

## Topological Effect on MO Energies, IV. The Total $\pi$ -Electron Energy of *S*- and *T*-Isomers

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A novel general property of the *S*- and *T*-isomers (a concept which has been introduced and elaborated elsewhere<sup>1,2</sup>) of alternant hydrocarbons is demonstrated, namely that due to the HMO total  $\pi$ -electron energy the *S*-isomer should always be more stable than the *T*-isomer. Some other classes of conjugated isomers are also constructed, for which similar inequalities are derived.

(*Keywords: Molecular topology; TEMO; Topologically related isomers; Total  $\pi$ -electron energies*)

*Topologischer Effekt bei MO-Energien, 4. Mitt.: Die  $\pi$ -Elektronen-Gesamtenergie von S- und T-Isomeren*

Es wird allgemein gezeigt, daß bei einem *S-T*-Isomerenpaar (beschrieben in<sup>1,2</sup>) eines alternierenden Kohlenwasserstoffes infolge der HMO  $\pi$ -Elektronen-Gesamtenergie das *S*-Isomere stets stabiler sein sollte als das *T*-Isomere. Weitere Klassen konjugierter Isomere werden konstruiert und ähnliche Ungleichungen angegeben.

### 1. Introduction

A topological effect on molecular orbitals (TEMO) which relates the MO energy patterns of the so-called *S*- and *T*-isomers has been recently discovered<sup>1</sup>. The conclusions derived within the simple *Hückel* MO model are in agreement with experimental data and *ab initio* calculations<sup>1,2</sup>.

The basic idea of Paper I<sup>1</sup> consists in considering the difference of the characteristic polynomials of  $S$  and  $T$ . As this difference is non-negative for all (real) values of the variable  $x$ , the *Hückel* MO energies of the  $S$ - and  $T$ -isomers obey an interlacing rule, called TEMO. In the present paper we wish to point out another property of the  $S$ - and  $T$ -isomers, closely related to TEMO. Namely, if  $S$  is an alternant hydrocarbon, then it has always greater total  $\pi$ -electron energy than its  $T$ -isomer. In Section 2 we offer a general result for the total  $\pi$ -electron energy (as calculated within the HMO model), which as a consequence will yield the inequality  $E(S) \geq E(T)$ . In Section 3 a number of additional classes of conjugated isomers are described, which have analogous TEMO behaviour. Several further inequalities for total  $\pi$ -electron energy and reference energy are also deduced.

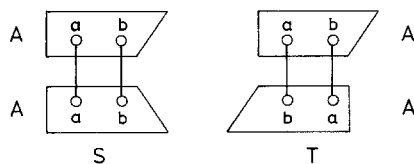
The results of the present paper could be of some use in predicting the relative stability of  $S$ - and  $T$ -isomers, especially when the isomers studied are not sterically crowded, since it is well-known<sup>3</sup>, HMO total  $\pi$ -electron energies of conjugated hydrocarbons correlate well with experimental heats of formation and enable their calculation with an error of some 0.1%.

In the following we will use a graph-theoretical terminology and formalism closely similar to that of Paper I. If  $G$  is a graph on  $n$  vertices, then  $\mu(G)$  denotes its  $\mu$ -polynomial<sup>4</sup>;  $\mu(G)$  is a polynomial of degree  $n$  in the variable  $x$ ; in addition  $\mu(G)$  depends on a parameter  $t$ . Therefore, we may write  $\mu(G) = \mu(G, t, x)$ . For  $t = 1$  the  $\mu$ -polynomial reduces to the characteristic polynomial  $\varphi(G)$  of the graph  $G$ . For  $t = 0$  the  $\mu$ -polynomial reduces to the matching polynomial  $\alpha(G)$  of the graph  $G$ . More details on the polynomials  $\mu(G)$ ,  $\varphi(G)$  and  $\alpha(G)$  can be found elsewhere<sup>4, 5</sup>.

If  $a$  is a vertex of  $G$ , then  $G - a$  denotes the subgraph obtained by deletion of  $a$  and all incident edges from  $G$ . The subgraph obtained by deletion of the vertices  $a$  and  $b$  from  $G$  is denoted by  $G - a - b$ , etc.

