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Research Notes on the Topological Effect on MO (TEMO) 2*

SOME STRUCTURAL REQUIREMENTS FOR THE CENTRAL SUBUNIT IN A PARTICULAR TOPOLOGICAL MODEL

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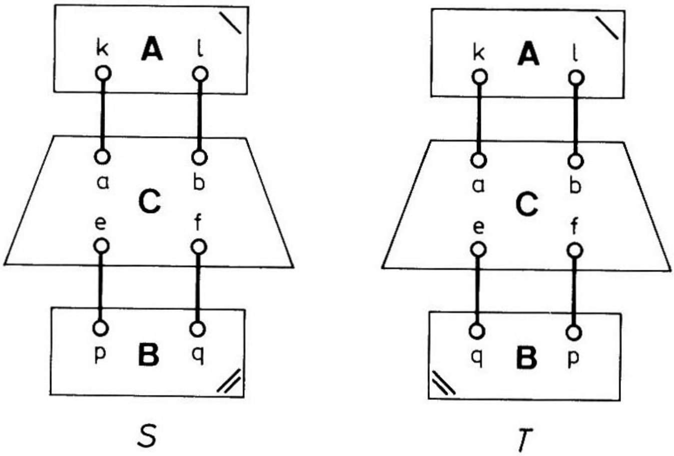
For the central subunit in the topological model depicted in Scheme 1 some structures are assumed and it is shown for which structure and under what conditions TEMO without inversions is assured.

* For Part 1 see reference [1].

1. Introduction

In the previous note a topological model has been treated (subsection 4,1 in [1]) in which the topologically related isomers are constructed in accord with the scheme 1 below:



Scheme 1

If the following conditions are supposed,

(i) the terminal subunits, A and B, are isomorphic and

(ii) the central subunit C possesses a structure such that the vertex a may be mapped automorphically onto the vertex b and simultanous the vertex e onto f and vice versa by an appropriate symmetry operator, P, i.e.:

$$Pa = b,\ Pb = a,\ Pe = f,\ Pf = e\ , \qquad (1)$$

then the difference polynomial Δ as defined by eq. (4) in [1] takes the form given by eq. (35) in [1], which reads as follows:

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

Evidently Δ and its factor $(C^{af}-C^{ae})$ have the same sign. Because $\Delta \geq 0$ is a sufficient condition for the appearance of TEMO without inversions one is interested in central moieties which have a structure such that $(C^{af}-C^{ae})$ is positive:

$$(C^{af}-C^{ae}) \geq 0 \quad . \tag{3}$$

Some particular examples for this are given in [2]. In the present note some general structures (I-V) for the central moiety C are considered with respect to eq. (3). Because the symmetry of C as expressed by eq. (1) is an essential precondition for obtaining eq. (2), all the general structures treated here must exhibit this symmetry.

The general structure I differs from the other ones in the following point: Only in I has the vertex subset {a,b,e,f} the property of a cut set: its removal decomposes I into four components. In II this subset is no cut set at all while in III-V certain intermediate situations are realized. It will turn out that only in the case of I, IV, and V are there real chances to achieve the demand given by eq. (3).

Throughout this note the same notation is used as in [1]; references 9 and 15 cited in [1] should be stressed as well as the convention of using the same symbols for any graph and the μ-polynomial associated with this graph.

2. Structure I

The general structure assumed here for the central moiety C is depicted in Figure 1. It consists of four unspecified subunits F, G, H, J, the vertices a, b, e, and f, and some edges which connect a with F and H, b with G and H, e with F and J, and finally f with G and J.

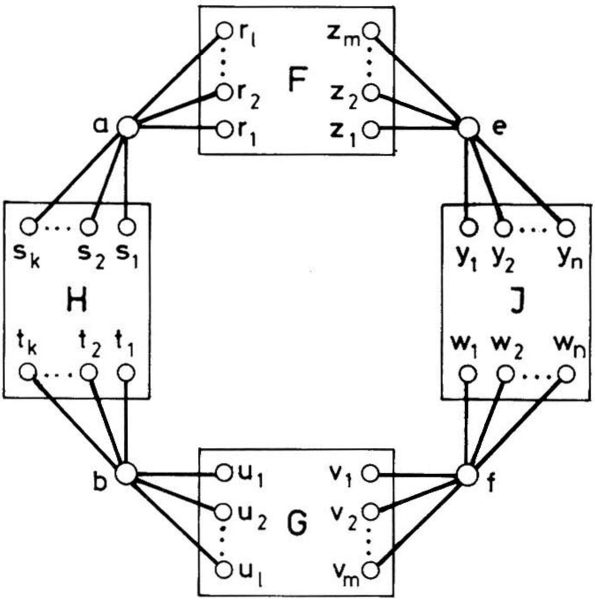


Figure 1: Structure I

Due to the symmetry operator P we have for the subunits F, G, H, and I the following relations additional to eq. (1):

$$PH = H \,, \qquad PJ = J \,,$$
$$PF = G \,, \qquad PG = F \,. \tag{4}$$

Eq. (4) requires that F and G are isomorphic and further, that H and J are symmetric with respect to the symmetry operation P.

A consequence of the isomorphism of F and G is that the number of edges which connect a with F and b with G, respectively, must be equal, the number of those edges which connects e with F and f with G must also be equal. This is accomplished by assuming

$$Pr_\lambda = u_\lambda, \quad Pu_\lambda = r_\lambda, \quad 1 \leq \lambda \leq l, \quad r_\lambda \in F, \quad u_\lambda \in G \,;$$
$$Pv_\mu = z_\mu, \quad Pz_\mu = v_\mu, \quad 1 \leq \mu \leq m, \quad z_\mu \in F, \quad v_\mu \in G \,; \tag{5}$$

where l and m are independent of each other.

The symmetry of H and J with respect to P demands

$$Ps_\kappa = t_\kappa, \quad Pt_\kappa = s_\kappa, \quad 1 \leq \kappa \leq k, \quad s_\kappa, t_\kappa \in H \,;$$
$$Pw_\nu = Y_\nu, \quad Py_\nu = w_\nu, \quad 1 \leq \nu \leq n, \quad w_\nu, y_\nu \in J \,. \tag{6}$$

Once again, k and n are independent numbers; they denote the number of edges which connect the vertex a(b) with H and the vertex e(f) with J, respectively.

An inspection of Fig. 1 shows that C^{af} and C^{ae} are disconnected graphs which consist of two components. In the case of C^{af} the one component is formed by the subunits F and J which are connected with each other via the vertex e; the other one is formed by G and H, connected via vertex b. The vertices b and f are articulations in their components; the cycles to which they belong are fully localized in one subunit. In the case of C^{ae} the one component is identical with F; the other one consists of the subunits G, H, and J which are connected with each other via b and f, respectively, in the same manner they are connected in C. The vertices b and f are articulations in this component. The cycles to which either b or f belongs are fully localized in one of the adjacent subunits. Apart from these there are cycles to which b as well as f belong; these cycles consist of two paths which connect u_λ with v_μ and $u_{\lambda'}$ with $v_{\mu'}$, respectively, and the edges $\{bu_\lambda\}$, $\{bu_{\lambda'}\}$, $\{fv_\mu\}$, and $\{fv_{\mu'}\}$.

