figure 1. Here and in the further figures black a circle represents a heteroatom. Let us further consider the isomers of M_A in which the first to heteroatom is moved out of the middle position to the new position $1 + p$ while the second heteroatom remains at its position 1. These isomers are represented by $B_p = (P_{2n-1}; n + p, 1; h_1, h_2)$, $p = 1, 2, \dots, 1 - n - 1$, and a representative is depicted in Figure 1.



The third factor on the right-hand side of eq. (3) is a nonnegative quantity. However, the parity of the second factor changes along x-axis and TEMO with inversions holds. The inversion points are easily calculated after the values of 1, p and h_2 are given and they don't depend on the length, $2n - 1$, of the considered hetero-substituted polyenes.

If the heteroatom h_2 is moved to the left side, $p < 0$, of the middle position, an equation analogous to eq. (3) can be derived by using the following well-known identity:

$$(P_{-k}; x) = -(P_{k-2}; x) \tag{4}$$

The same comment applies to the rest of this paper as well.

Class 2. — Let us now consider the situation where both heteroatoms are moved simultaneously by the same amount, p.

Let N be an even number, $N = 2n$. Let us consider the hetero-substituted isomer M_A whose graph is $A = (P_{2n}; n, 1; h_1, h_2)$. Let us further consider the isomers M_{B_p} of M_A which are represented by the graphs $B_p = (P_{2n}; n + p, 1 + p; h_1, h_2)$. The difference function is rather complicated. In the special case $1 = n + 1$, *i.e.* where two heteroatoms are neighbours in M_A and M_{B_p}, and for both heteroatoms being of the same kind, $h_1 = h_2 = h$, the difference function is simplified to the following form:

$$\Phi(B_p; x) - \Phi(A; x) = h(x - h)[\Phi(P_{p-1}; x)]^2 \tag{5}$$

$$p = 1, 2, \ldots, n - 1$$

The corresponding graphs are depicted in Figure 2.

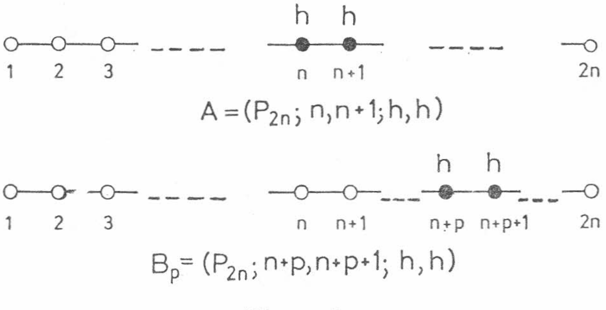


Figure 2.

Eq. (5) implies that TEMO with only one inversion point $x_{\text{inversion}} = h$, holds.

In the case of electron attracting heteroatoms, $h > 0$, the inversion point lies in the region of the bonding MO's. Up to the inversion point the regularity (2) holds where B stands for any of B_p's.

In the case of heteroatoms with $h < 0$, the inversion point lies in the region of the anti-bonding MO's. The regularity (2) holds in the whole region of bonding MO's but the symbols A and B have to interchange their places because $\Delta(A, B_p; x) \leq 0$ for $x \geq 0$.

SUBSTITUTED ANNULENES

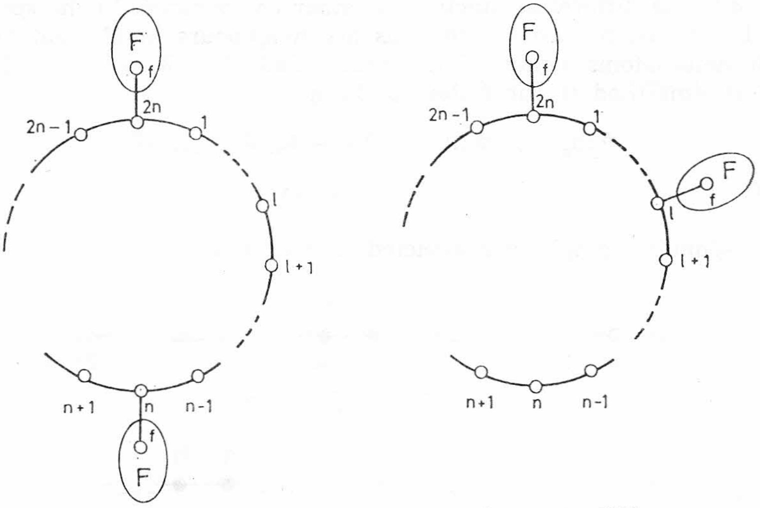
An annulene, C_NH_N, may be represented by the cycle graph, C_N, with N vertices.

Further, we consider three classes of substituted annulenes.

Class 3. — Let us represent the graph attached to the annulene C_NH_N by graph F. The linking site of the attached graph is represented by the vertex f. The graph obtained by deletion of f out from F is denoted by $F - f$.

Let us consider a substituted annulene where two graphs F_1 and F_2 are attached at the positions i and j, respectively. The corresponding graph is denoted by $(C_N; i, j; F_1, F_2)$.

