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Research Notes on the Topological Effect on MO (TEMO), 1. [1]

# ON THE CHARACTERISTIC POLYNOMIALS OF TOPOLOGICALLY RELATED ISOMERS FORMED WITHIN THREE DIFFERENT MODELS

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Explicit formulae are given for the characteristic polynomials of topologically related isomers, T and S, formed by means of three different models using a different number of bonds (l = 2, 3, 4) for the linkage of the building subunits. Furthermore, explicit expressions for the difference polynomial $\Delta = T - S$ are also given. The effect of the symmetry of the central subunit (if present) as well as that of the isomorphism of the terminal subunits are briefly discussed. The number of terms of specific types are enumerated combinatorially.

## 1. General remarks

The discovery of the topological effect on the molecular orbitals (TEMO) of topologically related isomers [2] has aroused interest in some technical details which are given in the present note. For the sake of clarity, the terminology used is reviewed at the beginning. Next a concise notation of the characteristic polynomials, used throughout this note is explained; finally, in subsequent sections, the TEMO formulae derived for some versions of three different topological models are presented.

The topological space associated with a given molecule is defined in terms of the families of subsets of the vertices of the molecular graph forming the neighbourhoods of all the distinct vertices, resulting in the umgebungs topology, $T_U$ [3]. In this topological space, connected parts of the molecule are represented by connected subspaces.

Isomers, which may be constructed from two or more subunits, A, B, C, ..., by linking them in a different manner, are called topologically related; usually, they are denoted by S and T, respectively, [2]. The topological spaces, associated with a pair of topologically related isomers, consist of subspaces which correspond to the building subunits and which are pairwise isomorphic; but they differ with respect to the connection between these subspaces. This is in accord with the fact that topologically related isomers differ only with respect to the linkage between their building moieties.

There are several ways in which pairs of topologically related isomers may be constructed; each one is called a topological model. A topological model is characterized by the number of subunits used as well as the number of bonds which link them. In order to generate a different but related topology in the isomers, one needs at least two bonds for the linkage of two moieties. In the first of the three models treated below two building moieties, A and B, in the other ones three moieties, A, B, and C, are used; the number of linking bonds between two subunits, l, is taken as l = 2, 3, 4.

The union of the MO eigenvalue spectra of a pair of topologically related isomers, S and T, is called their <u>TEMO pattern</u>. In the case of <u>TEMO without inversions</u>, the TEMO pattern is characterized by the interlacing of alternately two and no eigenvalues of T in the subsequent intervals given by the eigenvalues of S; this is realized when the difference of the characteristic polynomials of the isomers, T - S, is positiv in the complete range of their variable. <u>TEMO with inversions</u> may occur when this difference polynomial, T - S, also takes negative values; if the real roots of T - S = 0 are non-degenerate or of odd degeneracy they indicate the intervals in which the TEMO pattern is inverted; hence, they are called <u>inversion points</u>. Conclusions about the appearance of inversions may be drawn when the characteristic polynomials of S and T are expressed in terms of the characteristic polynomials of the building moieties and some of their derivatives [2,4,5]. Such expressions are obtained by the repeated application of Heilbronner´s formula [6] to all the edges linking the subunits in S or T:

$$(G) = (G-\{u,v\}) - (G-u-v) - 2t\sum(G-Z_{uv}), \qquad (1)$$

where, (G), (G-{u,v}), (G-u-v), and (G-$Z_{uv}$) are the characteristic polynomials of the original graph G and of those obtained from G by removing the edge {u,v}, or the vertices u and v (together with all their incident edges), or the cycle $Z_{uv}$ to which the edge {u,v} belongs, respectively; the summation runs over the set {$Z_{uv}$} and t takes the value [7] of t = 1 in case of characteristic poly nomials but t = 0 in case of acyclic polynomials. As has been shown [8] the result is essentially determined by the combinations of the linking edges (bonds) and the cycles in which they are involved; hence, the number of terms increases rapidly with the number, l, of the linking bonds. On the other hand, the fact that the complete sets of combinations lead to the expansion of the characteristic polynomial in terms of those of the constituting subunits offers a graphical method for the derivation of TEMO formulae used in [5].

The usual notations as employed in eq. (1) are space consuming; hence, their use is not advisable in our case where some of the formulae consist of more than a hundred terms. In order to develop the most concise notations one may profit from the following facts:

(i) Because eq. (1) is applied to all the linking edges between the subunits of the topologically related isomers but only to these, the removal of these edges need not be indicated explicitly.

(ii) As a consequence of this procedure, each term of the final result corresponds to a disconnected graph composed of certain subgraphs of the subunits used; hence, such a term is represented by the product of the characteristic polynomials of these subgraphs.

(iii) Since no misunderstanding can occur, these characteristic polynomials can be denoted by the same symbols which are used for the notation of the graphs.

(iv) Vertices removed from a graph can be denoted unequivocally by an upper index; e.g.: the term (G-u-v) of eq. (1) will be expressed by $G^{uv}$.

(v) The cycles, $Z_{uv}$, which appear in the last term of eq. (1) are composed of four different parts: first of all, there is the edge $\{u,v\}$, linking two moieties, say A and B, $u \in A$, $v \in B$; then, we have two paths, one in A and one in B, connecting the vertices u and v with the endpoints of another linking edge, say $\{s,t\}$, $s \in A$, $t \in B$, and finally this edge itself which closes the cycle:

$$Z_{st,uv} = \{u,v\} \cup P_{vt} \cup \{t,s\} \cup P_{su}. \tag{2}$$

In order to obtain the complete set $\{Z_{st,uv}\}$, one has to combine each member of the set $\{P_{vt}\}$ with each one of $\{P_{su}\}$. Suppose, the graph G consists of the two subunits A and B which are connected by the two edges $\{u,v\}$ and $\{s,t\}$ as described above

$$G = A \cup B \cup \{\{u,v\},\{s,t\}\}$$

then (in the usual notation) the term corresponding to the last one in eq. (1) is given as follows

$$\Sigma(G-Z_{st,uv}) = [\Sigma(A-P_{su})][\Sigma(B-P_{tv})]$$

wherein the summations run over the complete sets $\{Z_{st,uv}\}$, $\{P_{su}\}$, and $\{P_{tv}\}$, respectively. We will denote concisely the factors of the right-hand-side of this equation by $A_{su}$ and $B_{tv}$, respectively. Thus, the lower indices indicate not only the end points of the paths removed but also the summing up over all these paths [9]. In cases where two or more paths have been removed, the endpoints of the different paths are separated by commas; then one has to sum up independently over all sets of paths involved [9].

Combining the symbols explained in (iv) and (v) one may arrive at a symbol like

$G^{abc}_{mn,rt}$ ... it represents the sum of all characteristic polynomials corresponding to the graphs obtained from the given graph G by removing the vertices a, b, and c as well as the paths $P_{mn}$ and $P_{rt}$.

When four vertices, $\{m,n,r,t\} \in G$, have to be linked by two paths, there are three different possibilities to do so, leading to unequal terms like

$$G_{mn,rt} \neq G_{mr,nt} \neq G_{mt,nr} \quad . \tag{3}$$

It can be shown that in the expansion of the characteristic polynomials of the topologically related isomers S and T that out of these three possibilities only two may be realized if S and T correspond to planar graphs and the vertices involved belong to their perimeters. But in the formulae derived below no term is suppressed; thus, they also might be applied to systems which correspond to non-planar graphs.

The physical meaning of TEMO [2,5,11] and the quantum chemical treatment of inversion points [12-14] is discussed elsewhere.

## 2. Model 1

In this model the S and the T isomer are formed from two subunits, A and B, which are linked by 1 = 2, 3, or 4 edges; these three cases are treated separately.

In all cases A and B are first assumed to be different and the characteristic polynomials of T and S are given. Then the difference polynomial defined by

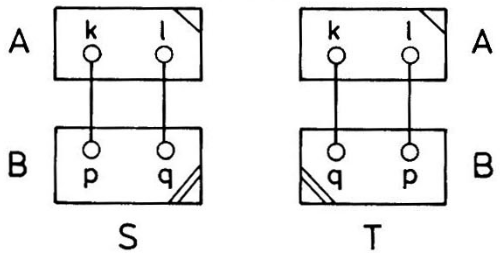
$$\Delta = T - S \tag{4}$$

is derived. Finally, the isomorphism of A = B is assumed and the resulting form of the difference polynomial, Δ, is given.

At the beginning of each subsection a schematic representation of the model is given which also exhibits the labelling of the vertices. Further, in a table the number of terms are listed which are generated by removing the endpoints of edges (note: according to eq. (1) none or both endpoints of an edge are removed!) or cycles. Some of these terms cancel each other when the difference polynomial is formed; their number is listed in another column. The last column shows the number of terms not vanishing in Δ contributed from T as well as from S; hence, Δ has just twice as many terms.

2.1. Model 1, l = 2

The subunits A and B are bivalent. They form the S and the T isomer as schematically depicted below:




The number of terms of the characteristic polynomials of S and T and those of the difference polynomial listed in Table 1, are determined by the combinations of removed endpoints of edges

Table 1: Number of terms in the case model 1, l=2:

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contri-buting to S and T | equal in S and T | contribu-ting to Δ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 2 | 0 | 2 |
| 0 | 2 | 1 | 1 | 0 |
| 1 | 0 | 1 | 1 | 0 |
| | | 5 | 3 | 2 |

and cycles resulting from the repeated application of eq. (1). In the present case, eq. (1) is applied two times.

The characteristic polynomial of S and T, each one consisting of five terms, are represented as follows:

$$T = AB - A^k B^q - A^l B^p + A^{kl} B^{pq} - 2tA_{kl}B_{pq}$$

$$S = AB - A^k B^p - A^l B^q + A^{kl} B^{pq} - 2tA_{kl}B_{pq} \qquad (5)$$

As already indicated in Table 1, there are three terms in T and S which are pairwise identically equal; hence, they cancel each other when the difference polynomial is expressed according to eq. (4):

$$\Delta = (A^k - A^l)(B^p - B^q) \ . \qquad (6)$$

This bilinear form takes negative values if one of the factors is negative and the other one positive; hence, the appearance of inversions in the TEMO pattern cannot be excluded.

If one assumes that A and B are isomorphic and that an isomorphic mapping of A onto B maps the vertex $k \in A$ onto $p \in B$, and $l \in A$ onto $q \in B$, respectively, one obtains the following equalities:

$$A^k = B^p, \qquad A^l = B^q \ .$$

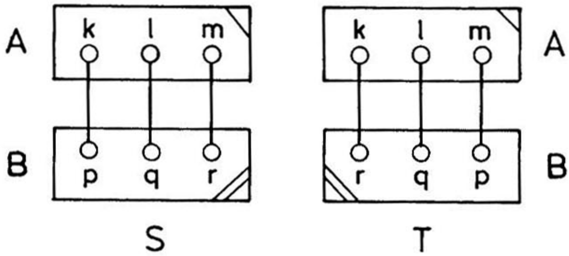
Inserting these in eq. (6) the difference polynomial takes the quadratic form

$$\Delta = (A^k - A^l)^2 \geq 0 \ . \qquad (7)$$

In the case of model 1, l=2 and A=B, Δ is positive in the complete range of its variable; hence, TEMO without inversions results in this case.

2.2. Model 1, l = 3

The subunits A and B are trivalent. They form the S and the T isomer as schematically depicted below:




In Table 2 the number of terms of T and S and those of Δ are given.