The removal of the vertices b and e from C^{af} and that of b and f from C^{ae}, respectively, results in a graph which consists of the four components, F, G, H, and J. Hence, the polynomials C^{af} and C^{ae} may be expressed as a sum of tetralinear terms made up of the polynomials associated with these graphs F, G, H, and J or with some of their partial graphs.

Recently a special formula for the polynomial of a graph G has been derived [3] for the case in which all the edges incident with an given vertex u, have been removed:

$$G = xG^{u}-\Sigma G^{uv}-2t\Sigma\Sigma G^{u}_{vv'} \quad . \tag{7}$$

where v and v′ denote vertices which are adjacent to the vertex u (the neighbours of u form the subset $\{v_\gamma \mid 1\leqq\gamma\leqq g\}$ where g denote the degree of the vertex u). The first summation runs over the set $\{v_\gamma\}$, the second one over all the pairs $\{\{v_\gamma, v_{\gamma'}\} | 1 \leq \gamma < \gamma' \leq g\}$ which may be formed from the set $\{v_\gamma\}$. This double sum represents the cyclic contributions (note: a cycle to which u belongs is composed of the edges $\{uv\}$, $\{uv'\}$, and the path $P_{vv'}$). The first term, xG^u, represents the product of the polynomials of the partial graphs which are generated by the removal of the edges $\{\{uv_\gamma\} | 1 \leq \gamma \leq g\}$; note that x represents the polynomial of the partial graph which consists of the single vertex u only. Eq. (7) describes the partition of the graph G at its vertex u.

The application of eq. (7) to the partition of C^{af} at the vertex b results in

$$C^{af} = xC^{abf} - \Sigma C^{abft} - \Sigma C^{abfu} - 2t\Sigma\Sigma C^{abf}_{tt'} - 2t\Sigma\Sigma C^{abf}_{uu'} . \tag{8}$$

The first two summations run over the vertices adjacent to b, namely $\{t_\kappa\}$ and $\{u_\lambda\}$, respectively. The last two summations run over the pairs $\{\{t_\kappa, t_{\kappa'}\} | 1 \leq \kappa < \kappa' \leq k\}$ and $\{\{u_\lambda, u_{\lambda'}\} | 1 \leq \lambda < \lambda' \leq l\}$, respectively; these two terms of eq. (8) are generated by the removal of the cycles to which b belongs and which are fully localized either in H or in G. All the terms of eq. (8) correspond to graphs which contain the vertex e. The partition of all these graphs at the vertex e results in

$$
\begin{aligned}
C^{af} = & \\
= x^2D \quad & - x\Sigma D^{t} \quad - x\Sigma D^{u} \quad - 2tx\Sigma D_{tt'} \quad - 2tx\Sigma D_{uu'} \\
- x\Sigma D^{y} \quad & + \Sigma D^{ty} \quad + \Sigma D^{uy} \quad + 2t\Sigma D^{y}_{tt'} \quad + 2t\Sigma D^{y}_{uu'} \\
- x\Sigma D^{z} \quad & + \Sigma D^{tz} \quad + \Sigma D^{uz} \quad + 2t\Sigma D^{z}_{tt'} \quad + 2t\Sigma D^{z}_{uu'} \\
- 2tx\Sigma D_{yy'} \quad & + 2t\Sigma D^{t}_{yy'} \quad + 2t\Sigma D^{u}_{yy'} \quad + 4t^2\Sigma D_{tt',yy'} \quad + 4t^2\Sigma D_{uu',yy'} \\
- 2tx\Sigma D_{zz'} \quad & + 2t\Sigma D^{t}_{zz'} \quad + 2t\Sigma D^{u}_{zz'} \quad + 4t^2\Sigma D_{tt',zz'} \quad + 4t^2\Sigma D_{uu',zz'} \ .
\end{aligned}
\tag{9}
$$

In order to reduce the number of indices which must be indicated, in these expression we use the abbreviation $D = C^{abef}$ (Note: D is a disconnected graph which consists of the components F, G, H, and J). Also double, triple and quadruple summations are not especially indicated; evidently, the summations must be carried out over the complete sets of the indicated vertices and pairs of vertices as has been discussed in the context of eq. (7).

Applying eq. (7) to C^{ae} in the same manner one obtains:

$$
\begin{aligned}
C^{ae} = & \\
= x^2D \quad & - x\Sigma D^{t} \quad - x\Sigma D^{u} \quad - 2tx\Sigma D_{tt'} \quad - 2tx\Sigma D_{uu'} \\
- x\Sigma D^{v} \quad & + \Sigma D^{tv} \quad + \Sigma D^{uv} \quad + 2t\Sigma D^{v}_{tt'} \quad + 2t\Sigma D^{v}_{uu'} \\
- x\Sigma D^{w} \quad & + \Sigma D^{tw} \quad + \Sigma D^{uw} \quad + 2t\Sigma D^{w}_{tt'} \quad + 2t\Sigma D^{w}_{uu'} \\
- 2tx\Sigma D_{vv'} \quad & + 2t\Sigma D^{t}_{vv'} \quad + 2t\Sigma D^{u}_{vv'} \quad + 4t^2\Sigma D_{tt',vv'} \quad + 4t^2\Sigma D_{uu',vv'} \\
- 2tx\Sigma D_{ww'} \quad & + 2t\Sigma D^{t}_{ww'} \quad + 2t\Sigma D^{u}_{ww'} \quad + 4t^2\Sigma D_{tt',ww'} \quad + 4t^2\Sigma D_{uu',ww'} \ .
\end{aligned}
\tag{10}
$$

The terms of the first row of eqs. (9) and (10) are pair-wise identical; hence, they cancel in $(C^{af}-C^{ae})$. But there are more terms in these two equations which are equal as a consequence of the presumed symmetry. This will be exemplified for

$$\Sigma D^{v} = \Sigma D^{z} \ .$$

Expanding these sums in terms of F, G, H, and J one obtains

$$\Sigma D^{v} = F(\Sigma G^{v})HJ$$
$$\Sigma D^{z} = (\Sigma F^{z})GHJ$$

Now from the isomorphism of F and G, as expressed in eq. (4) by PF=G and PG=F, it follows that their polynomials are equal, F=G. From the second line of eq. (5) it is obvious, that for each pair v_μ and z_μ there are equal polynomials contributed to the sums ΣG^{v} and ΣF^{z}, respectively. Therefore, the following equality holds

$$F(\Sigma G^{v}) = (\Sigma F^{z})G \ ,$$

which proves $\Sigma D^{v} = \Sigma D^{z}$, q.e.d.