In Paper I we considered molecules built from two fragments, connected by a certain number,  $l$ , of linking bonds. The special case arises when the both bonding fragments are the same and the linking

*Scheme 1*



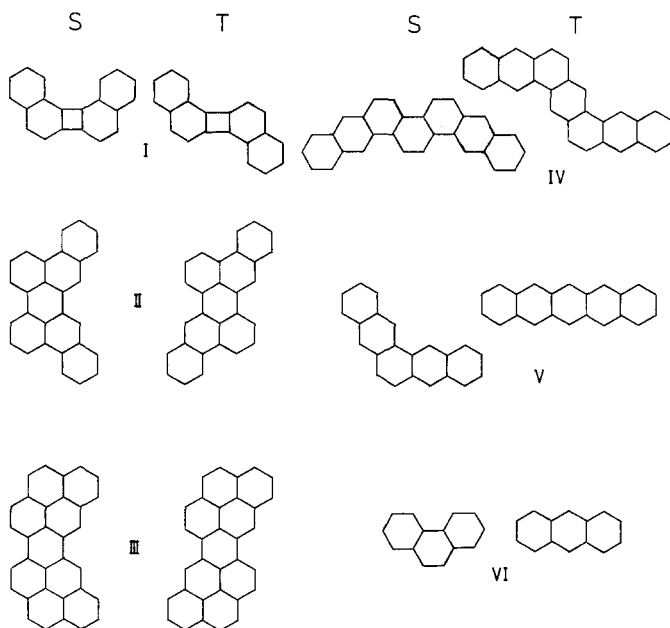
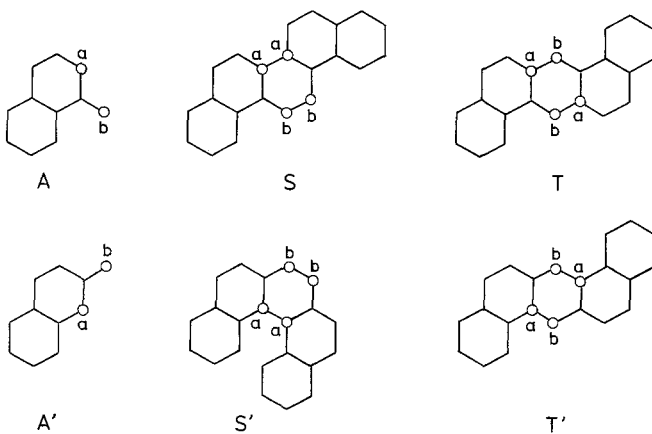


Fig. 1. Pairs of *S*- and *T*-isomers belonging to *Class I*; the Roman number used in Table I indicates the isomer under consideration

*Scheme 2*



bonds connect the same group of atoms in the both parts. The conjugated systems of the above type with  $l = 2$  will be referred as belonging to Class 1. They are presented by the graphs  $S$  and  $T$ . As a consequence of the construction, the isomer  $S$  possess a plane of symmetry while the isomer  $T$  has a center of inversion. The building fragment is denoted by  $A$ , two such fragments are connected through the vertices  $a$  and  $b$ . The number of vertices of  $A$  is  $n$ ; hence,  $S$  and  $T$  possess  $2n$  vertices (Scheme 1).

Some examples of  $S$ - and  $T$ -isomers are given in Fig. 1.

The examples below may illustrate the mode of the construction of such pairs (Scheme 2).

One sees that different fragments could lead to the same  $T$  graph.

The basic equations of Paper I are given as follows:

$$\begin{aligned} \mu(S) &= \mu(A)^2 - \mu(A - a)^2 - \mu(A - b)^2 + \\ &+ \mu(A - a - b)^2 - 2t[\sum \mu(A - P_{ab})]^2, \end{aligned} \quad (1)$$

$$\begin{aligned} \mu(T) &= \mu(A)^2 - 2\mu(A - a)\mu(A - b) + \\ &+ \mu(A - a - b)^2 - 2t[\sum \mu(A - P_{ab})]^2, \end{aligned} \quad (2)$$

where  $P_{ab}$  denotes a path connecting the vertices  $a$  and  $b$ , and the summation on the r.h.s. of both (1) and (2) ranges over all paths of  $A$ , connecting  $a$  and  $b$ . An immediate consequence of (1) and (2) is

$$\mu(T) - \mu(S) = [\mu(A - a) - \mu(A - b)]^2. \quad (3)$$

Hence,  $\mu(T) - \mu(S)$  is non-negative for all real values of the variable  $x$ . For  $t = 1$  and  $t = 0$  we obtain the following two special cases:

$$\begin{aligned} \varphi(T) - \varphi(S) &= [\varphi(A - a) - \varphi(A - b)]^2, \\ \alpha(T) - \alpha(S) &= [\alpha(A - a) - \alpha(A - b)]^2. \end{aligned} \quad (4)$$