Table 2: Number of terms in the case of model 1, l=3:

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contributing to T and S | equal in T and S | contributing to Δ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 3 | 1 | 2 |
| 0 | 2 | 3 | 1 | 2 |
| 0 | 3 | 1 | 1 | 0 |
| 1 | 0 | 3 | 1 | 2 |
| 1 | 1 | 3 | 1 | 2 |
| | | 14 | 6 | 8 |

For the characteristic polynomial of T and S the following expressions are obtained:

$$T = AB - A^kB^r - A^lB^q - A^mB^p + A^{kl}B^{qr} + A^{km}B^{pr} + A^{lm}B^{pq} - A^{klm}B^{pqr} - 2t( A_{kl}B_{qr} + A_{km}B_{pr} + A_{lm}B_{pq} - A^m_{kl}B^p_{qr} - A^l_{km}B^q_{pr} - A^k_{lm}B^r_{pq} )$$

(8)

$$S = AB - A^kB^p - A^lB^q - A^mB^r + A^{kl}B^{pq} + A^{km}B^{pr} + A^{lm}B^{qr} - A^{klm}B^{pqr} - 2t( A_{kl}B_{pq} + A_{km}B_{pr} + A_{lm}B_{qr} - A^m_{kl}B^r_{pq} - A^l_{km}B^q_{pr} - A^k_{lm}B^p_{qr} )$$

There are, indeed, six terms of T and S which are pairwise identically equal, namely those in which the factors derived from B have no indices or the indices are combinations of {q} and {p,r}. They cancel each other when according to eq. (4) $\Delta$ is formed resulting in

$$\Delta = (A^k - A^m)(B^p - B^r) - (A^{kl} - A^{lm})(B^{pq} - B^{qr}) + 2t(A_{kl} - A_{lm})(B_{pq} - B_{qr}) - 2t(A^m_{kl} - A^k_{lm})(B^r_{pq} - B^p_{qr}). \qquad (9)$$

In the case of isomorphic moieties, A = B, and the isomorphic mapping k ↔ p, l ↔ q, and m ↔ r, we have the following equalities

$$A^k = B^p , \quad A^m = B^r , \quad A^{kl} = B^{pq} , \quad A^{lm} = B^{qr} ,$$

$$A_{kl} = B_{pq} , \quad A_{lm} = B_{qr} , \quad A^m_{kl} = B^r_{pq} , \quad A^k_{lm} = B^p_{qr} ,$$

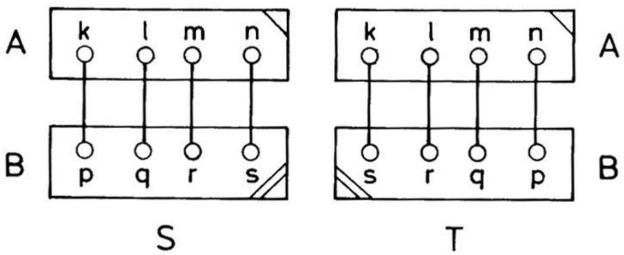
and eq. (9) takes the form

$$\Delta = (A^k - A^m)^2 - (A^{kl} - A^{lm})^2 + 2t(A_{kl} - A_{lm})^2 - 2t(A^m_{kl} - A^k_{lm})^2 \qquad (10)$$

Obviously, $\Delta$ can be negative in some intervals and, hence, the appearance of inversion points cannot be excluded.

2,3. Model 1, l = 4

The subunits A and B are tetravalent. They form the S and the T isomer as schematically depicted below:




Here we meet two types of terms which could not have appeared in the foregoing subsections. The first type is generated by the removal of a cycle from S or T which contains four linking edges. We denote their configuration by $e^4$ while to cycles which contain only two linking edges the configuration $e^2$ is assigned; in these notations, e stands for any member of the edge cut set formed by the linking edges. The other type is generated by the removal of two cycles, each one of the configuration $e^2$; this case will be denoted by $e^2+e^2$.

In both new types there are four vertices in A and in B, respectively, which have to be connected by two paths. As already mentioned in connection with eq. (3), this can be performed in three different ways. Table 3 shows these possibilities and also indicates what combinations correspond to $e^4$ and which ones to $e^2+e^2$ configurations.

Table 3: Cyclic configurations $e^4$ and $e^2+e^2$ in model 1, $l = 4$ :

| | $A_{kl,mn}$ | $A_{km,ln}$ | $A_{kn,lm}$ |
|---|---|---|---|
| $B_{pq,rs}$ | $e^2+e^2$ | $e^4$ | $e^4$ |
| $B_{pr,qs}$ | $e^4$ | $e^2+e^2$ | $e^4$ |
| $B_{ps,qr}$ | $e^4$ | $e^4$ | $e^2+e^2$ |

According to eq. (1), each contribution to T and S generated by removing a cycle is multiplied by 2t. Consequently, contributions to T and S generated by the removal of two independent cycles (as takes place in the case of $e^2+e^2$ configurations) are multiplied by $4t^2$. This shows that t is a useful ordering parameter although all powers of t have the same actual value [7].

In Table 4 the number of terms of T, S, and Δ are given in a similar way as in the foregoing subsections; in the first column only the configuration of single cyclic contributions, $e^2$ or $e^4$, are indicated. Terms in which the factors due to B have no indices or indices built up from the pairs (p,s) and (q,r) appear identically equal in T and S; hence, they cancel each other when Δ is formed according to eq. (4).

Table 4: Number of terms in the case of model 1, l=4:

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contributing to T and S | equal in T and S | contributing to Δ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 4 | 0 | 4 |
| 0 | 2 | 6 | 2 | 4 |
| 0 | 3 | 4 | 0 | 4 |
| 0 | 4 | 1 | 1 | 0 |
| 1 $e^2$ | 0 | 6 | 2 | 4 |
| 1 $e^4$ | 0 | 6 | 6 | 0 |
| 1 $e^2$ | 1 | 12 | 0 | 12 |
| 1 $e^2$ | 2 | 6 | 2 | 4 |
| 2 | 0 | 3 | 3 | 0 |
| | | 49 | 17 | 32 |

For the characteristic polynomial T and S one obtains:

$$
\begin{aligned}
T = {} & AB - A^{k}B^{s} - A^{l}B^{r} - A^{m}B^{q} - A^{n}B^{p} + A^{kl}B^{rs} + A^{km}B^{qs} + \\
& + A^{kn}B^{ps} + A^{lm}B^{qr} + A^{ln}B^{pr} + A^{mn}B^{pq} - A^{klm}B^{qrs} - \\
& - A^{kln}B^{prs} - A^{kmn}B^{pqs} - A^{lmn}B^{pqr} + A^{klmn}B^{pqrs} - \\
& - 2t( A_{kl}B_{rs} + A_{km}B_{qs} + A_{kn}B_{ps} + A_{lm}B_{qr} + A_{ln}B_{pr} + \\
& + A_{mn}B_{pq} + A_{kl,mn}B_{pr,qs} + A_{kl,mn}B_{ps,qr} + A_{km,ln}B_{pq,rs} + \\
& + A_{km,ln}B_{ps,qr} + A_{kn,lm}B_{pq,rs} + A_{kn,lm}B_{pr,qs} ) + \\
& + 2t( A^{m}_{kl}B^{q}_{rs} + A^{n}_{kl}B^{p}_{rs} + A^{l}_{km}B^{r}_{qs} + A^{n}_{km}B^{p}_{qs} + A^{l}_{kn}B^{r}_{ps} + A^{m}_{kn}B^{q}_{ps} + \\
& + A^{k}_{lm}B^{s}_{qr} + A^{n}_{lm}B^{p}_{qr} + A^{k}_{ln}B^{s}_{pr} + A^{m}_{ln}B^{q}_{pr} + A^{k}_{mn}B^{s}_{pq} + A^{l}_{mn}B^{r}_{pq} ) - \\
& - 2t( A^{mn}_{kl}B^{pq}_{rs} + A^{ln}_{km}B^{pr}_{qs} + A^{lm}_{kn}B^{qr}_{ps} + A^{kn}_{lm}B^{ps}_{qr} + A^{km}_{ln}B^{qs}_{pr} + A^{kl}_{mn}B^{rs}_{pq} ) + \\
& + 4t^{2}( A_{kl,mn}B_{pq,rs} + A_{km,ln}B_{pr,qs} + A_{kn,lm}B_{ps,qr} )
\end{aligned}
\qquad (11)
$$

$$
\begin{aligned}
S = {} & AB - A^{k}B^{p} - A^{l}B^{q} - A^{m}B^{r} - A^{n}B^{s} + A^{kl}B^{pq} + A^{km}B^{pr} + \\
& + A^{kn}B^{ps} + A^{lm}B^{qr} + A^{ln}B^{qs} + A^{mn}B^{rs} - A^{klm}B^{pqr} - \\
& - A^{kln}B^{pqs} - A^{kmn}B^{prs} - A^{lmn}B^{qrs} + A^{klmn}B^{pqrs} - \qquad (11) \\
& - 2t( A_{kl}B_{pq} + A_{km}B_{pr} + A_{kn}B_{ps} + A_{lm}B_{qr} + A_{ln}B_{qs} + \\
& + A_{mn}B_{rs} + A_{kl,mn}B_{pr,qs} + A_{kl,mn}B_{ps,qr} + A_{km,ln}B_{pq,rs} + \\
& + A_{km,ln}B_{ps,qr} + A_{kn,lm}B_{pq,rs} + A_{kn,lm}B_{pr,qs} ) + \\
& + 2t( A^{m}_{kl}B^{r}_{pq} + A^{n}_{kl}B^{s}_{pq} + A^{l}_{km}B^{q}_{pr} + A^{n}_{km}B^{s}_{pr} + A^{l}_{kn}B^{q}_{ps} + A^{m}_{kn}B^{r}_{ps} + \\
& + A^{k}_{lm}B^{p}_{qr} + A^{n}_{lm}B^{s}_{qr} + A^{k}_{ln}B^{p}_{qs} + A^{m}_{ln}B^{r}_{qs} + A^{k}_{mn}B^{p}_{rs} + A^{l}_{mn}B^{q}_{rs} ) - \\
& - 2t( A^{mn}_{kl}B^{rs}_{pq} + A^{ln}_{km}B^{qs}_{pr} + A^{lm}_{kn}B^{qr}_{ps} + A^{kn}_{lm}B^{ps}_{qr} + A^{km}_{ln}B^{pr}_{qs} + A^{kl}_{mn}B^{pq}_{rs} ) + \\
& + 4t^{2}( A_{kl,mn}B_{pq,rs} + A_{km,ln}B_{pr,qs} + A_{kn,lm}B_{ps,qr} )
\end{aligned}
$$

Indeed, there are 17 terms of T and S which are pairwise identically equal.

According to eq. (4) for the difference polynomial the following expression is obtained:

$$
\begin{aligned}
\Delta = {} & (A^{k} - A^{n})(B^{p} - B^{s}) + (A^{l} - A^{m})(B^{q} - B^{r}) - \\
& - (A^{kl} - A^{mn})(B^{pq} - B^{rs}) - (A^{km} - A^{ln})(B^{pr} - B^{qs}) + \\
& + (A^{klm} - A^{lmn})(B^{pqr} - B^{qrs}) + (A^{kln} - A^{kmn})(B^{pqs} - B^{prs}) + \\
& + 2t( (A_{kl} - A_{mn})(B_{pq} - B_{rs}) + (A_{km} - A_{ln})(B_{pr} - B_{qs}) ) - \\
& - 2t( (A^{m}_{kl} - A^{l}_{mn})(B^{r}_{pq} - B^{s}_{rs}) + (A^{n}_{kl} - A^{k}_{mn})(B^{s}_{pq} - B^{p}_{rs}) + \\
& + (A^{l}_{km} - A^{m}_{ln})(B^{q}_{pr} - B^{r}_{qs}) + (A^{n}_{km} - A^{k}_{ln})(B^{s}_{pr} - B^{p}_{qs}) + \qquad (12) \\
& + (A^{l}_{kn} - A^{m}_{kn})(B^{q}_{ps} - B^{r}_{ps}) + (A^{k}_{lm} - A^{n}_{lm})(B^{p}_{qr} - B^{s}_{qr}) ) + \\
& + 2t( (A^{mn}_{kl} - A^{kl}_{mn})(B^{rs}_{pq} - B^{pq}_{rs}) + (A^{ln}_{km} - A^{km}_{ln})(B^{qs}_{pr} - B^{pr}_{qs}) )
\end{aligned}
$$

When the isomorphism of the moieties, A = B, and the isomorphic mapping k ↔ p, l ↔ q, m ↔ r, and n ↔ s is assumed we have to insert the following equalities into eq. (12):

$$A^{k}=B^{p},\quad A^{l}=B^{q},\quad A^{m}=B^{r},\quad A^{n}=B^{s};$$

$$A^{kl}=B^{pq},\quad A^{km}=B^{pr},\quad A^{ln}=B^{qs},\quad A^{mn}=B^{rs};$$

$$A^{klm}=B^{pqr},\quad A^{kln}=B^{pqs},\quad A^{kmn}=B^{prs},\quad A^{lmn}=B^{qrs};$$

$$A_{kl}=B_{pq},\quad A_{km}=B_{pr},\quad A_{ln}=B_{qs},\quad A_{mn}=B_{rs};$$

$$A_{kl}^{m}=B_{pq}^{r},\quad A_{km}^{l}=B_{pr}^{q},\quad A_{ln}^{k}=B_{qs}^{p},\quad A_{mn}^{k}=B_{rs}^{p},$$

$$A_{kl}^{n}=B_{pq}^{s},\quad A_{km}^{n}=B_{pr}^{s},\quad A_{ln}^{m}=B_{qs}^{r},\quad A_{mn}^{l}=B_{rs}^{q};$$

$$A_{kn}^{l}=B_{ps}^{q},\quad A_{kn}^{m}=B_{ps}^{r},\quad A_{lm}^{k}=B_{qr}^{p},\quad A_{lm}^{n}=B_{qr}^{s};$$

$$A_{kl}^{mn}=B_{pq}^{rs},\quad A_{km}^{ln}=B_{pr}^{qs},\quad A_{ln}^{km}=B_{qs}^{pr},\quad A_{mn}^{kl}=B_{rs}^{pq}.$$

Thus, eq. (12) takes the following form:

$$\begin{aligned}
\Delta = \; & (A^{k} - A^{n})^{2} + (A^{l} - A^{m})^{2} - (A^{kl} - A^{mn})^{2} - (A^{km} - A^{ln})^{2} + \\
& + (A^{klm} - A^{lmn})^{2} + (A^{kln} - A^{kmn})^{2} + \\
& + 2t(\, (A_{kl} - A_{mn})^{2} + (A_{km} - A_{ln})^{2} \,) - \qquad (13) \\
& - 2t(\, (A_{kl}^{m} - A_{mn}^{l})^{2} + (A_{kl}^{n} - A_{mn}^{k})^{2} + (A_{km}^{l} - A_{ln}^{m})^{2} + \\
& + (A_{km}^{n} - A_{ln}^{k})^{2} + (A_{kn}^{l} - A_{kn}^{m})^{2} + (A_{lm}^{k} - A_{lm}^{n})^{2} \,) + \\
& + 2t(\, (A_{kl}^{mn} - A_{mn}^{kl})^{2} + (A_{km}^{ln} - A_{ln}^{km})^{2} \,)
\end{aligned}$$

Obviously, Δ could be negative in some intervals of its variable, hence, inversions in the TEMO pattern cannot be excluded.