In this manner the following equalities are derived:

$$\begin{gathered}
\Sigma D^{v} = \Sigma D^{z}, \quad \Sigma D^{w} = \Sigma D^{y}, \\
\Sigma D^{tv} = \Sigma D^{tz}, \quad \Sigma D^{tw} = \Sigma D^{ty}, \quad \Sigma D^{uw} = \Sigma D^{uy}, \\
\Sigma D_{vv'} = \Sigma D_{zz'}, \quad \Sigma D_{ww'} = \Sigma D_{yy'}, \\
\Sigma D^{v}_{tt'} = \Sigma D^{z}_{tt'}, \quad \Sigma D^{w}_{tt'} = \Sigma D^{y}_{tt'}, \quad \Sigma D^{w}_{uu'} = \Sigma D^{y}_{uu'}, \\
\Sigma D^{t}_{yy'} = \Sigma D^{t}_{ww'}, \quad \Sigma D^{t}_{zz'} = \Sigma D^{t}_{vv'}, \quad \Sigma D^{u}_{yy'} = \Sigma D^{u}_{ww'} \\
\Sigma D_{tt',vv'} = \Sigma D_{tt',zz'}, \quad \Sigma D_{tt',ww'} = \Sigma D_{tt',yy'}, \quad \Sigma D_{uu',ww'} = \Sigma D_{uu',yy'} \ .
\end{gathered} \tag{11}$$

Taking all these equalities into account, $(C^{af}-C^{ae})$ results in

$$(C^{af}-C^{ae}) = \Sigma D^{uz} - \Sigma D^{uv} + 2t(\Sigma D^{z}_{uu'} - \Sigma D^{v}_{uu'}) + 2t(\Sigma D^{u}_{zz'} - \Sigma D^{u}_{vv'})$$
$$+ 4t^{2}(\Sigma D_{uu',zz'} - \Sigma D_{uu',vv'}) \ .$$

This expression may be transformed into tetralinear terms made up from F, G, H, and J; if in addition the following equalities are considered

$$F = G, \quad \Sigma F^{z} = \Sigma G^{v}, \quad \Sigma F_{zz'} = \Sigma G_{vv'} \ , \tag{11a}$$

which arise from isomorphism of F and G, one obtains

$$\begin{aligned} C^{af} - C^{ae} = \\ = HJ\{[(\Sigma G^{u})(\Sigma G^{v}) - G\Sigma G^{uv}] + 2t[(\Sigma G^{v})(\Sigma G_{uu'}) \\ - G\Sigma G^{v}_{uu'} + (\Sigma G^{u})(\Sigma G_{vv'}) - G\Sigma G^{u}_{vv'}] + \\ + 4t^{2}[(\Sigma G_{uu'})(\Sigma G_{vv'}) - G\Sigma G_{uu',vv'}]\} \ . \end{aligned} \tag{12}$$

The number of terms with plus and with minus signs, respectively, are equal in eq. (12). Hence, it is impossible to conclude from eq. (12) wether eq. (3), i.e. $(C^{af} - C^{ae}) \geqq 0$, is satisfied or not. Thus, first of all, eq. (12) needs a transformation into a form which permits such a conclusion. For that purpose the terms in the brackets appearing in eq. (12) are now examined bracket by bracket.

In the first brackets the summations run indepently over the sets $\{u_{\lambda}\}$ and $\{v_{\mu}\}$, respectively. Hence, this term may be rewritten as follows:

$$\sum_{\{u_\lambda\}} \sum_{\{v_\mu\}} (G^u G^v - GG^{uv}) \ .$$

It has been shown [4,5], that the expression in the round brackets may be transformed for any pair u,v as follows:

$$G^u G^v - GG^{uv} = G_{uv}^2 \ . \tag{13}$$

Thus, for the first brackets of eq. (12) the following equality arises

$$[(\Sigma G^u)(\Sigma G^v) - G\Sigma G^{uv}] = \sum_u \sum_v [G_{uv}]^2 \tag{14a}$$

(Note that by definition G_{uv} involves a summation over the set of paths $\{P_{uv}\}$ which connect the vertices u and v in G). Because the right-hand-side (r.h.s.) of eq. (14a) represents a sum of squares, this term will be positive in the complete range of the variable.

In the second brackets of eq. (12) the summations run independently over the sets $\{v_\mu | 1 \leq \mu \leq m\}$ and $\{(u_\lambda, u_{\lambda'}) | 1 \leq \lambda < \lambda' \leq l\}$. Hence, this term may be rewritten as follows:

$$\sum_{\{v_\mu\}} \sum_{\substack{\{(u_\lambda, u_{\lambda'})\} \\ \lambda<\lambda'}} \sum (G^v G_{uu'} - GG^v_{uu'}) +$$
$$\sum_{\{u_\lambda\}} \sum_{\substack{\{(v_\mu, v_{\mu'})\} \\ \mu<\mu'}} \sum (G^u G_{vv'} - GG^u_{vv'}) \ .$$

Recently, it has been shown [6] that the expressions in the round brackets above can be transformed as follows

$$G^{v}G_{uu'} - GG^{v}_{uu'} = G_{uv}G_{u'v} \; ; \tag{15}$$

Thus, one obtains for the second brackets of eq. (12) the following equality:

$$2t[(\Sigma G^{v})(\Sigma G_{uu'}) - G\Sigma G^{v}_{uu'} + (\Sigma G^{u})(\Sigma G_{vv'}) - G\Sigma G^{u}_{vv'}] = \tag{14b}$$

$$= t \sum\sum_{vu \neq u'}\sum G_{uv}G_{u'v} + t \sum\sum_{uv \neq v'}\sum G_{uv}G_{uv'}$$

Because the r.h.s. of eq. (14b) represents a sum of bilinear terms which might be positive or negative for an arbitrary value of x it is not possible to conclude whether this term will be positive or negative.

The third brackets of eq. (12) may be rewritten as follows:

$$\sum_{\substack{\{(u_\lambda, u_{\lambda'})\} \\ \lambda < \lambda'}} \sum \; \sum_{\substack{\{(v_\mu, v_{\mu'})\} \\ \mu < \mu'}} \sum (G_{uu'}G_{vv'} - GG_{uu',vv'}).$$

The round brackets above cannot be expressed as a simple equality is available. Nevertheless, some kind of transformation can be performed by means of the Jacobi theorem [7]. Let Δ denote the secular determinant of the graph G, then one has the following identities

$$\Delta = G$$

$$\Delta_{u,u'} = \Delta_{u',u} = G_{uu'}, \quad \Delta_{v,v'} = \Delta_{v',v} = G_{v'},$$

$$\Delta_{uv,u'v'} = \Delta_{u'v',uv} = G_{uu',vv'} - G_{uv',u'v}$$

$$\Delta_{uv',u'v} = \Delta_{u'v,uv'} = G_{uu',vv'} - G_{uv,u'v'}$$

where $\Delta_{j,k}$ and $\Delta_{jj',kk'}$ denote Δ with rows j (and j'>j) and columns k (and k'>k) struck out; with the exception of Δ itself, they are all unsymmetric minors of Δ. It is worthwile noting that in the generation of the polynomials, e.g. $G_{uu'}$, the direction of any path removed, $P_{uu'}$, plays no role and remains undetermined. In contrast to that, due to its lack on symmetry, in $\Delta_{u,u'}$ all the paths $P_{uu'} \in \{P_{uu'}\}$ go from the vertex u' to the vertex u [8]. In general, all the paths removed in the course of the expansion of a minor start (end) at one of those vertices which correspond to the struck out columns (rows). This fact explains the difference between $\Delta_{uv,u'v'}$ and $\Delta_{uv',u'v}$ as notated abaove.