Note that in the general case the subgraphs  $A - a$  and  $A - b$  may possess cycles. Therefore, the corresponding matching and characteristic polynomials would differ.

As shown in Paper I<sup>1</sup> the following inequality is derived from eq. (4):

$$\begin{aligned} X_1^S &\leq X_1^T \leq X_2^T \leq X_2^S \leq \dots \\ \dots &\leq X_{2n-1}^S \leq X_{2n-1}^T \leq X_{2n}^T \leq X_{2n}^S. \end{aligned} \quad (5)$$

This equation expresses the interlacing rule mentioned above.

## 2. An Inequality Between the Total $\pi$ -Electron Energy of the $S$ - and $T$ -Isomers

We show here that if  $A$  represents an alternant hydrocarbon fragment, then for an arbitrary  $S, T$  pair the following inequality holds

$$E(S) \geq E(T), \quad (6)$$

where  $E(X)$  denotes the *Hückel* total  $\pi$ -electron energy of a conjugated system  $X$ , expressed in (negative)  $\beta$  units. Provided the contributions of the  $\sigma$ - and core electrons to the energy content of the  $S$ - and  $T$ -isomers are nearly the same, the energies of these isomers are discriminated by their  $\pi$ -electron contributions, which are well reproduced within the framework of the simple HMO model<sup>3</sup>. Hence, the isomer  $S$  is predicted to be thermodynamically not less stable than the isomer  $T$ .

We will prove, in fact, a slightly more general statement. In order to do this we need some additional definitions.

A polynomial  $R(x)$  is said to be even if  $R(-x) = R(x)$  and is said to be odd if  $R(-x) = -R(x)$ . A polynomial  $R(x)$  is said to be alternant if it can be written in the form

$$R(x) = x^m - r_1 x^{m-2} + r_2 x^{m-4} - r_3 x^{m-6} + \dots \\ \dots + (-1)^{[m/2]} r_{[m/2]} x^{m-2[m/2]}, \quad (7)$$

where  $[m/2] = m/2$  if  $m$  is even and  $[m/2] = (m-1)/2$  if  $m$  is odd, and  $r_i \geq 0$  for  $i = 1, 2, \dots, [m/2]$ . In other words  $R(x)$  is alternant if it is either even or odd and if its coefficients alternate in sign.

If all the zeros of an even or odd polynomial are real numbers, then this polynomial is necessarily alternant. The characteristic polynomial of an alternant hydrocarbon is, therefore, alternant. The matching polynomial of any conjugated hydrocarbon is alternant<sup>4, 6</sup>.

Let  $P(x)$  and  $Q(x)$  be two alternant polynomials of degree  $m$  having real zeros  $p_1, p_2, \dots, p_m$  and  $q_1, q_2, \dots, q_m$ , respectively. Let

$$\varepsilon(P) = \sum_{i=1}^m |p_i| \quad \text{and} \quad \varepsilon(Q) = \sum_{i=1}^m |q_i|. \quad (8)$$

If  $P(x)$  is the characteristic polynomial of an alternant hydrocarbon, then  $\varepsilon(P)$  represents the *Hückel* total  $\pi$ -electron energy. If  $P(x)$  is the matching polynomial of a hydrocarbon, then  $\varepsilon(P)$  represents its reference energy, as calculated within the topological resonance energy (TRE) model<sup>6</sup>, which neglects the cyclic contributions.