2.4. Summary: model 1

TEMO without inversions has to be expected within the model 1 only if the building subunits are isomorphic, A = B, and they are linked by exactly two bonds.

In all other cases the appearance of inversions in the TEMO pattern cannot be excluded definitely. But the inability to exclude inversions does not mean that they must occur in the TEMO pattern. It may easily be verified that inversions will be realized only if (i) the difference polynomial $\Delta = 0$ has real roots of an odd degeneracy (single roots, threefold roots, etc.) and (ii) the characteristic polynomials T and/or S have eigenvalues in at least one range of the variable where $\Delta$ is negative.

It should be mentioned here, that some pairs of topologically related isomers constructed by means of model 1, A=B, $l>2$, might be also obtained from other models, e.g. from those described in section 3 and 4 of this note. In some particular cases [5] inversions may be excluded if the other model is applied to such a pair.

In the last columns of the Tables 1, 2, and 4, the number of contributions to $\Delta$ are listed; these are terms of T and S, respectively, which do not cancel each other when $\Delta$ is formed according to eq. (4). Hence, $\Delta$ has just twice the number of terms as indicated in these columns. It follows from these Tables, for $l = 2, 3, 4$, that the number of the terms of $\Delta$ are 4, 16, and 64, respectively; this might be generalized to $4^{l-1}$. However, with increasing $l$ new types of terms are created; hence, $4^{l-1}$ is only the lower limit for the number of terms of the difference polynomial (for $l = 5$, $\Delta$ would consist of 336 terms, there are 80 terms more than would follow from $4^{l-1}$). Since about half of these terms are summed up to Δ with a positive sign, the other half with a negative sign, only in the case of $l = 2$ is there a real chance to draw conclusions about the non-appearance of inversions in the TEMO pattern. This fact is also the reason that TEMO formulae for $l>2$ have not been published until now.

## 3. Model 2

In this model the S and the T isomers are formed from three subunits: two terminal ones, A and B, and a central one, C. The terminal moieties are linked to the central one by l edges each, $l = 2, 3, 4$. Thus, there are two edge cut sets: the first one, denoted by $e = \{e_j | j = 1, 2, \ldots, l\}$, is formed from the edges linking A and C, the other one, $f = \{f_j | j = 1, 2, \ldots, l\}$, from those linking B and C. The edges $e_j$ and $f_j$ have one of their endpoints in common, namely the one which belongs to C.

We meet here another new type of term in the characteristic polynomials; the cycles removed according to the last term of eq. (1) may have either $e^2$ or $f^2$ or $e^2f^2$ configuration.

The central moiety, C, may be represented either by a connected or a disconnected graph. In order to derive the TEMO formulae, there is no need to specify this property of C because the characteristic polynomials of non-existent subgraphs are identically zero.

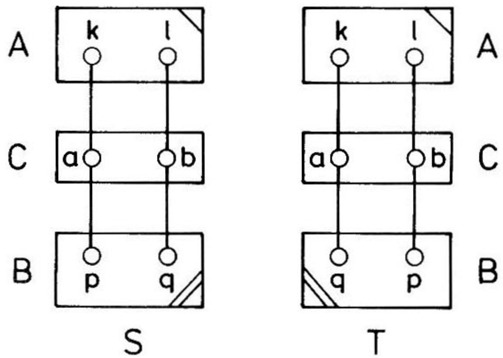
If eq. (1) is applied $2l$ times, then all the edges of the cut sets are removed. The resulting expressions of the characteristic polynomials T and S consist of a number of terms, each one a product of three characteristic polynomials corresponding to subgraphs of A, B, and C, respectively.

After setting up the difference polynomial Δ according to eq. (4), some symmetry in C is assumed; this usually reduces the number of terms of Δ. A further reduction is achieved if the isomorphism of the terminal moieties, A = B, is assumed, leading to the final result.

In the following subsections the value of l is specified. At the beginning of each subsection a schematic representation of the model is given which also exhibits the labelling of the vertices; in a Table the number and types of the different terms of T and S are indicated.

3.1. Model 2, l = 2

The general structure of the S and the T isomer formed within this model are schematically depicted below:




In Table 5 the number of the terms and their types are listed.

Table 5: Number and types of terms, model 2, l=2:

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contributing to T and S | equal in T and S | contributing to Δ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 4 | 2 | 2 |
| 0 | 2 | 4 | 2 | 2 |
| 1 $e^2$ | 0 | 1 | 1 | 0 |
| 1 $f^2$ | 0 | 1 | 1 | 0 |
| 1 $e^2f^2$ | 0 | 1 | 1 | 0 |
| | | 12 | 8 | 4 |

The characteristic polynomial T and S are obtained as follows:

$$T = ABC - A^kBC^a - A^lBC^b - AB^qC^a - AB^pC^b + A^{kl}BC^{ab} + A^kB^pC^{ab} + A^lB^qC^{ab} + AB^{pq}C^{ab} - 2t(A_{kl}BC_{ab} + AB_{pq}C_{ab} + A_{kl}B_{pq}C^{ab}) \quad (14)$$

$$S = ABC - A^kBC^a - A^lBC^b - AB^pC^a - AB^qC^b + A^{kl}BC^{ab} + A^kB^qC^{ab} + A^lB^pC^{ab} + AB^{pq}C^{ab} - 2t(A_{kl}BC_{ab} + AB_{pq}C_{ab} + A_{kl}B_{pq}C^{ab})$$

From this, according to eq. (4), the difference polynomial results in

$$\Delta = A(B^p - B^q)(C^a - C^b) + (A^k - A^l)(B^p - B^q)C^{ab} . \qquad (15)$$

If a symmetric structure of C is assumed which allows the automorphic mapping of the vertex a onto the vertex b, we have the equality

$$C^a = C^b ,$$

and consequently the first term of eq. (15) vanishes.
Thus, one obtains

$$\Delta = (A^k - A^l)(B^p - B^q)C^{ab} . \qquad (16)$$

Assuming now the isomorphism A = B (for details see subsection 2,1), eq. (16) takes the following form:

$$\Delta = (A^k - A^l)^2 C^{ab} . \qquad (17)$$

Obviously, the sign of Δ and the one of $C^{ab}$ must coincide, i.e., Δ will be positive in the complete range of the variable if and only if the same is true for $C^{ab}$.

One could imagine several structures of C which are in accord with that demand. But regarding C as a part of a chemical constitution, it will be of sufficient generality to consider only such structures of C in which the vertices a and b are articulations

[15]. In Figure 1 such a general structure is represented. Obviously, in the notations used there, one obtains

$$C^{ab} = FGH \ .$$

Let P denote the automorphic mapping of C mentioned above, i.e.: Pa = b and Pb = a. As may be seen from Fig. 1 this mapping implies

$$PF = G \ , \quad PG = F \ , \quad PH = H \ . \tag{18}$$

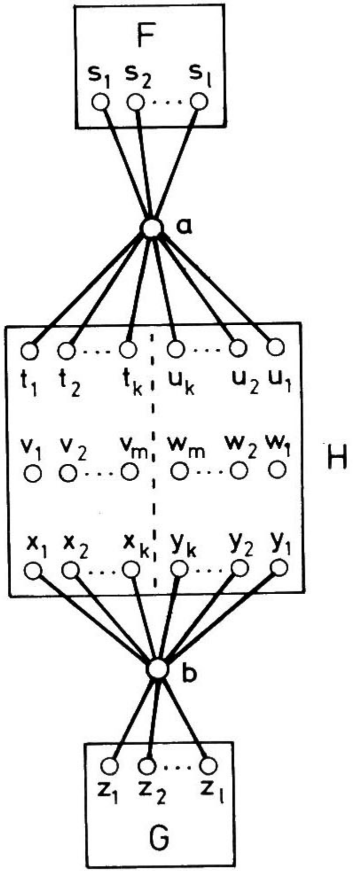



Figure 1: Schematic representation of the central subunit C in the case of model 2, $l = 2$.

From the first two of these relations one may conclude that F and G denote isomorphic subgraphs in Fig. 1; hence, their characteristic polynomials are identically equal, $F = G$, and consequently $C^{ab}$ takes the form

$$C^{ab} = F^2 H \ .$$

In order to obtain a quadratic form for $C^{ab}$, the characteristic polynomial H must be a square, say $H = [h(x)]^2$. This is achieved simply if H represents either (i) an empty graph the characteristic polynomial of which equals $1 = 1^2$ by definition (in this case the vertices a and b would be either disconnected or adjacent in C) or (ii) an even Möbius-cycle (or the union of an arbitrary number of even Möbius-cycles or pairs of odd Möbius- or even/odd Hückel-cycles) or (iii) a non-empty graph which may be partitioned into pairs of isomorphic components (as indicated in Fig. 1 by the broken line). Let $H_j$ and $H_{j'}$ denote such a pair of isomorphic components of H, $1 \leq j \leq J$, then their characteristic polynomials are identically equal, $H_{j'} = H_j$, and consequently H will take the following form

$$H = \prod_{j=1}^{J} H_j^2 \ . \tag{19}$$

In this way one really obtains a quadratic form for $C^{ab}$ as demanded, namely:

$$C^{ab} = F^2 \prod_{j=1}^{J} H_j^2 \ . \tag{20}$$

The condition stated in (ii) implies another symmetry operation, Q, which maps automorphically the pairwise isomorphic components, $H_{j'}$ and $H_j$, onto each other, but all the other vertices of C onto themselves. Thus the effect of Q is expressed by the following relations:

$$Qa = a \,, \qquad Qb = b \,;$$
$$QF = F \,, \qquad QG = G \,; \qquad (21)$$
$$QH_j = H_{j'} \,, \qquad QH_{j'} = H_j \,.$$

It may easily be verified that the two symmetry operators, P and Q, commute; thus, we have in addition

$$R = PQ = QP \,. \qquad (22)$$

Together with the identical mapping, E, these symmetry operators form a group, {E,P,Q,R}, which represents necessarily a subgroup of the automorphism group of the graph C,

$$\{E,P,Q,R\} \subseteq A(C) \,. \qquad (23)$$

In order to complete the discussion of the symmetry of the central moiety C, we briefly consider the cycle structure (cs) of P, Q, and R, respectively. Let 2n and 2h denote the number of vertices of C and H, respectively (it will turn out below that these numbers must be even!).

According to eq. (18) the symmetry operator P consists of permutations such as

$$\begin{pmatrix} a & b \\ b & a \end{pmatrix}, \begin{pmatrix} s_\lambda z_\lambda \\ z_\lambda s_\lambda \end{pmatrix}, \begin{pmatrix} t_\kappa x_\kappa \\ x_\kappa t_\kappa \end{pmatrix}, \begin{pmatrix} u_\kappa y_\kappa \\ y_\kappa u_\kappa \end{pmatrix}, \begin{pmatrix} v_\mu \\ v_\mu \end{pmatrix}, \begin{pmatrix} w_\mu \\ w_\mu \end{pmatrix}.$$

Thus, its cycle structure is expressed as

$$cs(P) = [2]^{n-m}[1]^{2m} \quad . \tag{24}$$

where m denotes the cardinalities of the vertex subsets $\{v_\mu\} \in H$ and $\{w_\mu\} \in H$. In these subsets those vertices are collected which are the only ones which are mapped identically onto themselves by the symmetry operator P.