From the Jacobi theorem the following relations are derived [7]:

$$\Delta_{u,u'}\Delta_{v,v'}-\Delta\Delta_{uv,u'v'} = \Delta_{u,v'}\Delta_{v,u'}, \tag{16a}$$

$$\Delta_{u',u}\Delta_{v,v'}-\Delta\Delta_{u'v,uv'} = \Delta_{u',v'}\Delta_{vu} \tag{16b}$$

which may be expressed in terms of the polynomials as follows:

$$G_{uu'}G_{vv'} - G(G_{uu',vv'} - G_{uv',u'v}) = G_{uv'}G_{u'v} , \tag{16a'}$$

$$G_{uu'}G_{vv'} - G(G_{uu',vv'} - G_{uv,u'v'}) = G_{uv}G_{u'v'} . \tag{16b'}$$

The addition of eq. (16a′) and (16b′) results in

$$\begin{aligned} &2(G_{uu'}G_{vv'} - GG_{uu',vv'}) = \\ &= G_{uv}G_{u'v'} + G_{uv'}G_{u'v} - G(G_{uv,u'v'} + G_{uv',u'v}) . \end{aligned} \tag{17}$$

The l.h.s. of eq. (17) represents one contribution to the third brackets of eq. (12); by the substitution of eq. (17) one obtains:

$$\begin{aligned} &4t^2[(\Sigma G_{uu'})(\Sigma G_{vv'}) - G\Sigma G_{uu',vv'}] = \\ &= 2t^2\sum_{u<u'}\sum\sum_{v<v'}\sum (G_{uv}G_{u'v'} + G_{uv'}G_{u'v}) - \\ &- 2t^2\sum_{u<u'}\sum\sum_{v<v'}\sum G(G_{uv,u'v'} + G_{uv',u'v}) = \\ &= t^2 \sum_{u\neq u'}\sum\sum_{v\neq v'}\sum G_{uv}G_{u'v'} - t^2\sum_{u\neq u'}\sum\sum_{v\neq v'}\sum GG_{uv,u'v'} . \end{aligned} \tag{14c}$$

Since the r.h.s. of eq. (14c) represents a sum of bilinear terms which might be positive or negative for an arbitrary value of x, it is impossible to conclude wether this term will be positive or negative.

Collecting the intermediate results, eqs. (14a-c), and inserting them in eq. (12) one finally obtains:

$$C^{af}-C^{ae} = HJ\{\sum_{uv}\sum G_{uv}^2 + t\sum\sum_{uv\neq v'}\sum G_{uv}G_{uv'} + t\sum_{u\neq u'}\sum_{v'}\sum G_{uv}G_{u'v} +$$

$$+ t^2 \sum_{u\neq u'}\sum \sum_{v\neq v'}\sum G_{uv}G_{u'v'} - t^2\sum_{u\neq u'}\sum \sum_{v\neq v'}\sum GG_{uv,u'v'} \}. \qquad (18)$$

To attain eq. (3), i.e. $(C^{af}-C^{ae}) \geq 0$, one has to require that the factor (HJ) as well as the expression in the curled brackets be positive in the complete range of the variable because it is very unlikely that both factors change their sign simultaneously; such a behaviour would demand that both factors have exactly the same zeros.

The requirement

$$HJ \geq 0 \qquad (19a)$$

is realized simply if H and J are either isomorphous or cospectral graphs; then one would have

$$HJ = H^2 \geq 0 \ . \qquad (19b)$$

The connection of H with the vertices a and b and the one of J with e and f plays no role with regard to eq. (18), i.e. no bijective mapping of the edges connecting H with a(b) onto the edges connecting J with e(f) is required; but, of course, both graphs as well as their embedding into C must exhibit that symmetry which is necessary for effecting the symmetry operation according to eq. (4-6). If the graph of the terminal subunits, A, is connected, H and J may be disconnected or even empty graphs; in case that H and J are disconnected, due to the symmetry P, both graphs consist of a pair of isomorphous components and, hence, both polynomials H and J are squares satisfying (19a).

For different graphs H and J, the requirement of eq. (19a) may also be realized if H and J represent either two even- or two odd-membered Hückel- or Möbius-cycles. Once again, the connection of H with the vertices a and b and the one of J with e and f plays no role with regard to eq. (18).

From the terms within the curled brackets of eq. (16) only the first term is not multiplied by any power of the discrimination parameter t [1,9], hence, in the case of acyclic polynomials (t=0) it will be the remaining term.

The first term represents a sum of squares and, hence, will be positive:

$$\sum_{uv}\sum G^2_{uv} \geq 0 \quad . \tag{20}$$

this allows one to state:

Result 1: *If T and S denote the acyclic polynomials of topologically related isomers constructed within scheme 1, the terminal subunits A and B are isomorphic, and the central moiety C is in agreement with the general structure shown in Figure 1, where H and J represent either a) isomorphic or b) cospectral or c) disconnected graphs which consist of pairs of isomorphic components or d) two even (odd) membered Hückel- (Möbius-)cycles, then (T-S) $\geq$ 0 will hold in the complete range of the variable.*

But in the case of characteristic polynomials the value t=1 has to be set [1,9] and all the terms of the curled brackets in eq. (18) have to be considered.

Obviously, the first four terms form a square, namely

$$\sum\sum_{uv} G_{uv}^2 + \sum\sum_{uv \neq v'} \sum G_{uv} G_{uv'} + \sum_{u \neq u'} \sum_{v} \sum G_{uv} G_{u'v} + \tag{21}$$

$$+ \sum_{u \neq u'} \sum \sum_{v \neq v'} \sum G_{uv} G_{u'v'} = [\sum\sum_{uv} G_{uv}]^2 \geq 0$$

But in this case the last term of eq. (18) remains and prevents a conclusion as to whether the expression in the curled brackets of eq. (18) will be positive or not. To the best of our knowledge there is no way to transform the last terms of eq. (18) into any satisfactory form.

For what follows it is necessary to recall the origin of this troublesome term. Tracing them back to eq. (12), it is evident that it arises from the the bicyclic contributions to $(C^{af}-C^{ae})$. If the general structure of C as shown in Figure 1 is altered such that no bicyclic contribution at all can be generated in the course of the partitioning of C^{af} and C^{ae}, respectively, then these difficulties would be eliminated at once. This is performed simply if one demands that one of the vertex sets $\{u_\lambda\}$ and $\{v_\mu\}$ has the cardinality 1. With regard to eqs. (12), (18), and (21) we choose $|\{u_\lambda\}|=1$. In this case, with regard to eqs. (19) and (21), eq. (2) will finally take the following form

$$C^{af}-C^{ae} = H^2[\sum_{v} G_{uv}]^2 \geq 0 \ . \tag{22}$$

Having derived eq. (22) one may state (see also Figure 2):

Result 2: *Let S and T denote the characteristic polynomials of the topologically related isomers S and T according to Scheme 1; their differerence will be positive in the complete range of the variable,*

$(T-S) \geq 0$,

if

(1) the terminal subunits, A and B, are isomorphic;

(2) the central subunit C, is agreement in principle with the general structure shown in Figure 1 and satisfies the following conditions:

(2.1) C exhibits a symmetry such that the symmetry operator P, defined by Pa=b, Pb=a, Pe=f, Pf=e, and eqs. (4)-(6) belongs to the automorphism group of C;

(2.2) the subgraphs H and J are either a) isomorphic or b) cospectral or c) disconnected or d) two even (odd) membered Hückel-(Möbius)-cycles;

(2.3) at least one of the vertex sets $\{u_\lambda\}$ *and* $\{v_\mu\}$ *has the cardinality 1.*

This alteration of the structure shown in Figure 1 is illustrated by Figure 2.