The following result holds:

If the difference of the polynomials  $P(x)$  and  $Q(x)$  can be presented as

$$Q(x) - P(x) = R_1(x) \cdot [R_2(x)]^2, \quad (9)$$

where  $R_1(x)$  is an alternant and  $R_2(x)$  an even or odd (but not necessarily alternant) polynomial, then

$$\begin{aligned} \varepsilon(P) \geq \varepsilon(Q) & \quad \text{if } m - m_1 - 2m_2 \equiv 2 \pmod{4} \\ \varepsilon(P) \leq \varepsilon(Q) & \quad \text{if } m - m_1 - 2m_2 \equiv 0 \pmod{4} \end{aligned} \quad (10)$$

where  $m_1$  is the degree of  $R_1(x)$  and  $m_2$  is the degree of  $R_2(x)$ .

Note that the condition  $Q(x) \geq P(x)$  needs not be fulfilled for all  $x$  as it is required in TEMO<sup>1</sup>. This condition holds in the special case  $m_1 = 0$ .

In order to prove (10), we introduce first a polynomial  $R^+(x)$ , associated with the polynomial  $R(x)$  in the following way:

$$R^+(x) = i^{-m} R(ix). \quad (11)$$

Now, if  $R(x)$  is alternant, then by eq. (7),

$$R^+(x) = x^m + r_1 x^{m-2} + r_2 x^{m-4} + \dots + r_{[m/2]} x^{m-2[m/2]} \quad (12)$$

and  $R^+(x)$  is positive for all  $x > 0$ . In addition, if  $R(x)$  is either even or odd, then  $R^+(x)$  is a polynomial with real coefficients. Then  $[R^+(x)]^2$  is non-negative for all real values of  $x$ . Having these relations in mind, we get from (9)

$$[Q(ix) - P(ix)] \cdot i^{m-m_1-2m_2} = R_1^+(x) [R_2^+(x)]^2. \quad (13)$$

The right-hand side of (13) is positive for all  $x > 0$ . Therefore,  $Q(ix) - P(ix) \geq 0$  if  $m - m_1 - 2m_2$  is divisible by four and  $Q(ix) - P(ix) \leq 0$  if  $m - m_1 - 2m_2$  is even, but not divisible by four.

Now, the application of *Coulson's* integral formula<sup>7</sup>

$$\varepsilon(P) - \varepsilon(Q) = \frac{2}{\pi} \int_0^\infty \ln \left| \frac{P(ix)}{Q(ix)} \right| dx \quad (14)$$

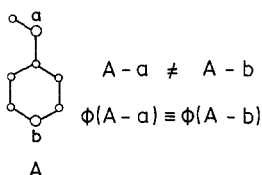
completes the proof of the relations (10).

The proof of the inequality (6) is now immediate. From (4) we see that the polynomials  $\varphi(T)$  and  $\varphi(S)$  obey the conditions (9) whenever the fragment  $A$  is an alternant hydrocarbon. Namely then  $\varphi(A-a)$  and  $\varphi(A-b)$  are alternant polynomials of degree  $n-1$  and their difference is an even or odd polynomial of degree  $n-1-2k$ , with  $k$  being a certain positive integer. Then  $m = 2n$ ,  $m_1 = 0$  and  $m_2 = n-1-2k$ . Thus,

relation (6) is a special case of the relations (10) which have already been proved.

From the above analysis it is evident that the difference  $E(S) - E(T)$  vanishes if and only if  $\varphi(A - a) \equiv \varphi(A - b)$ . A trivial case when this occurs is when  $a$  and  $b$  are equivalent centers; then the  $S$ - and  $T$ -isomers coincide. A non-trivial case occurs when  $A - a \neq A - b$ , but  $\varphi(A - a) \equiv \varphi(A - b)$ . Then also the  $S$ - and  $T$ -isomers (which are different) have equal characteristic polynomials. A simple example of this type, but of only limited chemical relevance, is offered by  $A$  representing the skeleton of vinylbenzene (Scheme 3).

Scheme 3



In the great majority of cases the polynomials  $\varphi(A - a)$  and  $\varphi(A - b)$  are different, and then (6) will be a strict inequality.

Our results are illustrated in Table 1, where *Hückel* total  $\pi$ -electron energies of some pairs of alternant  $S$ - and  $T$ -isomers are presented.