As seen from eq. (21) the symmetry operator Q is constructed from permutations such as

$$\begin{pmatrix} a \\ a \end{pmatrix}, \begin{pmatrix} b \\ b \end{pmatrix}, \begin{pmatrix} s_\lambda \\ s_\lambda \end{pmatrix}, \begin{pmatrix} z_\lambda \\ z_\lambda \end{pmatrix}, \begin{pmatrix} t_\kappa u_\kappa \\ u_\kappa t_\kappa \end{pmatrix}\begin{pmatrix} x_\kappa y_\kappa \\ y_\kappa x_\kappa \end{pmatrix}\begin{pmatrix} v_\mu w_\mu \\ w_\mu v_\mu \end{pmatrix}.$$

Thus, for the cycle structure of Q one obtains

$$cs(Q) = [2]^{h}[1]^{2n-2h} \quad . \tag{25}$$

It may easily be verified that the symmetry operator R = PQ = QP consists of permutations such as

$$\begin{pmatrix} a & b \\ b & a \end{pmatrix}, \begin{pmatrix} s_\lambda z_\lambda \\ z_\lambda s_\lambda \end{pmatrix}, \begin{pmatrix} t_\kappa y_\kappa \\ y_\kappa t_\kappa \end{pmatrix}, \begin{pmatrix} u_\kappa y_\kappa \\ x_\kappa u_\kappa \end{pmatrix}, \begin{pmatrix} v_\mu w_\mu \\ w_\mu v_\mu \end{pmatrix}.$$

Thus, its cycle structure is expressed as

$$cs(R) = [2]^{n} \quad . \tag{26}$$

From eq. (26) it immediately follows that the number of vertices of C must be even and equal 2n. This implies that the number of vertices of the subunit H must also be even and equal 2h, because the other two subunits are isomorphic, F = G, and hence, they must have together an even number of vertices; this is clearly in accord with the conclusion drawn from eq. (25). The subsets $\{v_\mu\}$ and $\{w_\mu\}$ may be empty or not, but in any case they must have the same cardinality m, in order to make the symmetry operations Q and R = PQ = QP feasible. It should be noted that the existence of the symmetry operation Q is necessary for obtaining a quadratic form for the characteristic polynomial H as given by eq. (19).

Some examples of moieties C which exhibit the symmetry described above are given elsewhere [5].

Summarizing, one may conclude: TEMO without inversions is expected within model 2, if all the following conditions are satisfied:

(i) The terminal subunits are isomorphic, A = B.

(ii) Each terminal subunit is linked by two edges (bonds) to the central one.

(iii) the symmetry of the central moiety, C, complies with eq. (23).

It should be noted, that the symmetry described by eq. (23) is sufficient but not necessary in order to achieve $C^{ab} \geq 0$ in the complete range of the variable.

3.2. Model 2, l = 3

The general structure of the S and the T isomer formed within this model is schematically depicted below:

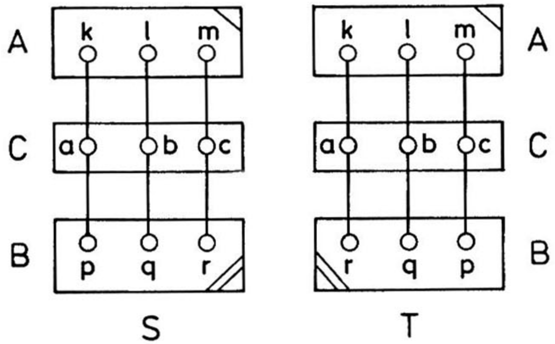



Table 6 lists the number of terms and their types.

Table 6 : Number and types of terms, model 2, l = 3 :

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contributing to T and S | equal in T and S | contributing to Δ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 6 | 4 | 2 |
| 0 | 2 | 12 | 6 | 6 |
| 0 | 3 | 8 | 4 | 4 |
| 1 $e^2$ | 0 | 3 | 3 | 0 |
| 1 $f^2$ | 0 | 3 | 1 | 2 |
| 1 $e^2f^2$ | 0 | 9 | 3 | 6 |
| 1 $e^2$ | 1 | 6 | 4 | 2 |
| 1 $f^2$ | 1 | 6 | 2 | 4 |
| 1 $e^2f^2$ | 1 | 6 | 2 | 4 |
| | | 60 | 30 | 30 |

The characteristic polynomials T and S have the following forms:

$$
\begin{aligned}
T = {} & ABC - A^{k}BC^{a} - A^{l}BC^{b} - A^{m}BC^{c} - AB^{r}C^{a} - AB^{q}C^{b} - AB^{p}C^{c} + \\
& + A^{kl}BC^{ab} + A^{km}BC^{ac} + A^{lm}BC^{bc} + A^{k}B^{q}C^{ab} + A^{k}B^{p}C^{ac} + \\
& + A^{l}B^{r}C^{ab} + A^{l}B^{p}C^{bc} + A^{m}B^{r}C^{ac} + A^{m}B^{q}C^{bc} + AB^{qr}C^{ab} + \\
& + AB^{pr}C^{ac} + AB^{pq}C^{bc} - A^{klm}BC^{abc} - A^{kl}B^{p}C^{abc} - A^{km}B^{q}C^{abc} - \\
& - A^{lm}B^{r}C^{abc} - A^{k}B^{pq}C^{abc} - A^{l}B^{pr}C^{abc} - A^{m}B^{qr}C^{abc} - \\
& - AB^{pqr}C^{abc} - 2t( A_{kl}BC_{ab} + A_{km}BC_{ac} + A_{lm}BC_{bc} + \\
& + AB_{qr}C_{ab} + AB_{pr}C_{ac} + AB_{pq}C_{bc} + A_{kl}B_{qr}C^{ab} + A_{kl}B_{pr}C^{a}_{bc} + \\
& + A_{kl}B_{pq}C^{b}_{ac} + A_{km}B_{qr}C^{a}_{bc} + A_{km}B_{pr}C^{ac} + A_{km}B_{pq}C^{c}_{ab} + \qquad (27) \\
& + A_{lm}B_{qr}C^{b}_{ac} + A_{lm}B_{pr}C^{c}_{ab} + A_{lm}B_{pq}C^{bc} ) + \\
& + 2t( A^{m}_{kl}BC^{c}_{ab} + A^{l}_{km}BC^{b}_{ac} + A^{k}_{lm}BC^{a}_{bc} + A_{kl}B^{p}C^{c}_{ab} + \\
& + A_{km}B^{q}C^{b}_{ac} + A_{lm}B^{r}C^{a}_{bc} + A^{m}B_{qr}C^{c}_{ab} + A^{l}B_{pr}C^{b}_{ac} + A^{k}B_{pq}C^{a}_{bc} + \\
& + AB^{p}_{qr}C^{c}_{ab} + AB^{q}_{pr}C^{b}_{ac} + AB^{r}_{pq}C^{a}_{bc} + A^{m}_{kl}B_{qr}C^{abc} + A_{kl}B^{p}_{qr}C^{abc} + \\
& + A^{l}_{km}B_{pr}C^{abc} + A_{km}B^{q}_{pr}C^{abc} + A^{k}_{lm}B_{pq}C^{abc} + A_{lm}B^{r}_{pq}C^{abc} )
\end{aligned}
$$

$$
\begin{aligned}
S = {} & ABC - A^{k}BC^{a} - A^{l}BC^{b} - A^{m}BC^{c} - AB^{p}C^{a} - AB^{q}C^{b} - AB^{r}C^{c} + \\
& + A^{kl}BC^{ab} + A^{km}BC^{ac} + A^{lm}BC^{bc} + A^{k}B^{q}C^{ab} + A^{k}B^{r}C^{ac} + \\
& + A^{l}B^{p}C^{ab} + A^{l}B^{r}C^{bc} + A^{m}B^{p}C^{ac} + A^{m}B^{q}C^{bc} + AB^{pq}C^{ab} + \\
& + AB^{pr}C^{ac} + AB^{qr}C^{bc} - A^{klm}BC^{abc} - A^{kl}B^{r}C^{abc} - A^{km}B^{q}C^{abc} - \\
& - A^{lm}B^{p}C^{abc} - A^{k}B^{qr}C^{abc} - A^{l}B^{pr}C^{abc} - A^{m}B^{pq}C^{abc} - \\
& - AB^{pqr}C^{abc} - 2t(\, A_{kl}BC_{ab} + A_{km}BC_{ac} + A_{lm}BC_{bc} + \\
& + AB_{pq}C_{ab} + AB_{pr}C_{ac} + AB_{qr}C_{bc} + A_{kl}B_{pq}C^{ab} + A_{kl}B_{pr}C^{a}_{bc} + \\
& + A_{kl}B_{qr}C^{b}_{ac} + A_{km}B_{pq}C^{a}_{bc} + A_{km}B_{pr}C^{ac} + A_{km}B_{qr}C^{c}_{ab} + \\
& + A_{lm}B_{pq}C^{b}_{ac} + A_{lm}B_{pr}C^{c}_{ab} + A_{lm}B_{qr}C^{bc} \,) + \\
& + 2t(\, A^{m}_{kl}BC^{c}_{ab} + A^{l}_{km}BC^{b}_{ac} + A^{k}_{lm}BC^{a}_{bc} + A_{kl}B^{r}C^{c}_{ab} + \\
& + A_{km}B^{q}C^{b}_{ac} + A_{lm}B^{p}C^{a}_{bc} + A^{m}B_{pq}C^{c}_{ab} + A^{l}B_{pr}C^{b}_{ac} + A^{k}B_{qr}C^{a}_{bc} + \\
& + AB^{r}_{pq}C^{c}_{ab} + AB^{q}_{pr}C^{b}_{ac} + AB^{p}_{qr}C^{a}_{bc} + A^{m}_{kl}B_{pq}C^{abc} + A_{kl}B^{r}_{pq}C^{abc} + \\
& + A^{l}_{km}B_{pr}C^{abc} + A_{km}B^{q}_{pr}C^{abc} + A^{k}_{lm}B_{qr}C^{abc} + A_{lm}B^{p}_{qr}C^{abc} \,)
\end{aligned}
\tag{27}
$$

Inserting these expressions into eq. (4) one obtains:

$$
\begin{aligned}
\Delta = {} & A(B^{p} - B^{r})(C^{a} - C^{c}) + (A^{k} - A^{m})(B^{p} - B^{r})C^{ac} - \\
& - A^{l}(B^{p} - B^{r})(C^{ab} - C^{bc}) - A(B^{pq} - B^{qr})(C^{ab} - C^{bc}) - \\
& - (A^{kl} - A^{lm})(B^{p} - B^{r})C^{abc} - (A^{k} - A^{m})(B^{pq} - B^{qr})C^{abc} + \\
& + 2t(\, A(B_{pq} - B_{qr})(C_{ab} - C_{bc}) + A_{kl}(B_{pq} - B_{qr})(C^{ab} - C^{b}_{ac}) + \\
& + A_{km}(B_{pq} - B_{qr})(C^{a}_{bc} - C^{c}_{ab}) - A_{lm}(B_{pq} - B_{qr})(C^{bc} - C^{b}_{ac}) \,) + \\
& + 2t(\, A_{kl}(B^{p} - B^{r})C^{c}_{ab} - A_{lm}(B^{p} - B^{r})C^{a}_{bc} + A^{k}(B_{pq} - B_{qr})C^{a}_{bc} - \\
& - A^{m}(B_{pq} - B_{qr})C^{c}_{ab} - (A^{m}_{kl} - A^{k}_{lm})(B_{pq} - B_{qr})C^{abc} + \\
& + A(B^{r}_{pq} - B^{p}_{qr})(C^{a}_{bc} - C^{c}_{ab}) - (A_{kl} - A_{lm})(B^{r}_{pq} - B^{p}_{qr})C^{abc} \,)
\end{aligned}
\tag{28}
$$

We now assume that the central moiety has a symmetry such that the vertex a can be mapped automorphically onto the vertex b. Then we have to consider the following equalities:

$$C^a = C^c,\ C^{ab} = C^{bc},\ C_{ab} = C_{bc},\ C^c_{ab} = C^a_{bc}.$$

By insertion of these, eq. (28) takes the form:

$$\begin{aligned}\Delta = \ & (A^k - A^m)(B^p - B^r)C^{ac} - (A^{kl} - A^{lm})(B^p - B^r)C^{abc} - \\ & - (A^k - A^m)(B^{pq} - B^{qr})C^{abc} + \\ & + 2t[\ (A_{kl} - A_{lm})(B_{pq} - B_{qr})(C^{ab} - C^b_{ac})\ ) + \\ & + 2t(\ (A_{kl} - A_{lm})(B^p - B^r)C^c_{ab} + (A^k - A^m)(B_{pq} - B_{qr})C^c_{ab} - \\ & - (A^m_{kl} - A^k_{lm})(B_{pq} - B_{qr})C^{abc} - (A_{kl} - A_{lm})(B^r_{pq} - B^p_{qr})C^{abc}]\end{aligned} \tag{29}$$

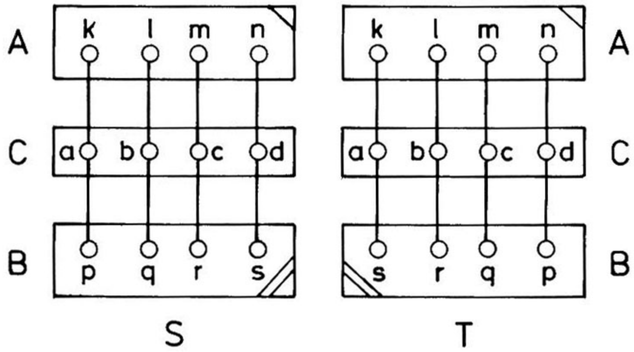
In the case of isomorphic terminal moieties, A = B (for details see subsection 2,2), eq. (29) takes the form:

$$\begin{aligned}\Delta = \ & (A^k - A^m)^2C^{ac} - 2(A^k - A^m)(A^{kl} - A^{lm})C^{abc} + \\ & + 2t[\ (A_{kl} - A_{lm})^2(C^{ab} - C^b_{ac}) + 2(A^k - A^m)(A_{kl} - A_{lm})C^c_{ab} - \\ & - 2(A_{kl} - A_{lm})(A^m_{kl} - A^k_{lm})C^{abc}\ ]\end{aligned} \tag{30}$$

According to this expression the appearance of inversions in the TEMO pattern cannot be excluded.