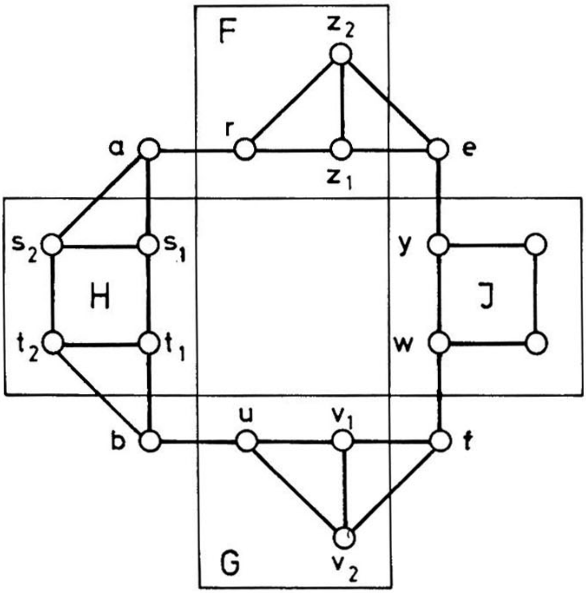


Figure 2, illustrating result 2: In the case of this particular structure one obtains $(C^{af}-C^{ae}) = [2(x^4-x^3-4x^2+4x)]^2 = 4x^2(x-1)^2(x+2)^2(x-2)^2 \geqq 0$.

Before this section is closed a brief remark should be made about the non-equivalence of the vertex sets $\{u_\lambda\}$ and $\{v_\mu\}$ as displayed in eqs. (12), (18), and (21): According to eq. (7) a vertex $u_\lambda(v_\mu)$ can be removed from G only together with its adjacent vertex b(f). Hence, vertices of the set $\{u_\lambda\}$ are removed from G in the partitioning of C^{af} as well as C^{ae} because both graphs contain the vertex b; in contrast to this, vertices of the set $\{v_\mu\}$ are removed from G only in the partitioning of C^{ae} because the vertex f belongs to C^{ae} but not to C^{af}. On the other hand, also according to eq. (7), a vertex $r_\lambda(z_\mu)$ can be removed from F only together with its adjacent vertex a(e). Because the vertex a is not present either in C^{af} or in C^{ae}, no vertex r_λ can actually be removed in the partitioning of these graphs. But the vertices of the set $\{z_\mu\}$ will be removed from F in the partitioning of C^{af}; this result is then expressed in terms of $G^{f(\{v_\mu\})}$ according to eq. (11a). Thus, the factors $G^{g(\{u_\lambda\})}$ are generated directly by removing u_λ´s in the partitioning of either C^{af} or C^{ae}; in contrast to that, the factors $G^{f(\{v_\mu\})}$ are generated either by removing v_μ from G in the partitioning of C^{ae} or by removing z_μ from F in the partitioning of C^{af} and the subsequent transformation of the result into terms of $G^{f(\{v_\mu\})}$. As a consequence of the procedures described, for example the term G^uG^v is obtained in the partitioning of C^{af}, but the term GG^{uv} in the partitioning of C^{ae}.

Finally it should be mentioned that the introduction of an additional symmetry operator, Q, defined by

$$Qa = e, \quad Qe = a, \quad Qb = f, \quad Qf = b \ ,$$

which was necessary in another case [10] contradicts the condition (2.3) if both sets do not have cardinality 1, $|\{u_\lambda\}|=|\{v_\mu\}|=1$.

3. Structure II

The structure I treated in the preceding section has been constructed on the basic assumption that the vertices $\{a,b,e,f\} \in C$ to which the terminal moieties are linked (see Scheme 1) form a cut set. This assumption is dropped now. On the contrary, each pair of adjacent subunits, F, G, H, and J, which is linked in C via one of the vertices a, b, e, or f, is linked by an additional edge. The resulting structure II is shown in Figure 3. Its symmetry is assumed such that eqs. (1) and (4) are satisfied. Furthermore, for simplicity it is assumed that the vertices a, b, e, and f have the degree 2 in C.

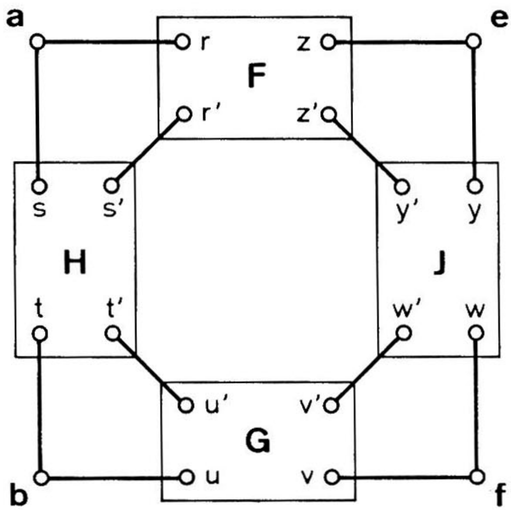


Figure 3: General Structure II

In contrast to the previous section where $D = C^{abef}$ has represented a disconnected graph consisting of the four components F, G, H, and J, here $D = C^{abef}$ is a connected graph in which the subunits F and H, H and G, G and J, and finally J and F are linked by one edge respectively; we will refer briefly to these four edges by the term additional linking edges.

Besides some cycles which are fully localized in one of the subunits there is here in D a set of other cycles to which the additional linking edges belong and which are, hence, fully delocalized over all the subunits, i.e. such a cycle consists of the four additional linking edges and four paths, from each subunit one path.

In $C^{af}(C^{ae})$, due to the presence of the vertices b and e (b and f) there are additional cycles to which at least one of these vertices belongs. They are either fully or incompletely delocalized as may be seen from Figure 3. There are 9 different types of such cycles; in Figure 4 the numbers 1 to 9 are assigned to them. The types 1 and 2 are feasible in C^{af} as well as in C^{ae}; the types 3-5 can only occur in C^{af}, the types 6-9 only in C^{ae}. The assignment of the types of cycles will also be used in the concise notation of the polynomials. Thus, D_1 will denote the sum of all polynomials associated with those partial graphs which are generated from C^{af} or C^{ae} by the removal of one cycle of type 1 and the vertex e or f, respectively. Similarly, $D_{1,4}(D_{1,8})$ denotes the sum of bicyclic contributions corresponding to the removal of one cycle of type 1 and one cycle of type 4(8) from $C^{af}(C^{ae})$; etc.