Table 1. *Hückel* total  $\pi$ -electron energies (in  $\beta$  units) of alternant  $S$ - and  $T$ -isomers of Class 1 [as the number of centers increases the density of the MO's increases too and as the result the difference between  $E(S)$  and  $E(T)$  might become negligible small]

Pair	$E(S)$	$E(T)$	Pair	$E(S)$	$E(T)$
(I)	27.819	27.816	(IV)	42.242	42.196
(II)	39.76886	39.76880	(V)	30.762	30.544
(III)	45.91474	45.91400	(VI)	19.448	19.313

In a completely analogous manner we deduce from (5)

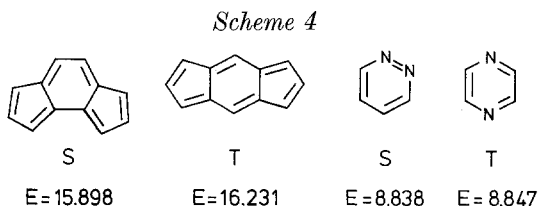
$$E^R(S) \geq E^R(T), \quad (15)$$

where  $E^R(X)$  is the reference energy of the molecule  $X$  in the TRE model<sup>6</sup>. Contrary to (6), the inequality (15) holds for both alternant and non-alternant conjugated hydrocarbons.

The result (6) holds for the total  $\pi$ -electron energies of dications and dianions of alternant hydrocarbons if their number of electrons equals

4 *r*. In that case the absolute value of the energy of HOMO (LUMO) is in *S* smaller or equal than in *T*<sup>1</sup>, hence the difference  $E(S) - E(T)$  is either enlarged or unchanged for the diions as compared with the neutral compounds.

But it is not possible to extend the result (6) to non-alternant hydrocarbons and/or heteroconjugated compounds. For such systems, namely, examples can be found where the *T*-isomer has greater *Hückel* total energy than the *S*-isomer. Two such isomeric pairs are given in Scheme 4.

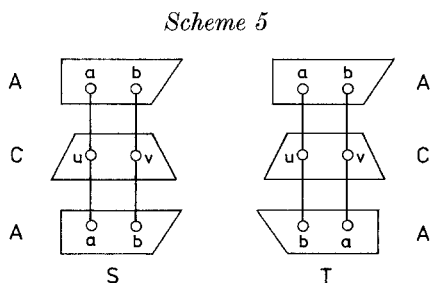


### 3. More Classes of Isomers and More Inequalities for Total $\pi$ -Electron Energy

Relations (10) can be applied not only to *S*- and *T*-isomers of Paper I, but to many other isomeric pairs, the characteristic or the matching polynomials of which fulfil the condition (9). In the present section we describe a few such classes of isomers and then apply (10) in order to obtain inequalities for their total  $\pi$ -electron and reference energies. As already mentioned, the *S*- and *T*-isomers of Paper I are said to belong to *Class 1*.

#### *Class 2*

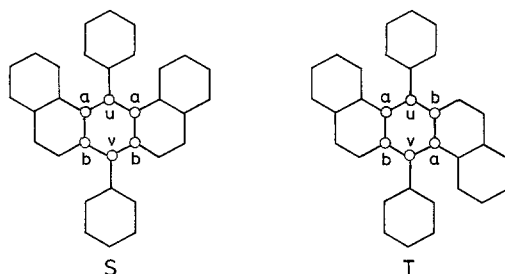
Let *C* be a graph possessing two equivalent vertices *u* and *v*. In other words, let the subgraphs  $C - u$  and  $C - v$  be isomorphic. Then the isomers of *Class 2* are defined by the graphs shown in Scheme 5.





An example is depicted in Scheme 6.

*Scheme 6*



Using the same methods as before, it can be proved that the *S*- and *T*-isomers of Class 2 obey the relation

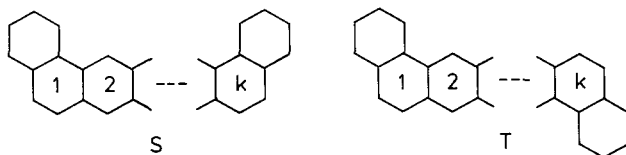
$$\mu(T) - \mu(S) = \mu(C - u - v) [\mu(A - a) - \mu(A - b)]^2. \quad (16)$$

An important special case of Class 2 isomers is obtained by choosing *C* to possess just two vertices *u* and *v*, irrespective of whether they are connected or not. Then  $\mu(C - u - v) \equiv 1$  and one has

$$\mu(T) - \mu(S) = [\mu(A - a) - \mu(A - b)]^2. \quad (17)$$

An example of this kind are the two isomeric dibenzopolyacenes shown in Scheme 7.