### 3.3. Model 2, l = 4

The general structure of the S and the T isomer formed within this model is schematically depicted below:




In Table 7 the number and the types of the terms of the polynomials T, S, and Δ are given. We here meet new types of cyclic contributions, namely five monocyclic and six bicyclic ones.

As indicated in Table 7 the characteristic polynomials T and S consist of 396 terms each. Because of the length of these formulae they are not given explicitely. Out of the 396 terms there are 144 which are identically equal in T and S; they cancel each other when the difference polynomial Δ is formed according to eq. (4). Thus, the difference polynomial Δ consists of 504 terms in all, half of them contributed from T and from S, respectively. Again, in view of the length of this formulae, it is not given here explicitely.

Table 7: Number and types of terms, model 2, l = 4 :

| There have been removed | | | number of terms | | |
|---|---|---|---|---|---|
| cycles | | endpoints of edges | contributing to T and S | equal in T and S | contributing to |
| | 0 | 0 | 1 | 1 | 0 |
| | 0 | 1 | 8 | 4 | 4 |
| | 0 | 2 | 24 | 8 | 16 |
| | 0 | 3 | 32 | 8 | 24 |
| | 0 | 4 | 16 | 4 | 12 |
| 1 | $e^2$ | 0 | 6 | 6 | 0 |
| 1 | $f^2$ | 0 | 6 | 2 | 4 |
| 1 | $e^4$ | 0 | 6 | 6 | 0 |
| 1 | $e^2f^2$ | 0 | 42 | 14 | 14 |
| 1 | $f^4$ | 0 | 6 | 6 | 0 |
| 1 | $e^4f^2$ | 0 | 12 | 4 | 8 |
| 1 | $e^2f^4$ | 0 | 12 | 12 | 0 |
| 1 | $e^4f^4$ | 0 | 6 | 6 | 0 |
| 1 | $e^2$ | 1 | 24 | 12 | 12 |
| 1 | $f^2$ | 1 | 24 | 4 | 20 |
| 1 | $e^2f^2$ | 1 | 72 | 12 | 60 |
| 1 | $e^2$ | 2 | 24 | 8 | 16 |
| 1 | $f^2$ | 2 | 24 | 4 | 20 |
| 1 | $e^2f^2$ | 2 | 24 | 4 | 20 |
| 2 | $e^2+e^2$ | 0 | 3 | 3 | 0 |
| 2 | $e^2+f^2$ | 0 | 6 | 2 | 4 |
| 2 | $f^2+f^2$ | 0 | 3 | 3 | 0 |
| 2 | $e^2f^2+e^2$ | 0 | 6 | 2 | 4 |
| 2 | $e^2f^2+f^2$ | 0 | 6 | 6 | 0 |
| 2 | $e^2f^2+e^2f^2$ | 0 | 3 | 3 | 0 |
| | | | 396 | 144 | 252 |

Suppose, the central subunit, C, has a symmetry such that the vertices a and b may be mapped automorphically onto the vertices c and d, respectively,

$$a \leftrightarrow d \,, \qquad b \leftrightarrow c \,.$$

Then one has the following equalities (among others):

$$\begin{array}{llll} C^a = C^d \,, & C^b = C^c \,; & C^{ab} = C^{cd} \,, & C^{ac} = C^{bd} \,; \\ C^{abc} = C^{bcd} \,, & C^{abd} = C^{acd} \,; & C_{ab} = C_{cd} \,, & C_{ac} = C_{bd} \,; \\ C^c_{ab} = C^b_{cd} \,, & C^d_{ab} = C^a_{cd} \,, & C^b_{ac} = C^c_{bd} \,, & C^d_{ac} = C^a_{bd} \,, \\ C^b_{ad} = C^c_{ad} \,, & C^a_{bc} = C^d_{bc} \,; & C^{cd}_{ab} = C^{ab}_{cd} \,, & C^{bd}_{ac} = C^{ac}_{bd} \,. \end{array}$$

Inserting these equalities into the expression obtained for $\Delta$, there are 168 terms which cancel each other and the number of terms of the difference polynomial is reduced in this way to 336 terms; of these 64 terms are non-cyclic, 264 terms monocyclic, and 8 terms bicyclic. Once again, in view of the length of this formula, it is not given here explicitely.

In case that A and B are isomorphic, A = B (for details see subsection 2,3), one finally obtains:

$$\begin{aligned} \Delta = \; & (A^k - A^n)^2 C^{ad} + (A^l - A^m)^2 C^{bc} - \\ & - 2(A^k - A^n)(A^l - A^m)(C^{ab} - C^{ac}) - \\ & - 2(A^k - A^n)(A^{kl} + A^{km} - A^{ln} - A^{mn})C^{abd} - \\ & - 2(A^l - A^m)(A^{kl} + A^{km} - A^{ln} - A^{mn})C^{abc} + \\ & + 2(A^k - A^n)(A^{klm} - A^{lmn})C^{abcd} + \\ & + 2(A^l - A^m)(A^{kln} - A^{kmn})C^{abcd} + \\ & + 2t \, [\, (A_{kl} - A_{mn})^2 (C^{ab} - C_{ac,bd} - C_{ad,bc}) + \\ & + (A_{km} - A_{ln})^2 (C^{ac} - C_{ab,cd} - C_{ad,bc}) - \end{aligned} \qquad (31)$$

$$- 2(A_{kl} - A_{mn})(A_{km} - A_{ln})(C^{b}_{ad} - C^{a}_{bc}) +$$

$$+ 2(A^{k} - A^{n})(A_{kl} - A_{mn})C^{d}_{ab} + 2(A^{k} - A^{n})(A_{km} - A_{ln})C^{d}_{ac} +$$

$$+ 2(A^{l} - A^{m})(A_{kl} - A_{mn})C^{c}_{ab} - 2(A^{l} - A^{m})(A_{km} - A_{ln})C^{b}_{ac} -$$

$$- 2(A_{kl} - A_{mn})(A^{m}_{kl} - A^{l}_{mn})C^{abc} - 2(A_{kl} - A_{mn})(A^{n}_{kl} - A^{k}_{mn})C^{abd} -$$

$$- 2(A_{km} - A_{ln})(A^{l}_{km} - A^{m}_{ln})C^{abc} - 2(A_{km} - A_{ln})(A^{n}_{km} - A^{k}_{ln})C^{abd} +$$

$$+ 2(A_{km} - A_{ln})(A^{m}_{kn} - A^{l}_{kn} - A^{n}_{lm} + A^{k}_{lm})C^{cd}_{ab} +$$

$$+ 2(A_{kl} - A_{mn})(A^{l}_{kn} - A^{m}_{kn} - A^{n}_{lm} + A^{k}_{lm})C^{bd}_{ac} +$$

$$+ 2(A_{kl} - A_{mn})(A^{l}_{km} - A^{m}_{ln})C^{bc}_{ad} + 2(A_{km} - A_{ln})(A^{m}_{kl} - A^{l}_{mn})C^{bc}_{ad} -$$

$$- 2(A_{kl} - A_{mn})(A^{n}_{km} - A^{k}_{ln})C^{ad} - 2(A_{km} - A_{ln})(A^{n}_{kl} - A^{k}_{mn})C^{ad}_{bc} +$$

$$+ (A^{k} - A^{n})(A^{n}_{km} - A^{k}_{ln} + A^{l}_{km} - A^{m}_{ln})C^{bd}_{ab} -$$

$$- 2(A^{k} - A^{n})(A^{m}_{kl} - A^{l}_{mn})C^{cd}_{ab} - 2(A^{k} - A^{n})(A^{k}_{lm} - A^{n}_{lm})C^{ad}_{bc} -$$

$$- 2(A^{l} - A^{m})(A^{n}_{kl} - A^{k}_{mn})C^{cd}_{ab} + 2(A^{l} - A^{m})(A^{n}_{km} - A^{k}_{ln})C^{bd}_{ac} -$$

$$- 2(A^{l} - A^{m})(A^{l}_{kn} - A^{m}_{kn})C^{bc} -$$

$$- 2(A^{kl} - A^{mn})(A_{kl} - A_{mn})C^{cd}_{ab} - 2(A^{km} - A^{ln})(A_{km} - A_{ln})C^{bd}_{ac} +$$

$$+ 2(A_{kl} - A_{mn})(A^{mn}_{kl} - A^{kl}_{mn})C^{abcd} +$$

$$+ 2(A_{km} - A_{ln})(A^{ln}_{km} - A^{km}_{ln})C^{abcd} +$$

$$+ 2(A^{n}_{kl} - A^{k}_{mn})(A^{m}_{kl} - A^{l}_{mn})C^{abcd} +$$

$$+ 2(A^{l}_{km} - A^{m}_{ln})(A^{n}_{km} - A^{k}_{ln})C^{abcd} - \qquad (31)$$

$$- [(A^{l}_{kn} - A^{m}_{kn})^2 C^{abcd} - (A^{k}_{lm} - A^{n}_{lm})^2 C^{abcd}] +$$

$$+ 4t^2[(A_{kl} - A_{mn})^2 C_{ab,cd} + (A_{km} - A_{ln})^2 C_{ac,bd}]$$

Obviously, from this expression the appearance of inversions in the TEMO pattern cannot be excluded.

### 3,4. Summary: model 2

In the case of this model one can only exclude definitely the appearance of inversions in the TEMO pattern if the terminal moieties are isomorphic, A = B, and linked to the central moiety C by not more than two bonds, i.e.: l = 2, and, in addition, the central moiety, C, exhibits a symmetric structure such that the polynomial corresponding to $C^{ab}$ has the form of a square. The structural conditions for this are briefly discussed in subsection 3,1; some concrete examples for such structures are given in [5].

## 4. Model 3

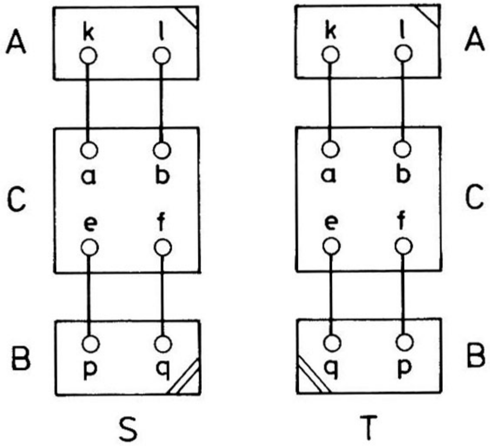
This model resembles model 2. Here again the S and the T isomer are formed from three subunits: two terminal ones, A and B, and a central one, C. The terminal subunits are linked by l edges each to the central one, l = 2, 3, 4. Thus, there are again two edge cut sets, $e = \{e_j | j = 1, 2, \ldots, l\}$ and $f = \{f_j | j = 1, 2, \ldots, l\}$, collecting the linking edges between A and C and those between B and C, respectively. But in contrast to model 2, the edges of these two cut sets have no endpoint in common. the endpoints of the edges $e_j$ belonging to C will be denoted by a, b, c, d and those of $f_j$ by e, f, g, h. In order that the isomers S and T correspond to a connected graph, there must be some connections in C between at least two vertices of the first subset {a, b, c, d} and two of {e, f, g, h}. In the case of model 2 it was not necessary to introduce such a condition because the connection of the graphs was guaranted by the fact that the edges $e_j$ and $f_j$ have a common endpoint within model 2.

The types of terms which appear here are similar to those met already in the case of model 2. There is only a slight increase in the number of degrees of freedom of combinations here: While in model 2 the simultaneous removal of the endpoints of $e_j$ and $f_j$ is impossible because this pair of edges has by definition an endpoint in common, such a simultaneous removal can be carried out within the present model and must be considered for the sake of the completeness of the set of combinations. Certainly, this leads to a higher number of terms in the polynomial considered.

In all other details the models 2 and 3 are very close to each other; hence, model 3 is treated similarly to model 2.

## 4.1. Model 3, $l = 2$

The general structure of the S and the T isomer formed within this model is schematically depicted below:




In Table 8 the number of the terms and their types are listed. Apart from non-cyclic and monocyclic terms there is also a bicyclic term. The characteristic polynomials T and S consist of 27 terms each, the difference polynomial Δ of 2 x 10 = 20 terms.