Applying eq. (7) twice to C^{af} and C^{ae}, respectively, one obtains:

$$
\begin{aligned}
C^{af} = \\
&= x^2D - xD^t - xD^u - 2txD_1 - 2txD_2 \\
&- xD^y + D^{ty} + D^{uy} + 2tD_1^y + 2tD_2^y \\
&- xD^z + D^{tz} + D^{uz} + 2tD_1^z + 2tD_2^y \\
&- 2txD_4 + 2tD_4^t + 2tD_4^u + 4t^2D_{1,4} \\
&- 2txD_5 + 2tD_5^t + 2tD_5^u \qquad - 2tD_3
\end{aligned}
\tag{23}
$$

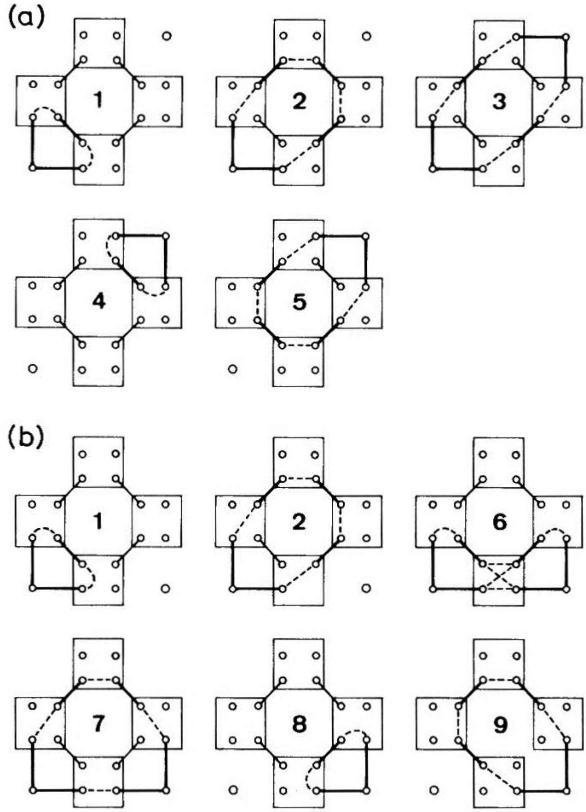


Figure 4: The types of cycles which can be constructed in C^{af} (a) and in C^{ae} (b), respectively, but not in $D=C^{abef}$. The heavy lines indicates the edges, the broken heavy lines the paths of which these cycles consist. For the composition of the cycles of type 6 one may alternatively use either the paths P_{uv} and $P_{u'v'}$ or the paths $P_{uv'}$ and $P_{u'v}$; in D_6 all these paths have to be considered.

and

$$
\begin{aligned}
C^{ae} &= \\
&= x^2D - xD^t - xD^u - 2txD_1 - 2txD_2 \\
&- xD^v + D^{tv} + D^{uv} + 2tD_1^v + 2tD_2^v \\
&- xD^w + D^{tw} + D^{uw} + 2tD_1^w + 2tD_2^w \\
&- 2txD_8 + 2D_8^t + 2tD_8^u + 4t^2D_{1,8} \\
&- 2txD_9 + 2tD_9^t + 2tD_9^u \quad - 2tD_6 - 2tD_7 \ .
\end{aligned} \tag{24}
$$

The terms of the first row of eqs. (23) and (24) are identical; hence, they cancel each other in (C^{af}-C^{ae}). But there are more terms which equal each other due to the presumed symmetry, namely:

$$
\begin{aligned}
D^v &= D^z \ , \qquad D^w = D^y \ , \\
D_4 &= D_8 \ , \qquad D_5 = D_9 \ ;
\end{aligned}
$$

these are the first terms in the other rows of eqs. (23) and (24). Taking all these equalities into account, one obtains

$$
\begin{aligned}
C^{af} - C^{ae} &= \\
&= -[D^{tv} + D^{tw} - D^{ty} - D^{tz} + D^{uv} + D^{uw} - D^{uy} - D^{uz}] - \\
&- 2t\{[D_1^v + D_1^w - D_1^y - D_1^z] + [D_2^v + D_2^w - D_2^y - D_2^z] + \\
&+ D_3 - [D_4^t + D_4^u - D_8^t - D_8^u] - [D_5^t + D_5^u - D_9^t - D_9^u] - \\
&- D_6 - D_7\} + 4t^2\{D_{1,4} - D_{1,8}\} \ .
\end{aligned} \tag{25}
$$

Each graph which is associated with one of the terms composing the r.h.s. of eq. (25) contains at least one of the additional linking edges. Thus, in order to express eq. (25) in terms of the polynomials associated with the subunits F, G, H, and J, the additional linking edges must be removed.

The notation of the eight terms composing the first brackets of eq. (25) may be generalized to $D^{\alpha\beta}$ where $\alpha \in \{t,u\}$ and $\beta \in \{v,w,y,z\}$. The removal of all the additional linking edges from one of these terms results in

$$
\begin{aligned}
D^{\alpha\beta} = [FGHJ &- F^{z'}GHJ^{y'} + F^{z'}G^{v'}HJ^{w'y'} \\
&- FG^{v'}HJ^{w'} + F^{z'}G^{u'}H^{t'}J^{y'} \\
&- FG^{u'}H^{t'}J + F^{r'z'}GH^{s'}J^{y'} \\
&- F^{r'}GH^{s'}J + FG^{u'v'}H^{t'}J^{w'} \\
&\qquad + F^{r'}G^{v'}H^{s'}J^{w'} \\
&\qquad + F^{r'}G^{u'}H^{s't'}J \\
&- F^{z'}G^{u'v'}H^{t'}J^{w'y'} \\
&- F^{r'z'}G^{v'}H^{s'}J^{w'y'} \\
&- F^{r'z'}G^{u'}H^{s't'}J^{y'} \\
&- F^{r'}G^{u'v'}H^{s't'}J^{w'} + F^{r'z'}G^{u'v'}H^{s't'}J^{w'y'} \\
&-2t\, F_{r'z'}G_{u'v'}H_{s't'}J_{w'y'}]^{\alpha\beta}
\end{aligned}
\tag{26}
$$

the superscripts $\alpha\beta$ outside the brackets indicate that the indices α and β have to be added in the proper way to each term within the brackets; in the case where $\alpha\beta$ stands for tv, for instance the first and last term are altered to $FG^{v}H^{t}J$ and $-2tF_{r'z'}G^{v}_{u'v'}H^{t}_{s't'}J_{w'y'}$, respectively.

In order to simplify the notation for the cyclic contribution in eq. (26) the following abbreviation will be used

$$[F_{r'z'}G_{u'v'}H_{s't'}J_{w'y'}]^{\alpha\beta} = D_{10}^{\alpha\beta} \tag{27}$$

On inspection one recognizes that terms of eq. (26) have 2,4,6,8 and 10 different indices (used as superscripts), respectively. Thus, with regard to eq. (26) one may express the first brackets of eq. (25) as follows

$$[1/(25)] = -2t \sum_{\alpha\beta} D_{10}^{\alpha\beta} + \sum_{v=1}^{5} O^{2v} \quad ; \tag{28}$$

where 2v indicates the number of indices which form the superscript and O^{2v} denotes the sum of all such (non-cyclic) terms (the signs have to be in accord with eqs. (25) and (26), of course). It should be noted, that the indices α and β must be contained in each supercript; with regard to eq. (25) they influence the resulting sign of the term as follows:

α:	t	t	t	t	u	u	u	u
β:	v	w	y	z	v	w	y	z
sign:	-	-	+	+	-	-	+	+

In the next steps the sums O^2, O^4, etc. are considered.