*Scheme 7*



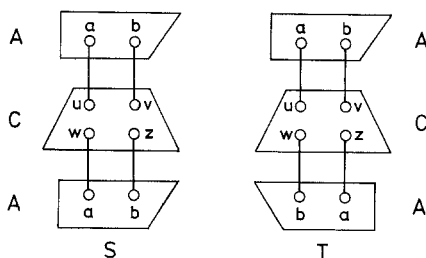
### *Class 3*

If *C* has two pairs of equivalent vertices *u*, *v* and *w*, *z*, then the *S*- and *T*-isomers of Class 3 are constructed as depicted in Scheme 8.

It can be shown that in this case

$$\begin{aligned} & \mu(T) - \mu(S) = \\ & = [\mu(C - u - z) - \mu(C - u - w)] \cdot [\mu(A - a) - \mu(A - b)]^2. \end{aligned} \quad (18)$$

Scheme 8

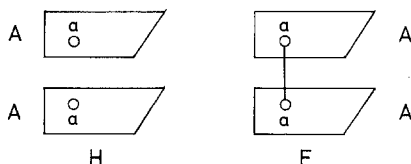


If one identifies the vertices  $u$  and  $w$ , and  $v$  and  $z$ , then  $\mu(C - u - w) \equiv 0$  and eq. (18) reduces to eq. (16). Hence, the isomers of Class 2 can be understood as special cases of isomers of Class 3.

## Class 4

Let the graph  $H$  be composed of two disconnected components, each being isomorphic to  $A$ . Let the graph  $F$  be obtained by joining the two vertices denoted by  $a$  in  $H$  (Scheme 9).

Scheme 9



It is easy to derive that

$$\mu(H) - \mu(F) = \mu(A - a)^2. \quad (19)$$

The formal equivalence of the eqs. (19) and (4) implies the interlacing of the double degenerate MO's of  $H$  between pairs of the MO's of  $F$  as expressed by eq. (5). This is in accordance with the well known fact that the MO's of two isolated molecules split under the bond formation.

## Class 5

Let  $v_1, v_2, \dots, v_k$  and  $w_1, w_2, \dots, w_k$  be arbitrary (but distinct) vertices of the cycle  $C_n$ ,  $n \geq 2k$ . Let further  $V_1, V_2, \dots, V_k$  and  $W_1, W_2, \dots, W_k$  be two collections of rooted trees. By identifying the root of  $V_i$  with the vertex  $v_i$  and the root of  $W_i$  with the vertex  $w_i$ ,  $i = 1, 2, \dots, k$ , a graph is obtained which will be denoted by  $Z$ .

Since  $V_1, V_2, \dots, V_k$  and  $W_1, W_2, \dots, W_k$  are acyclic by definition, the graph  $Z$  is unicyclic. Because of Corollary 1.2 given in the paper<sup>4</sup> one has

$$\mu(Z) = \alpha(Z) - 2t \prod_{i=1}^k \mu(V_i) \cdot \mu(W_i), \quad (20)$$

where  $V_i$  and  $W_i$  denote the graphs obtained by deletion of the roots from  $V_i$  and  $W_i$ , respectively. From (20) follows that the difference  $\mu(Z) - \alpha(Z)$  is independent of the choice of the vertices  $v_1, v_2, \dots, v_k$  and  $w_1, w_2, \dots, w_k$ . If, in addition, the rooted trees  $V_i$  and  $W_i$  are isomorphic for all  $i = 1, 2, \dots, k$ , then

$$\alpha(Z) - \mu(Z) = 2t \left[ \prod_{i=1}^k \mu(V_i) \right]^2. \quad (21)$$

This equation is of interest for  $t = 1$ :

$$\alpha(Z) - \varphi(Z) = 2 \left[ \prod_{i=1}^k \varphi(V_i) \right]^2. \quad (22)$$

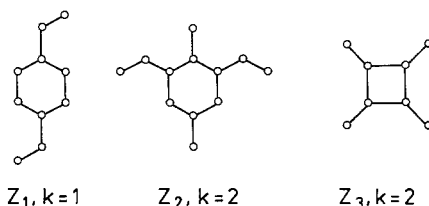
In this case we say that  $Z$  belongs to Class 5. The above equation has the consequence that the zeros of the characteristic and the matching polynomial of a conjugated system of Class 5 are related in the same way as the eigenvalues of the  $S$ - and  $T$ -isomers of Class 1.