Table 8: Number and types of terms, model 3, l = 2 :

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contributing to T and S | equal in T and S | contributing to Δ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 4 | 2 | 2 |
| 0 | 2 | 6 | 2 | 4 |
| 0 | 3 | 4 | 2 | 2 |
| 0 | 4 | 1 | 1 | 0 |
| 1 $e^2$ | 0 | 1 | 1 | 0 |
| 1 $f^2$ | 0 | 1 | 1 | 0 |
| 1 $e^2f^2$ | 0 | 2 | 2 | 0 |
| 1 $e^2$ | 1 | 2 | 0 | 2 |
| 1 $f^2$ | 1 | 2 | 2 | 0 |
| 1 $e^2$ | 2 | 1 | 1 | 0 |
| 1 $f^2$ | 2 | 1 | 1 | 0 |
| 2 $e^2+f^2$ | 0 | 1 | 1 | 0 |
| | | 27 | 17 | 10 |

The characteristic polynomials are obtained as follows:

$$
\begin{aligned}
T \; = \; & ABC - A^{k}BC^{a} - A^{l}BC^{b} - AB^{q}C^{e} - AB^{p}C^{f} + A^{kl}BC^{ab} + A^{k}B^{q}C^{ae} + \\
& + A^{k}B^{p}C^{af} + A^{l}B^{q}C^{be} + A^{l}B^{p}C^{bf} + AB^{pq}C^{ef} - A^{kl}B^{q}C^{abe} - \\
& - A^{kl}B^{p}C^{abf} - A^{k}B^{pq}C^{aef} - A^{l}B^{pq}C^{bef} + A^{kl}B^{pq}C^{abef} - \\
& - 2t\,[\, A_{kl}BC_{ab} + AB_{pq}C_{ef} + A_{kl}B_{pq}C_{ae,bf} + A_{kl}B_{pq}C_{af,be} - \\
& - A_{kl}B^{q}C^{e}_{ab} - A_{kl}B^{p}C^{f}_{ab} - A^{k}B_{pq}C^{a}_{ef} - A^{l}B_{pq}C^{b}_{ef} + A_{kl}B^{pq}C^{ef}_{ab} + \\
& + A^{kl}B_{pq}C^{ab}_{ef} \,] + 4\,t^{2}\, A_{kl}B_{pq}C_{ab,ef}
\end{aligned}
\qquad (32)
$$

$$S = ABC - A^kBC^a - A^lBC^b - AB^pC^e - AB^qC^f + A^{kl}BC^{ab} + A^kB^pC^{ae} + A^kB^qC^{af} + A^lB^pC^{be} + A^lB^qC^{bf} + AB^{pq}C^{ef} - A^{kl}B^pC^{abe} - A^{kl}B^qC^{abf} - A^kB^{pq}C^{aef} - A^lB^{pq}C^{bef} + A^{kl}B^{pq}C^{abef} - 2t\,( A_{kl}BC_{ab} + AB_{pq}C_{ef} + A_{kl}B_{pq}C_{ae,bf} + A_{kl}B_{pq}C_{af,be} - A_{kl}B^pC^e_{ab} - A_{kl}B^qC^f_{ab} - A^kB_{pq}C^a_{ef} - A^lB_{pq}C^b_{ef} + A_{kl}B^{pq}C^{ef}_{ab} + A^{kl}B_{pq}C^{ab}_{ef} ) + 4\,t^2\,A_{kl}B_{pq}C_{ab,ef} \qquad (32)$$

Inserting eq. (32) into eq. (4), for the difference polynomial the following expression results:

$$\Delta = A(B^p - B^q)(C^e - C^f) - A^k(B^p - B^q)(C^{ae} - C^{af}) - A^l(B^p - B^q)(C^{be} - C^{bf}) + A^{kl}(B^p - B^q)(C^{abe} - C^{abf}) - 2t\,A_{kl}(B^p - B^q)(C^e_{ab} - C^f_{ab}) \qquad (33)$$

Assuming now that the central subunit C has a symmetric structure such that the vertex a may be mapped automorphically onto the vertex b and simultaneous the vertex e onto f and vice versa by an appropriate symmetry operator, P, i.e.:

Pa = b ,   Pb = a ,   Pe = f ,   Pf = e ,

then the following equalities have to be taken into account in eq. (33):

$$C^{e} = C^{f} \ , \quad C^{abe} = C^{abf} \ , \quad C^{e}_{ab} = C^{f}_{ab} \ ;$$
$$C^{ae} = C^{bf} \ , \quad C^{af} = C^{be} \ .$$

As a consequence of the first three equalities above, three of the five terms of eq. (33) vanish, the remaining two terms might be assembled into a single one as a consequence of the last two equalities. Thus, for the difference polynomial (under the condition of the symmetry of C as described above) one obtains

$$\Delta = (A^{k} - A^{l})(B^{p} - B^{q})(C^{af} - C^{ae}) \ . \qquad (34)$$

For the case of isomorphic terminal subunits A = B, eq. (34) takes the following form:

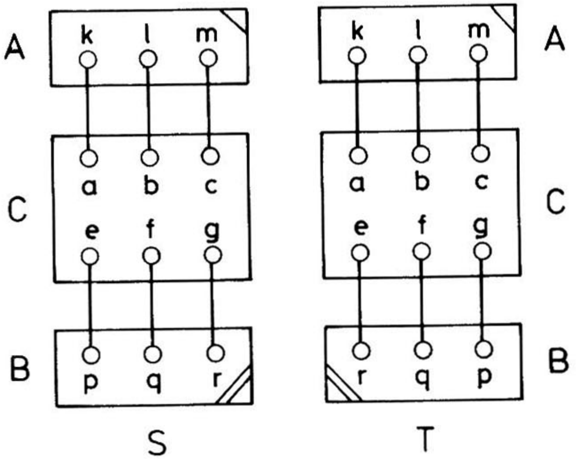
$$\Delta = (A^{k} - A^{l})^{2}(C^{af} - C^{ae}) \ . \qquad (35)$$

Obviously, $\Delta$ will be positive in the complete range of its variable if the same is true for $(C^{af}-C^{ae})$. The general structural conditions necessary for such a behaviour are rather complex; they are treated to some extent in the next note of this series [16]. In [5] some particular structures of C are given for which $(C^{af} - C^{ae})$ is positive in the complete range of the variable.

One should note that the difference polynomial $\Delta$ vanishes if $C^{ae}=C^{af}$, i.e.: the characteristic polynomial T and S are identically equal in this case. This would be realized for example if the subunit C represents a tetrahedron where, indeed, $C^{ae}=C^{af}$. In this very example the isomers S and T would correspond to two stereoisomers of one and the same compound and not to topologically related isomers.

4.2. Model 3, l = 3

The general structure of the S and the T isomer formed within this model is schematically depicted below:




In Table 9 the number of the terms and their types are listed; there are the same types of terms as in the case l = 2. But in contrast to the foregoing subsection, the bicyclic contributions to the difference polynomial Δ do not completely cancel each other.

As indicated in Table 9 the characteristic polynomials T and S consist of 268 terms each. Because of the length of these formula they are not given here explicitely. Among the 268 terms of T and S, respectively, there are 108 terms which are identically equal in T and in S. They cancel each other when the difference polynomial Δ is formed according to eq. (4). Thus, this polynomial consists of 2 x 160 = 320 terms, namely, 64 non-cyclic, 208 monocyclic, and 48 bicyclic terms.

Table 9: Number and types of terms, model 3 , $l = 3$ :

| There have been removed | | | number of terms | | |
|---|---|---|---|---|---|
| cycles | | endpoints of edges | contributing to T and S | equal in T and S | contributing to Δ |
| | 0 | 0 | 1 | 1 | 0 |
| | 0 | 1 | 6 | 4 | 2 |
| | 0 | 2 | 15 | 7 | 8 |
| | 0 | 3 | 20 | 8 | 12 |
| | 0 | 4 | 15 | 7 | 8 |
| | 0 | 5 | 6 | 4 | 2 |
| | 0 | 6 | 1 | 1 | 0 |
| 1 | $e^2$ | 0 | 3 | 3 | 0 |
| 1 | $f^2$ | 0 | 3 | 1 | 2 |
| 1 | $e^2f^2$ | 0 | 18 | 6 | 12 |
| 1 | $e^2$ | 1 | 12 | 6 | 6 |
| 1 | $f^2$ | 1 | 12 | 4 | 8 |
| 1 | $e^2f^2$ | 1 | 36 | 12 | 24 |
| 1 | $e^2$ | 2 | 18 | 6 | 12 |
| 1 | $f^2$ | 2 | 18 | 6 | 12 |
| 1 | $e^2f^2$ | 2 | 18 | 6 | 12 |
| 1 | $e^2$ | 3 | 12 | 6 | 6 |
| 1 | $f^2$ | 3 | 12 | 4 | 8 |
| 1 | $e^2$ | 4 | 3 | 3 | 0 |
| 1 | $f^2$ | 4 | 3 | 1 | 2 |
| 2 | $e^2+f^2$ | 0 | 9 | 3 | 6 |
| 2 | $e^2+f^2$ | 1 | 18 | 6 | 12 |
| 2 | $e^2+f^2$ | 2 | 9 | 3 | 6 |
| | | | 268 | 108 | 160 |

For the difference polynomial $\Delta$ the following expression is obtained:

$$
\begin{aligned}
\Delta = {} & (B^{p} - B^{r})\,[A(C^{e} - C^{g}) - A^{k}(C^{ae} - C^{ag}) - A^{l}(C^{be} - C^{bg}) - \\
& - A^{m}(C^{ce} - C^{cg}) + A^{kl}(C^{abe} - C^{abg}) + A^{km}(C^{ace} - C^{acg}) + \\
& + A^{lm}(C^{bce} - C^{bcg}) - A^{klm}(C^{abce} - C^{abcg})] - \\
& - (B^{pq} - B^{qr})\,[A(C^{ef} - C^{fg}) - A^{k}(C^{aef} - C^{afg}) - \\
& - A^{l}(C^{bef} - C^{bfg}) - A^{m}(C^{cef} - C^{cfg}) + A^{kl}(C^{abef} - \\
& - C^{abfg}) + A^{km}(C^{acef} - C^{acfg}) + A^{lm}(C^{bcef} - C^{bcfg}) - \\
& - A^{klm}(C^{abcef} - C^{abcfg})] - \\
& - 2t\ \{(B^{p} - B^{r})\,[A_{kl}(C^{e}_{ab} - C^{g}_{ab}) + A_{km}(C^{e}_{ac} - C^{g}_{ac}) + \\
& + A_{lm}(C^{e}_{bc} - C^{g}_{bc}) - A^{m}_{kl}(C^{ce}_{ab} - C^{cg}_{ab}) - A^{l}_{km}(C^{be}_{ac} - C^{bg}_{ac}) - \\
& - A^{k}_{lm}(C^{ae}_{bc} - C^{ag}_{bc})] - \qquad (36) \\
& - (B^{pq} - B^{qr})\,[A_{kl}(C^{ef}_{ab} - C^{fg}_{ab}) + A_{km}(C^{ef}_{ac} - C^{fg}_{ac}) + \\
& + A_{lm}(C^{ef}_{bc} - C^{fg}_{bc}) - A^{m}_{kl}(C^{cef}_{ab} - C^{cfg}_{ab}) - A^{l}_{km}(C^{bef}_{ac} - C^{bfg}_{ac}) - \\
& - A^{k}_{lm}(C^{aef}_{bc} - C^{afg}_{bc})] - \\
& - (B_{pq} - B_{qr})\ [A(C_{ef} - C_{fg}) - A^{k}(C^{a}_{ef} - C^{a}_{fg}) - \\
& - A^{l}(C^{b}_{ef} - C^{b}_{fg}) - A^{m}(C^{c}_{ef} - C^{c}_{fg}) + A^{kl}(C^{ab}_{ef} - C^{ab}_{fg}) + \\
& + A^{km}(C^{ac}_{ef} - C^{ac}_{fg}) + A^{lm}(C^{bc}_{ef} - C^{bc}_{fg}) - A^{klm}(C^{abc}_{ef} - C^{abc}_{fg}) + \\
& + A_{kl}(C_{ae,bf} - C_{af,bg} + C_{af,be} - C_{ag,bf}) + \\
& + A_{km}(C_{ae,cf} - C_{af,cg} + C_{af,ce} - C_{ag,cf}) + \\
& + A_{lm}(C_{be,cf} - C_{bf,cg} + C_{bf,ce} - C_{bg,cf}) - \\
& - A^{m}_{kl}(C^{c}_{ae,bf} - C^{c}_{af,bg} + C^{c}_{af,be} - C^{c}_{ag,bf}) - \\
& - A^{l}_{km}(C^{b}_{ae,cf} - C^{b}_{af,cg} + C^{b}_{af,ce} - C^{b}_{ag,cf}) - \\
& - A^{k}_{lm}(C^{a}_{be,cf} - C^{a}_{bf,cg} + C^{a}_{bf,ce} - C^{a}_{bg,cf})] +
\end{aligned}
$$