Obviously, O^2 is generated by $[FGHJ]^{\alpha\beta}$, i.e.:

$$O^2 = \sum_{\alpha\beta} [FGHJ]^{\alpha\beta} \ .$$

Thus, one obtains:

$$O^2 = - FG^vH^tJ - FGH^tJ^w + FGH^tJ^y + F^zGH^tJ$$

$$- FG^{uv}HJ - FG^{u}HJ^{w} + FG^{u}HJ^{y} + FG^{u}HJ^{z} .$$

Taking into account the following equalities

$$F = G , \qquad F^{z} = G^{v} ,$$
$$J^{w} = J^{y} , \quad FG^{v} = F^{z}G ,$$

which are caused by the symmetry as expressed in eqs. (4-6), O^2 results with regard to eq. (13) in

$$O^{2} = HJ(G^{u}G^{v}-GG^{uv}) = HJG^{2}_{uv} . \qquad (29a)$$

In a similar manner, O^4 is given by

$$O^{4} = \sum_{\alpha\beta} [-F^{z'}GHJ^{y'}-FG^{v'}HJ^{w'}-FG^{u'}H^{t'}J-F^{r'}GH^{s'}J]^{\alpha\beta}$$

and consists of $4 \cdot 8 = 32$ individual terms; taking into account the equalities caused by symmetry the number of individual terms is reduced to 16 and O^4 takes the following intermediate form

$$\begin{aligned} O^{4} = & [G^{u'}G^{v} - GG^{u'v}](H^{s't} - H^{t't})J + \\ & + [G^{u}G^{v'} - GG^{uv'}]H(J^{wy'} - J^{yy'}) - \\ & - [G^{u}G^{vv'} + G^{v}G^{uv'} - G^{v'}G^{uv} - GG^{uvv'}]HJ^{y'} - \\ & - [G^{u}G^{u'v} + G^{v}G^{uu'} - G^{u'}G^{uv} - GG^{uu'v}]H^{t'}J . \end{aligned}$$

To the brackets of the first two terms eq. (13) may be applied; recently, the following equality has been derived [6]:

$$G^kG^{lm} + G^lG^{km} - G^mG^{kl} - GG^{klm} = 2G_{kl}G^m_{kl} \ , \tag{30}$$

which may be applied to the brackets of the last two terms. Thus, O^4 results in

$$O^4 = G^2_{u'v}(H^{s't}-H^{t't})J + G^2_{uv'}H(J^{wy'}-J^{yy'}) - - 2G_{uv}G^{v'}_{uv}HJ^{w'} - 2G_{uv}G^{u'}_{uv}H^{t'}J \ . \tag{29b}$$

The sum O^6 is originally composed of 48 individual terms; by the presumed symmetry their number is reduced to 40. They may be condensed to 6 terms to which the eqs. (13), (30) and the following one (also recently derived [6]):

$$\begin{aligned} &G^kG^{lmn} + G^lG^{kmn} - G^mG^{kln} - G^nG^{klm} - \\ &- G^{kl}G^{mn} + G^{km}G^{ln} + G^{kn}G^{lm} - GG^{klmn} = \\ &= 2(G^m_{kl}G^n_{kl} + G_{kl}G^{mn}_{kl}) \end{aligned} \tag{31}$$

may be applied. Thus, one finally obtains

$$\begin{aligned} O^6 = &G^2_{u'v'}(H^{t't}-H^{s't})(J^{w'w}-J^{w'y}) + \\ &+ 2G_{u'v}G^{v'}_{u'v}(H^{t't}-H^{s't})J^{w'} + 2G_{uv'}G^{u'}_{uv'}H^{t'}(J^{w'w}-J^{y'w}) + \\ &+ (G^{v'}_{uv})^2 HJ^{w'y'} + (G^{u'}_{uv})^2 H^{s't'}J + \\ &+ 2(G^{u'}_{uv}G^{v'}_{uv} + G_{uv}G^{u'v'}_{uv})H^{t'}J^{w'} \ . \end{aligned} \tag{29c}$$

In the case of O^8 the originally 32 individual terms are reduced to 16 by means of the symmetry presumed; they may be contracted to four terms. After the application of eqs. (13) and (30) one obtains

$$O^8 = -(G^{v'}_{u'v})^2(H^{t't}-H^{s't})J^{w'y'} - (G^{u'}_{uv'})^2 H^{s't'}(J^{w'w}-J^{w'y}) - 2G^{v'}_{uv}G^{u'v'}_{uv}H^{t'}J^{w'y'} - 2G^{u'}_{uv}G^{u'v'}_{uv}H^{s't'}J^{w'} \quad . \qquad (29d)$$

Finally, O^{10} consists originally of 8 terms of which 6 terms are pairwise equal due to the symmetry presumed. Applying eq. (13) one obtains

$$O^{10} = (G^{u'v'}_{uv})^2 H^{s't'}J^{w'y'} \quad . \qquad (29e)$$

In order to finish the transformation of the first brackets of eq. (25) one has to consider its cyclic term

$$\sum_{\alpha\beta} D^{\alpha\beta}_{10} = \sum_{\alpha\beta}[F_{r'z'}, G_{u'v'}, H_{s't'}, J_{w'y'}]^{\alpha\beta}$$

which originally consists of 8 individual terms; 6 of these cancel each other due to the symmetry presumed. Without transforming the remaining terms [11] one obtains

$$\sum_{\alpha\beta} D^{\alpha\beta}_{10} = (G^{u}_{u'v'}G^{v}_{u'v'} - G_{u'v'}G^{uv}_{u'v'})H_{s't'}J_{w'y'} \quad . \qquad (29f)$$

Collecting all the partial results, eqs. (29a-f), the first brackets of eq. (25) results in

$$\begin{aligned} -[D^{tv} + D^{tw} - D^{ty} - D^{tz} + D^{uv} + D^{uw} - D^{uy} - D^{uz}] = \\ = G^2_{uv}HJ + G^2_{uv'}(H^{s't}-H^{t't})J + G^2_{u'v}H(J^{y'w}-J^{w'w}) - \\ - 2G_{uv}G^{u'}_{uv}H^{t'}J - 2G_{uv}G^{v'}_{uv}HJ^{w'} + G^2_{u'v'}(H^{s't}-H^{t't})(J^{w'y}-J^{w'w}) - \\ - 2G_{u'v}G^{v'}_{u'v}(H^{s't}-H^{t't})J^{w'} - 2G_{uv'}G^{u'}_{uv'}H^{t'}(J^{y'w}-J^{w'w}) + \end{aligned} \qquad (32)$$

$$+ (G^{v'}_{uv})^2 HJ^{w'y'} + (G^{u'}_{uv})^2 H^{s't} J + 2(G^{u'}_{uv}G^{v'}_{uv} + G_{uv}G^{u'v'}_{uv})H^{t'}J^{w'} +$$
$$+ (G^{v'}_{uv})^2 (H^{s't} - H^{t't})J^{w'y'} + (G^{u'}_{uv'})^2 H^{s't'}(J^{y'w} - J^{w'w}) -$$
$$- 2G^{v'}_{uv}G^{u'v'}_{uv}H^{t'}J^{w'y'} - 2G^{u'}_{uv}G^{u'v'}_{uv}H^{s't'}J^{w'} + (G^{u'v'}_{uv})^2 H^{s't'}J^{w'y'} -$$
$$- 2t(G^{u}_{u'v'}G^{v}_{u'v'} - G_{u'v'}G^{uv}_{u'v'})H_{s't'}J_{w'y'} .$$