Let N be an even number, $N = 2n$. Let us further take: $F_1 = F_2 = F$. Let us consider the substituted annulene M_B which is represented by graph $B = (C_{2n}; n, 2n; F, F)$ of Figure 3. If the graphs are attached at arbitrary positions, a series of isomers M_{A_l} is obtained which are represented by graphs $A_l = (C_{2n}; l, 2n; F, F)$, $l = 1, 2, \ldots, n-1$. A representative of the series is depicted in Figure 3.



$B = (C_{2n}; n, 2n; F, F)$ $A_l = (C_{2n}; n, 2n; F, F)$

Figure 3.

The difference function is non-negative for the whole series:

$$\Phi(B; x) - \Phi(A_l; x) = 3\,[\Phi(F - f; x)]^2 \cdot [\Phi(P_{n-l}; x)]^2 > 0 \qquad (6)$$

$$l = 1, 2, \ldots, n-1$$

Consequently, TEMO without inversions (2) applies if MO energies of any of isomers M_{A_l} are compared with MO energies of the starting isomer M_B.

Let us note that B and A_l's together represent n isomers. By using the terminology of TEMO[1] $A_1, A_3, \ldots$, represent S-isomers of Model 2[3] as they possess the planes of symmetry $\Sigma_1, \Sigma_2, \ldots$. Similarly, $A_2, A_4, \ldots$, represent S-isomers of Model 3[3] as they possess the planes of symmetry $\sigma_1, \sigma_2, \ldots$, which pass through a pair of vertices. Altogether, there are $(n-1)$ S-isomers, $[n/2]$ of them are of Σ-type and $\left[\frac{n-1}{2}\right]$ of σ-type. B represents T-isomer[1] with regard to any of $(n-1)$ S-isomers. The situation is clarified in Figure 4.

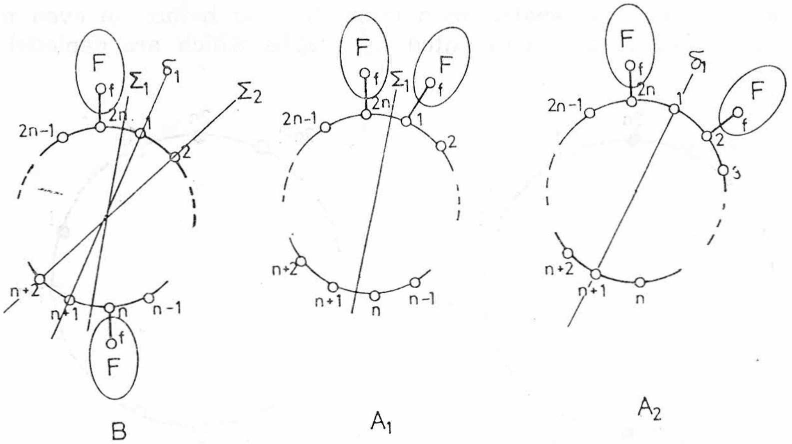


Figure 4.

Class 4. — Let us consider substituted annulenes whose graphs are shown in Figure 5. Let further N be an even number, $N = 2n$.

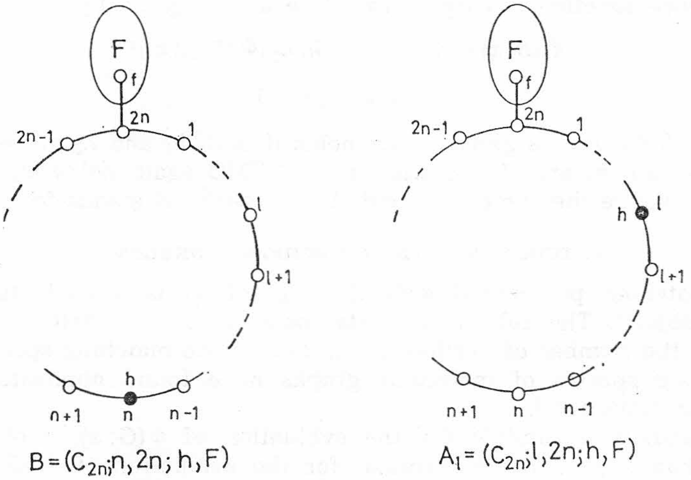


Figure 5.

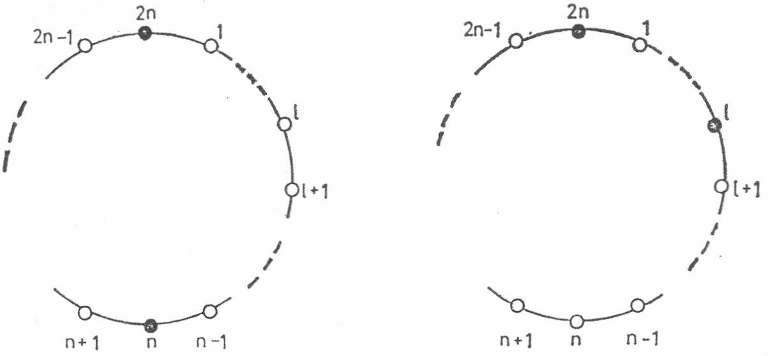
The difference function for the isomer represented by B and for S isomer represented by some of A_l's is given by:

$$\Phi(B;x) - \Phi(A_l;x) = h \cdot \Phi(F-f;x) \cdot [\Phi(P_{n-l};x)]^2 \tag{7}$$

$$l = 1, 2, \ldots, n-1$$

Consequently, TEMO with inversions holds where the inversion points are the roots of $\Phi(F - f; x)$ which is easy to calculate after the attached graph represented by F is specified.