A special case of (22) is

$$\alpha(C_n) - \varphi(C_n) = 2. \quad (23)$$

A few examples of molecular graphs belonging to Class 5 are depicted in Scheme 10.

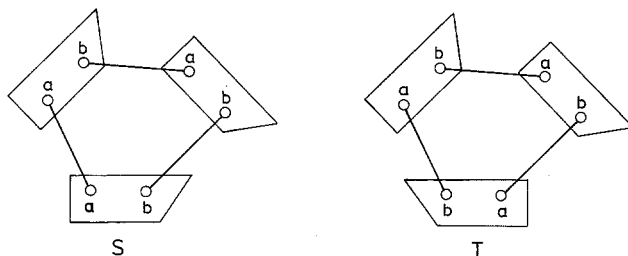
*Scheme 10*



*Class 6*

$S$ - and  $T$ -like isomers of Class 6 are represented by the graphs shown in Scheme 11.

## Scheme 11



A successive removal of the edges connecting the three fragments of type  $A$  gives<sup>8</sup>

$$\mu(T) - \mu(S) = [\mu(A) - \mu(A - a - b)] \cdot [\mu(A - a) - \mu(A - b)]^2. \quad (24)$$

Now we apply successively the result (10) to the above classes of molecular graphs. One arises to the following conclusions:

*Class 2.*  $E(S) \leq E(T)$  provided  $A$  and  $C$  are alternant hydrocarbon fragments, i.e.  $S$  is predicted to be less stable than  $T$ . The inequality holds irrespective of the size and the nature of the fragment  $C$ . Equality holds under the precisely same conditions as in the case of the relation (6).

From (16) also the inequality  $E^R(S) \leq E^R(T)$  follows. It holds for both alternant and non-alternant  $S, T$  pairs.

*Class 3.* From (18) we gain the very same conclusions about the total  $\pi$ -electron energy of  $S$  and  $T$  as in the previous case, provided the expression  $\mu(C - u - z) - \mu(C - u - w)$  is an alternant polynomial. However, this latter polynomial needs not be alternant even when  $C$  is alternant and  $t = 1$  or  $t = 0$ .

*Class 4.* From (19) we deduce the two trivial relations  $E(H) < E(F)$  and  $E^R(H) < E^R(F)$ .

*Class 5.* Eq. (20) enables one to compare the energy and the reference energy of a molecule  $Z$ . It follows that the actual form of the inequality obtained depends only on the size of the cycle  $C_n$ . In particular

$$\begin{aligned} E(Z) > E^R(Z) \text{ and } \text{TRE}(Z) > 0 & \text{ if } n \equiv 2 \pmod{4} \\ E(Z) < E^R(Z) \text{ and } \text{TRE}(Z) < 0 & \text{ if } n \equiv 0 \pmod{4} \end{aligned} \quad (25)$$

irrespective of the nature of the attached side groups  $V_i$  and  $W_i$ . This, however, is an already known result<sup>9</sup>.

*Class 6.*  $E(S) \geq E(T)$  provided  $A$  is an alternant hydrocarbon fragment.  $E^R(S) \geq E^R(T)$  irrespective of the nature of the fragment  $A$ .

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- <sup>5</sup> The  $\mu$ -polynomial depends, in fact, on a vector  $t = (t_1, t_2, \dots, t_r)$ . In the present paper, however, a special case of the  $\mu$ -polynomial is considered, namely when  $t_1 = t_2 = \dots = t_r = t$ . The same assumption was made also in Paper I.
- <sup>6</sup> *Aihara J.*, J. Amer. Chem. Soc. **98**, 2750 (1976); *Gutman I., Milun M., Trinajstić N.*, J. Amer. Chem. Soc. **99**, 1692 (1977).
- <sup>7</sup> *Coulson C. A.*, J. Chem. Soc. **1954**, 3111.
- <sup>8</sup> *Polansky O. E., Graovac A.*, Match (Mülheim) No. **13**, 151 (1982).
- <sup>9</sup> *Gutman I. M.*, Bull. Soc. Chim. Beograd **44**, 173 (1979).