$$
\begin{aligned}
&+ (B^{r}_{pq} - B^{p}_{qr}) \; [A(C^{g}_{ef} - C^{e}_{fg}) - A^{k}(C^{ag}_{ef} - C^{ae}_{fg}) - \\
&- A^{l}(C^{bg}_{ef} - C^{be}_{fg}) - A^{m}(C^{cg}_{ef} - C^{ce}_{fg}) + A^{kl}(C^{abg}_{ef} - C^{abe}_{fg}) + \\
&+ A^{km}(C^{acg}_{ef} - C^{ace}_{fg}) + A^{lm}(C^{bcg}_{ef} - C^{bce}_{fg}) - \\
&- A^{klm}(C^{abcg}_{ef} - C^{abce}_{fg}) + \\
&+ A_{kl}(C^{g}_{ae,bf} - C^{e}_{af,bg} + C^{g}_{af,be} - C^{e}_{ag,bf}) + \\
&+ A_{km}(C^{g}_{ae,cf} - C^{e}_{af,cg} + C^{g}_{af,ce} - C^{e}_{ag,cf}) + \\
&+ A_{lm}(C^{g}_{be,cf} - C^{e}_{bf,cg} + C^{g}_{bf,ce} - C^{e}_{bg,cf}) - \\
&- A^{m}_{kl}(C^{cg}_{ae,bf} - C^{ce}_{af,bg} + C^{cg}_{af,be} - C^{ce}_{ag,bf}) - \\
&- A^{l}_{km}(C^{bg}_{ae,cf} - C^{be}_{af,cg} + C^{bg}_{af,ce} - C^{be}_{ag,cf}) - \\
&- A^{k}_{lm}(C^{ag}_{be,cf} - C^{ae}_{bf,cg} + C^{ag}_{bf,ce} - C^{ae}_{bg,cf})]\} \quad - \\
&- 4t^{2} \quad \{(B_{pq} - B_{qr}) \; [A_{kl}(C_{ab,ef} - C_{ab,fg}) + \\
&+ A_{km}(C_{ac,ef} - C_{ac,fg}) + A_{lm}(C_{bc,ef} - C_{bc,fg}) - \\
&- A^{m}_{kl}(C^{c}_{ab,ef} - C^{c}_{ab,fg}) - A^{l}_{km}(C^{b}_{ac,ef} - C^{b}_{ac,fg}) - \\
&- A^{k}_{lm}(C^{a}_{bc,ef} - C^{a}_{bc,fg})] \quad - \\
&- (B^{r}_{pq} - B^{p}_{qr}) \; [A_{kl}(C^{g}_{ab,ef} - C^{e}_{ab,fg}) + \\
&+ A_{km}(C^{g}_{ac,ef} - C^{e}_{ac,fg}) + A_{lm}(C^{g}_{bc,ef} - C^{e}_{bc,fg}) - \\
&- A^{m}_{kl}(C^{cg}_{ab,ef} - C^{ce}_{ab,fg}) - A^{l}_{km}(C^{bg}_{ac,ef} - C^{be}_{ac,fg}) - \\
&- A^{k}_{lm}(C^{ag}_{bc,ef} - C^{ae}_{bc,fg})]\}
\end{aligned}
\tag{36}
$$

Assuming now that the central subunit C has a symmetry such that simultaneously the vertices a and e may be mapped automorphically onto the vertices c and g, respectively; then, in eq. (36) the following equalities have to be considered:

$$C^{e} = C^{g}\,, \qquad C^{be} = C^{bg}\,, \qquad C^{ef} = C^{fg}\,,$$

$$C^{bef} = C^{bfg}\,, \qquad C^{abce} = C^{abcg}\,, \qquad C^{acef} = C^{acfg}\,,$$

$$C^{abcef} = C^{abcfg}\;;$$

$$C_{ef} = C_{fg}\,, \qquad C^{e}_{ac} = C^{g}_{ac}\,, \qquad C^{b}_{ef} = C^{b}_{fg}\,,$$

$$C^{g}_{ef} = C^{e}_{fg}\,, \qquad C^{be}_{ac} = C^{bg}_{ac}\,, \qquad C^{ef}_{ac} = C^{fg}_{ac}\,,$$

$$C^{ac}_{ef} = C^{ac}_{fg}\,, \qquad C^{bg}_{ef} = C^{be}_{fg}\,, \qquad C^{bef}_{ac} = C^{bfg}_{ac}\,,$$

$$C^{abc}_{ef} = C^{abc}_{fg}\,, \qquad C^{acg}_{ef} = C^{acf}_{fg}\,, \qquad C^{abcg}_{ef} = C^{abce}_{fg}\;:$$

$$C_{ac,ef} = C_{ac,fg}\,, \quad C_{ae,cf} = C_{af,cg}\,, \quad C_{af,ce} = C_{ag,cf}\,,$$

$$C^{b}_{ac,ef} = C^{b}_{ac,fg}\,, \quad C^{g}_{ac,ef} = C^{e}_{ac,fg}\,, \quad C^{b}_{ae,cf} = C^{b}_{af,cg}\,,$$

$$C^{g}_{ae,cf} = C^{e}_{af,cg}\,, \quad C^{b}_{af,ce} = C^{b}_{ag,cf}\,, \quad C^{g}_{af,ce} = C^{e}_{ag,cf}\,,$$

$$C^{bg}_{ac,ef} = C^{be}_{ac,fg}\,, \quad C^{bg}_{ae,cf} = C^{be}_{af,cg}\,, \quad C^{bg}_{af,ce} = C^{be}_{ag,cf}\,.$$

The insertion of these equalities into eq. (36) causes the corresponding terms to vanish. But there are further equalities derived from the symmetry of C which permit uniting several terms into a single one; these equalities are listed below:

$$C^{ae} - C^{ag} = -\,(C^{ce} - C^{cg})\,,$$

$$C^{abe} - C^{abg} = -\,(C^{bce} - C^{bcg}) = C^{aef} - C^{afg} = -\,(C^{cef} - C^{cfg})\,,$$

$$C^{abef} - C^{abfg} = -\,(C^{bcef} - C^{bcfg})\;:$$

$$C^{e}_{ab} - C^{g}_{ab} = -\,(C^{e}_{bc} - C^{g}_{bc}) = C^{a}_{ef} - C^{a}_{fg} = -\,(C^{c}_{ef} - C^{c}_{fg})\,,$$

$$C^{ce}_{ab} - C^{cg}_{ab} = -\,(C^{ae}_{bc} - C^{ag}_{bc}) = C^{ag}_{ef} - C^{ae}_{fg} = -\,(C^{cg}_{ef} - C^{ce}_{fg})\,,$$

$$C_{ab}^{cef} - C_{ab}^{cfg} = -(C_{bc}^{aef} - C_{bc}^{afg}) = C_{ef}^{abg} - C_{fg}^{abe} =$$
$$= -(C_{ef}^{bcg} - C_{fg}^{bce}) ,$$

$$C_{ae,bf} - C_{af,bg} + C_{af,be} - C_{ag,bf} =$$
$$= -(C_{be,cf} - C_{bf,cg} + C_{bf,ce} - C_{bg,cf}) ,$$

$$C^{c}_{ae,bf} - C^{c}_{af,bg} + C^{c}_{af,be} - C^{c}_{ag,bf} =$$
$$= -(C^{a}_{be,cf} - C^{a}_{bf,cg} + C^{a}_{bf,ce} - C^{a}_{bg,cf}) =$$
$$= C^{g}_{ae,bf} - C^{e}_{af,bg} + C^{g}_{af,be} - C^{e}_{ag,bf} =$$
$$= -(C^{g}_{be,cf} - C^{e}_{bf,cg} + C^{g}_{bf,ce} - C^{e}_{bg,cf}) ,$$

$$C^{cg}_{ae,bf} - C^{ce}_{af,bg} + C^{cg}_{af,be} - C^{ce}_{ag,bf} =$$
$$= -(C^{ag}_{be,cf} - C^{ae}_{bf,cg} + C^{ag}_{bf,ce} - C^{ae}_{bg,cf}) ;$$

$$C_{ab,ef} - C_{ab,fg} = -(C_{bc,ef} - C_{bc,fg}) ,$$

$$C^{c}_{ab,ef} - C^{c}_{ab,fg} = -(C^{a}_{bc,ef} - C^{a}_{bc,fg}) =$$
$$= C^{g}_{ab,ef} - C^{e}_{ab,fg} = -(C^{g}_{bc,ef} - C^{e}_{bc,fg}) ,$$

$$C^{cg}_{ab,ef} - C^{ce}_{ab,fg} = -(C^{ag}_{bc,ef} - C^{ae}_{bc,fg}) .$$

Taking into account all these relations, the difference polynomial $\Delta$ now takes on the following form:

$$
\begin{aligned}
\Delta = \; & -(A^{k} - A^{m})(B^{p} - B^{r})(C^{ae} - C^{ag}) + \\
& + [(A^{k} - A^{m})(B^{pq} - B^{qr}) + (A^{kl} - A^{lm})(B^{p} - B^{r})] \cdot \\
& \qquad \cdot (C^{abe} - C^{abg}) - \\
& - (A^{kl} - A^{lm})(B^{pq} - B^{qr})(C^{abef} - C^{abfg}) - \\
& - 2t \, \{[(A^{k} - A^{m})(B_{pq} - B_{qr}) + (A_{kl} - A_{lm})(B^{p} - B^{r})] \cdot \\
& \qquad \cdot (C^{e}_{ab} - C^{g}_{ab}) - \\
& - [(A^{k} - A^{m})(B^{r}_{pq} - B^{p}_{qr}) + (A^{m}_{kl} - A^{k}_{lm})(B^{p} - B^{r})] \cdot \\
& \qquad \cdot (C^{ce}_{ab} - C^{cg}_{ab}) - \\
& - [(A^{kl} - A^{lm})(B_{pq} - B_{qr}) + (A_{kl} - A_{lm})(B^{pq} - B^{qr})] \cdot \\
& \qquad \cdot (C^{ef}_{ab} - C^{fg}_{ab}) + \\
& + [(A^{kl} - A^{lm})(B^{r}_{pq} - B^{p}_{qr}) + (A^{m}_{kl} - A^{k}_{lm})(B^{pq} - B^{qr})] \cdot \\
& \qquad \cdot (C^{cef}_{ab} - C^{cfg}_{ab}) - \\
& - (A_{kl} - A_{lm})(B_{pq} - B_{qr})(C_{ae,bf} - C_{af,bg} + C_{af,be} - \\
& \qquad \qquad - C_{ag,bf}) + \\
& + [(A_{kl} - A_{lm})(B^{r}_{pq} - B^{p}_{qr}) + (A^{m}_{kl} - A^{k}_{lm})(B_{pq} - B_{qr})] \cdot \\
& \qquad \cdot (C^{c}_{ae,bf} - C^{c}_{af,bg} + C^{c}_{af,be} - C^{c}_{ag,bf}) - \\
& - (A^{m}_{kl} - A^{k}_{lm})(B^{r}_{pq} - B^{p}_{qr})(C^{cg}_{ae,bf} - C^{ce}_{af,bg} + C^{cg}_{af,be} - \\
& \qquad \qquad - C^{ce}_{ag,bf})\} - \\
& - 4t^{2} \, \{(A_{kl} - A_{lm})(B_{pq} - B_{qr})(C_{ab,ef} - C_{ab,fg}) - \\
& - [(A_{kl} - A_{lm})(B^{r}_{pq} - B^{p}_{qr}) + (A^{m}_{kl} - A^{k}_{lm})(B_{pq} - B_{qr})] \cdot \\
& \qquad \qquad \cdot (C^{c}_{ab,ef} - C^{c}_{ab,fg}) + \\
& + (A^{m}_{kl} - A^{k}_{lm})(B^{r}_{pq} - B^{p}_{qr})(C^{cg}_{ab,ef} - C^{ce}_{ab,fg})\} \quad .
\end{aligned}
$$