Class 5. — The isomers of this class can be understood as a special case of Class 3 isomers. They contain two, generally different, heteroatoms with the values h_1 and h_2 associated with them. N is as before an even number, $N = 2n$. The isomers are represented by graphs which are depicted in Figure 6.



$B = (C_{2n}; n, 2n; h, h)$ $A_l = (C_{2n}; l, 2n; h, h)$

Figure 6.

The difference function is easy to calculate and is given by

$$\Phi(B; x) - \Phi(A_l; x) = h_1 h_2 [\Phi(P_{n-l}; x)]^2 \tag{8}$$

$$l = 1, 2, \ldots, n - 1$$

As a result, TEMO as is given by (2) holds if both h_1 and h_2 are of the same parity. If h_1 and h_2 are of opposite parity, TEMO again holds but in (2) one has to interchange the symbols B and A. Obviously, A stands for any of A_l's.

MATCHING SPECTRA OF BRIDGED ANNULENES

The matching polynomial $\alpha(G; x)$ of graph G is a well studied combinatorial object[8]. The collection of its roots, $x_1^{(m)}(G)$, $x_2^{(m)}(G), \ldots, x_N^{(M)}(G)$, where N is the number of vertices in G, defines the matching spectrum of G. The matching spectra of molecular graphs have found applications in the theory of aromaticity[9,10].

The recursive formula[8,9] for the evaluation of $\alpha(G; x)$ is of a simpler structure than the recursive formula[5] for the evaluation of $\Phi(G; x)$. Therefore, the matching spectra exhibit an analogon of TEMO for wider classes of isomers than the MO energies. We present now such a class.

Class 6. — The isomers of this class are bridged annulenes. Let N be an even number, $N = 2n$. If the bridge is established between positions n and l we denote the corresponding graph by B_l, $l = 1, 2, \ldots, n - 1$. For $l = 2n$, we write $A = B_l$. Graph A and a representative of the series of B_l's are depicted in Figure 7.

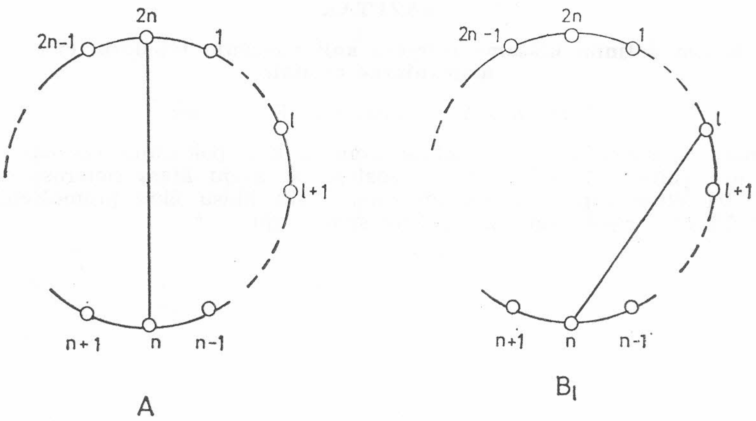


Figure 7.

By comparing the matching polynomial of A with the matching polynomial of any of B_l's the following result is obtained:

$$\alpha (B_l; x) - \alpha (A; x) = [\alpha (P_{l-1}; x)]^2 \geq 0 \tag{9}$$

where: $\alpha (P_k; x) \equiv \Phi (P_k; x)$. Inequality (9) implies that the following analogon of TEMO (2):

$$x_1^{(m)} (A) \geq x_1^{(m)} (B) \geq x_2^{(m)} (B) \geq x_2^{(m)} (A) \geq \ldots \geq$$
$$\geq x_{2k-1}^{(m)} (A) \geq x_{2k-1}^{(m)} (B) \geq x_{2k}^{(m)} (B) \geq x_{2k}^{(m)} (A) \geq \ldots \tag{10}$$

holds where B stands for any of B_l, $l = 1, 2, \ldots, n - 1$.

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SAŽETAK

O nekim daljnim klasama izomera koji pokazuju topološki efekt na molekularne orbitale

J. Hoxha, A. Graovac i O. E. Polansky

Razmatrane su neke daljnje klase izomera koji pokazuju topološki efekt na molekularne orbitale (TEMO). One se sastoje od dviju klasa heterosupstituiranih poliena i tri klase supstituiranih anulena. Šestu klasu čine premošteni anuleni kod kojih TEMO vrijedi samo za spektre sparivanja.