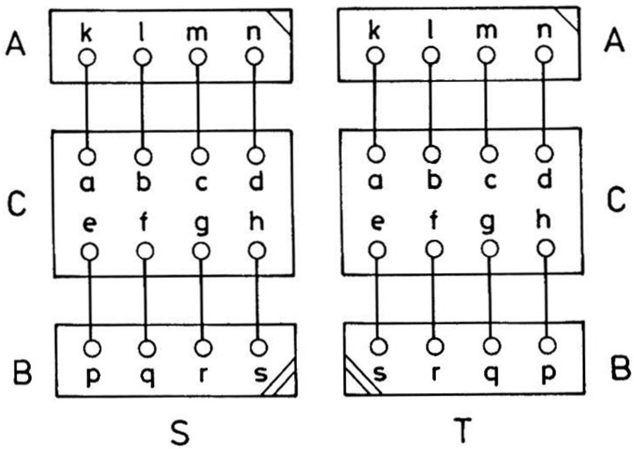
If the terminal moieties are isomorphic, A = B (for details see subsection 2,3), eq. (37) finally takes on the following form:

$$\begin{aligned}
\Delta = & - (A^{k} - A^{m})^{2}(C^{ae} - C^{ag}) + \\
& + 2(A^{k} - A^{m})(A^{kl} - A^{lm})(C^{abe} - C^{abg}) - \\
& - (A^{kl} - A^{lm})^{2}(C^{abef} - C^{abfg}) - \\
& - 2t \; \{ \; 2(A^{k} - A^{m})(A_{kl} - A_{lm})(C^{e}_{ab} - C^{g}_{ab}) - \\
& - 2(A^{k} - A^{m})(A^{m}_{kl} - A^{k}_{lm})(C^{ce}_{ab} - C^{cg}_{ab}) - \\
& - 2(A^{kl} - A^{lm})(A_{kl} - A_{lm})(C^{ef}_{ab} - C^{fg}_{ab}) + \\
& + 2(A^{kl} - A^{lm})(A^{m}_{kl} - A^{k}_{lm})(C^{cef}_{ab} - C^{cfg}_{ab}) - \qquad (38) \\
& - (A_{kl} - A_{lm})^{2}(C_{ae,bf} - C_{af,bg} + C_{af,be} - C_{ag,bf}) + \\
& + 2(A_{kl} - A_{lm})(A^{m}_{kl} - A^{k}_{lm})(C^{c}_{ae,bf} - C^{c}_{af,bg} + \\
& \qquad\qquad + C^{c}_{af,be} - C^{c}_{ag,bf}) - \\
& - (A^{m}_{kl} - A^{k}_{lm})^{2}(C^{cg}_{ae,bf} - C^{ce}_{af,bg} + C^{cg}_{af,be} - C^{ce}_{ag,bf}) \} - \\
& - 4t^{2} \; \{ (A_{kl} - A_{lm})^{2}(C_{ab,ef} - C_{ab,fg}) - \\
& - 2(A_{kl} - A_{lm})(A^{m}_{kl} - A^{k}_{lm})(C^{c}_{ab,ef} - C^{c}_{ab,fg}) + \\
& + (A^{m}_{kl} - A^{k}_{lm})^{2}(C^{cg}_{ab,ef} - C^{ce}_{ab,fg}) \} \quad .
\end{aligned}$$

Obviously, Δ can be negative in some intervals and, hence, the appearance of inversions cannot be excluded.

4.3. Model 3, l = 4

The general structure of the S and the T isomer formed within this model is schematically depicted below:




In Table 10 the number of the terms and their types are listed. There are some new types of terms, namely, tri- and tetracyclic ones.

As indicated in Table 10, the characteristic polynomials T and S consists of 6217 terms each. In the course of the formation of the difference polynomial Δ according to eq. (4), there are 2553 terms of T and S which cancel each other. Thus, each of these polynomials contributes 3664 terms to Δ; hence the difference polynomial consists of 7328 terms in all.

Certainly, this number will be lowered when the central moiety C possesses some useful symmetry; but the number of the remaining terms will still be too high to permit a general conclusion concerning the TEMO pattern. Hence, it is not worthwhile expanding the characteristic polynomial T and S in the present case.

Table 10: Number and types of terms, model 3 , l = 4

| There have been removed | | number of terms | | |
|---|---|---|---|---|
| cycles | endpoints of edges | contributing to T and S | equal in T and S | contributing to $\Delta$ |
| 0 | 0 | 1 | 1 | 0 |
| 0 | 1 | 8 | 4 | 4 |
| 0 | 2 | 28 | 8 | 20 |
| 0 | 3 | 56 | 12 | 44 |
| 0 | 4 | 70 | 14 | 56 |
| 0 | 5 | 56 | 12 | 44 |
| 0 | 6 | 28 | 8 | 20 |
| 0 | 7 | 8 | 4 | 4 |
| 0 | 8 | 1 | 1 | 0 |
| 1 $e^2$ | 0 | 6 | 6 | 0 |
| 1 $f^2$ | 0 | 6 | 2 | 4 |
| 1 $e^4$ | 0 | 6 | 6 | 0 |
| 1 $f^4$ | 0 | 6 | 6 | 0 |
| 1 $e^2f^2$ | 0 | 72 | 24 | 48 |
| 1 $e^4f^2$ | 0 | 144 | 48 | 96 |
| 1 $e^2f^4$ | 0 | 144 | 144 | 0 |
| 1 $e^4f^4$ | 0 | 432 | 432 | 0 |
| 1 $e^2$ | 1 | 36 | 12 | 24 |
| 1 $f^2$ | 1 | 36 | 8 | 28 |
| 1 $e^4$ | 1 | 24 | 0 | 24 |
| 1 $f^4$ | 1 | 24 | 24 | 0 |
| 1 $e^2f^2$ | 1 | 288 | 48 | 240 |
| 1 $e^4f^2$ | 1 | 288 | 0 | 288 |
| 1 $e^2f^4$ | 1 | 288 | 288 | 0 |
| 1 $e^2$ | 2 | 90 | 42 | 48 |
| 1 $f^2$ | 2 | 90 | 14 | 76 |
| 1 $e^4$ | 2 | 36 | 12 | 24 |
| 1 $f^4$ | 2 | 36 | 36 | 0 |
| 1 $e^2f^2$ | 2 | 432 | 48 | 384 |
| 1 $e^4f^2$ | 2 | 144 | 48 | 96 |
| 1 $e^2f^4$ | 2 | 144 | 144 | 0 |

Table 10 (continued)

| | | | | | |
|---|---|---|---|---|---|
| 1 | $e^2$ | 3 | 120 | 12 | 108 |
| 1 | $f^2$ | 3 | 120 | 8 | 112 |
| 1 | $e^4$ | 3 | 24 | 0 | 24 |
| 1 | $f^4$ | 3 | 24 | 24 | 0 |
| 1 | $e^2f^2$ | 3 | 288 | 48 | 240 |
| 1 | $e^2$ | 4 | 90 | 42 | 48 |
| 1 | $f^2$ | 4 | 90 | 14 | 76 |
| 1 | $e^4$ | 4 | 6 | 6 | 0 |
| 1 | $f^4$ | 4 | 6 | 6 | 0 |
| 1 | $e^2f^2$ | 4 | 72 | 24 | 48 |
| 1 | $e^2$ | 5 | 36 | 12 | 24 |
| 1 | $f^2$ | 5 | 36 | 8 | 28 |
| 1 | $e^2$ | 6 | 6 | 6 | 0 |
| 1 | $f^2$ | 6 | 6 | 2 | 4 |
| 2 | $e^2+e^2$ | 0 | 3 | 3 | 0 |
| 2 | $e^2+f^2$ | 0 | 36 | 12 | 24 |
| 2 | $f^2+f^2$ | 0 | 3 | 3 | 0 |
| 2 | $e^4+f^2$ | 0 | 36 | 12 | 24 |
| 2 | $e^2+f^4$ | 0 | 36 | 36 | 0 |
| 2 | $e^2f^2+e^2$ | 0 | 72 | 24 | 48 |
| 2 | $e^2f^2+f^2$ | 0 | 72 | 24 | 48 |
| 2 | $e^4f^2+f^2$ | 0 | 144 | 48 | 96 |
| 2 | $e^2f^4+e^2$ | 0 | 144 | 144 | 0 |
| 2 | $e^2f^2+e^2f^2$ | 0 | 144 | 48 | 96 |
| 2 | $e^4+f^4$ | 0 | 36 | 36 | 0 |
| 2 | $e^2+e^2$ | 1 | 12 | 0 | 12 |
| 2 | $e^2+f^2$ | 1 | 144 | 24 | 120 |
| 2 | $f^2+f^2$ | 1 | 12 | 12 | 0 |
| 2 | $e^4+f^2$ | 1 | 72 | 0 | 72 |
| 2 | $e^2+f^4$ | 1 | 72 | 72 | 0 |
| 2 | $e^2f^2+e^2$ | 1 | 144 | 0 | 144 |
| 2 | $e^2f^2+f^2$ | 1 | 144 | 48 | 96 |
| 2 | $e^2+e^2$ | 2 | 18 | 6 | 12 |
| 2 | $e^2+f^2$ | 2 | 216 | 24 | 192 |
| 2 | $f^2+f^2$ | 2 | 18 | 18 | 0 |
| 2 | $e^4+f^2$ | 2 | 36 | 12 | 24 |
| 2 | $e^2+f^4$ | 2 | 36 | 36 | 0 |

Table 10 (continued)

| | | | | | |
|---|---|---|---|---|---|
| 2 | $e^2f^2+e^2$ | 2 | 72 | 24 | 48 |
| 2 | $e^2f^2+f^2$ | 2 | 72 | 24 | 48 |
| 2 | $e^2+e^2$ | 3 | 12 | 0 | 12 |
| 2 | $e^2+f^2$ | 3 | 144 | 24 | 120 |
| 2 | $f^2+f^2$ | 3 | 12 | 12 | 0 |
| 2 | $e^2+e^2$ | 4 | 3 | 3 | 0 |
| 2 | $e^2+f^2$ | 4 | 36 | 12 | 24 |
| 2 | $f^2+f^2$ | 4 | 3 | 3 | 0 |
| 3 | $e^2+e^2+f^2$ | 0 | 18 | 6 | 12 |
| 3 | $e^2+f^2+f^2$ | 0 | 18 | 18 | 0 |
| 3 | $e^4+f^2+f^2$ | 0 | 18 | 6 | 12 |
| 3 | $e^2+e^2+f^4$ | 0 | 18 | 18 | 0 |
| 3 | $e^2f^2+e^2+f^2$ | 0 | 72 | 24 | 48 |
| 3 | $e^2+e^2+f^2$ | 1 | 36 | 0 | 36 |
| 3 | $e^2+f^2+f^2$ | 1 | 36 | 36 | 0 |
| 3 | $e^2+e^2+f^2$ | 2 | 18 | 6 | 12 |
| 3 | $e^2+f^2+f^2$ | 2 | 18 | 18 | 0 |
| 4 | $e^2+e^2+f^2+f^2$ | 0 | 9 | 9 | 0 |
| | | | 6217 | 2553 | 3664 |

## 4.4. Summary, model 3

TEMO without inversions may be expected in case of this model only if the terminal subunits, A and B, are bivalent (l = 2) and isomorphic (A = B) and the central moiety C has a structure such that $(C^{af} - C^{ae})$ is positive in the complete range of the variable. Some examples for such structures are given in [5] while in [16] some general conditions for such behaviour are discussed.

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References and Annotations:

[1] In this series of notes the more formal and, hence, mathematical aspects of the topological effect on molecular orbitals (TEMO) are treated; they usually cannot be adequately discussed in papers devoted to the display of TEMO in molecular physics and chemistry. For the physical significance of TEMO see for example [2,5,11] and the papers cited therein.

[2] O.E. Polansky and M. Zander, J. Mol. Struct. 84 (1982) 361

[3] O.E. Polansky, Chapter I in: Application of Graph theory in Chemistry (in Bulgarian); edited by N. Tyutyulkov and D. Bonchev, Science and Arts Publ., Sofia, (in the press)

[4] A. Graovac, I. Gutman and O.E. Polansky, Mh. Chemie, 115 (1984), 1

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[6] E. Heilbronner, Helv. Chim. Acta, 36 (1953) 170

[7] I. Gutman and O.E. Polansky, Theor. Chim. Acta (Berlin), 60 (1981), 203

[8] O.E. Polansky and A. Graovac, Match 13 (1982), 151

[9] One should note: In constrast to the symbol $A^{rs}$ which denotes the partial graph obtained from A by the removal of the vertices r and s (together with all their incident edges) as well as the characteristic polynomial of that partial graph, the symbol $A_{rs}$ does not correspond to a single graph at all; on the contrary, it denotes a sum of characteristic polynomials of certain partial graphs of A as defined in the text. Let $\Delta$ here be the secular determinant of the graph A; then $A^{rs}$ equals the main minor $\Delta_{rs,rs}$ but $A_{rs}$ equals the (non-symmetrical) minor $\Delta_{r,s}$ [10]. In this context it should also

be mentioned that $\Delta_{rt,su} = A_{rs,tu} - A_{ru,st}$, but $\Delta_{ru,st} = A_{rs,tu} - A_{rt,su}$.

[10] C.A. Coulson, H.C. Longuet-Higgins, Proc. Roy. Soc. A 191 (1947), 39

[11] O.E. Polansky, J. Mol. Struct. 113 (1984), 281

[12] I. Motoc, J.N. Silverman, and O.E. Polansky, Phys. Rev. A, 28 (1983), 3673

[13] I. Motoc, J.N. Silverman, and O.E. Polansky, Chem. Phys. Lett. 103 (1984), 285

[14] I. Motoc, J.N. Silverman, O.E. Polansky, and G. Olbrich, Theor. Chim. Acta, in press

[15] A vertex of a connected simple graph is called an articulation if its removal results in a disconnected graph. In this manner an articulation represents a vertex cut set of cardinality 1 as similarly a bridge represents an edge cut set of cardinality 1.

[16] O.E. Polansky, Match, this issue, next paper.