Assuming that H and J are isomorphic such that the following equalities hold

$$H = J, \qquad H^{t'} = J^{w'} , \qquad H^{s't'} = J^{w'y'} \tag{33}$$
$$H^{s't} = J^{y'w} , \quad H^{t't} = J^{w'w} , \quad H_{s't'} = J_{w'y'} ,$$

the r.h.s. of eq. (32) takes the following form:

$$G^2_{uv}H^2 + (G^2_{uv'} + G^2_{u'v})H(H^{s't} - H^{t't}) - 2G_{uv}(G_{uv} + G_{u'v})H^{t'}(H^{s't} - H^{t't}) +$$
$$+ G^2_{u'v'}(H^{s't} - H^{t't})^2 - 2(G_{u'v}G^{v'}_{u'v} + G_{uv'}G^{u'}_{uv'})H^{t'}(H^{s't} - H^{t't}) +$$
$$+ [(G^{u'}_{uv})^2 + (G^{v'}_{uv})^2]HH^{s't'} + 2(G^{u'}_{uv}G^{v'}_{uv} + G_{uv}G^{u'v'}_{uv})(H^{t'})^2 + \tag{34}$$
$$+ [(G^{u'}_{uv'})^2 + (G^{v'}_{u'v})^2]H^{s't'}(H^{s't} - H^{t't}) -$$
$$- 2(G^{u'}_{uv} + G^{v'}_{uv})G^{u'v'}_{uv}H^{t'}H^{s't'} + (G^{u'v'}_{uv})^2(H^{s't'})^2 -$$
$$- 2t(G^{u}_{u'v'}G^{v}_{u'v'} - G_{u'v'}G^{uv}_{u'v'})H^2_{s't'} .$$

Obviously, these terms cannot be contracted to a square, even if G were assumed to be symmetric such that

$$G_{uv}^{u'} = G_{uv'}^{v'}, \quad G_{uv'} = G_{u'v'}, \quad G_{uv'}^{u'} = G_{u'v}^{v'} . \tag{35}$$

But no final conclusion can be drawn concerning this without considering the cyclic contributions in eq. (25).

For the cyclic contributions in eq. (25) which are generated by the removal of the cycles of type 1 (see Figure 4), one obtains by neglecting of eq. (33) and (35):

$$\begin{aligned} - [D_1^v + D_1^w - D_1^y - D_1^z] = \\ = G_{uv}G_{u'v}H_{t't}J - G_{uv'}G_{u'v'}H_{t't}J^{w'w} - \\ - (G_{uv}^{v'}G_{u'v} + G_{uv}G_{u'v}^{v'})H_{t't}J^{w} + G_{uv'}G_{u'v'}H_{t't}J^{w'y} - \\ - G_{uv}^{u'}G_{u'v}H_{t't}^{s'}J + G_{uv}^{v'}G_{u'v}^{v'}H_{t't}J^{w'y'} + G_{uv'}^{u'}G_{u'v'}H_{t't}^{s'}J^{w'w} + \\ + (G_{uv}^{u'v'}G_{u'v} + G_{uv}^{u'}G_{u'v}^{v'})H_{t't}^{s'}J^{w'} - G_{uv'}^{u'}G_{u'v'}H_{t't}^{s'}J^{w'y} - \\ - G_{uv}^{u'v'}G_{u'v}^{v'}H_{t't}^{s'}J^{w'} . \end{aligned} \tag{36}$$

In order to achieve this result the equalities caused by the symmetry operator P have been taken into account and eq. (15) as well as the following equations derived recently [6]

$$G^{kl}G_{em} - G^{l}G_{lm}^{k} = G_{kl}G_{km}^{l} , \tag{37}$$

$$G^{kn}G_{lm} + G^{k}G_{lm}^{n} - G^{n}G_{lm}^{k} - GG_{lm}^{kn} = G_{kl}^{n}G_{mk} + G_{kl}G_{km}^{n} , \tag{38}$$

$$G^{kln}G_{lm} + G^{kl}G_{lm}^{n} - G^{ln}G_{lm}^{k} - G^{l}G_{lm}^{kn} = G_{kl}G_{km}^{ln} + G_{kl}^{n}G_{km}^{l} \tag{39}$$

have been applied.

In a very similar manner the following intermediate results are obtained:

$$-[D_2^v+D_2^w-D_2^y-D_2^z] = \tag{40}$$

$$= (G_{uv'}G^{v}_{u'v'}-G^{v}_{uv'}G_{u'v'})H_{s't}J_{w'y'} - (G^{u'}_{uv'}G^{v}_{u'v'}-G^{u'v}_{uv'}G_{u'v'})H^{t'}_{s't}J_{w'y'};$$

$$D_3 = G_{uv'}G_{u'v}H_{s't}J_{w'y} - G_{uv'}G^{v'}_{u'v}H_{s't}J^{y'}_{w'y} - \tag{41}$$

$$- G^{u'}_{uv'}G_{u'v}H^{t'}_{s't}J_{w'y} + G^{u'}_{uv'}G^{v'}_{u'v}H^{t'}_{s't}J^{y'}_{w'y};$$

$$[D_4^t + D_4^u - D_8^t - D_8^u] = \tag{42}$$

$$= G_{uv}G_{uv'}HJ_{ww'} - G^{v'}_{uv}G_{uv'}HJ^{y}_{ww'} - (G^{u'}_{uv}G_{uv'}+G_{uv}G^{u'}_{uv'})H^{t'}J_{ww'} +$$

$$+ (G^{v'}_{nv}G^{u'}_{uv'}+G^{u'v'}_{uv}G_{uv'})H^{t'}J^{y'}_{ww'} - G^{u'}G_{vu'}H^{t't}J_{ww'} + G^{v'}G_{vu'}H^{s't}J_{ww'} +$$

$$+ G^{u'}_{uv}G^{u'}_{uv'}H^{s't}J_{ww'} - G^{u'v'}_{uv}G^{u'}_{uv'}H^{s't'}J^{y'}_{ww'} + G^{u'v'}(H^{t't}-H^{s't})J^{y'}_{ww'};$$

$$[D_5^t + D_5^u - D_9^t - D_9^u] = (G_{u'v}G^{u}_{u'v'}-G^{u}_{u'v}G_{u'v'})H_{s't'}J_{w'y'} - \tag{43}$$

$$- (G^{v'}_{u'v}G^{u}_{u'v'}-G^{uv'}_{u'v}G_{u'v'})H_{s't'}J^{w'}_{wy'};$$

$$D_6 = GG_{u'v'}H_{t't}J_{ww'} - G^{u'}G_{u'v'}H^{s'}_{t't}J_{w'w}; \tag{44}$$

$$D_7 = G_{uv}G_{u'v'}H_{s't}J_{y'w} - G_{uv}^{u'}G_{u'v'}H_{s't}^{t'}J_{y'w} -$$
$$- G_{uv}^{v'}G_{u'v}H_{s't}J_{y'w}^{w'} + G_{uv}^{u'v'}G_{u'v'}H_{s't}^{t'}J_{y'w}^{w'} . \qquad (45)$$

Finally the bicyclic contributions of eq. (25) are given as follows:

$$[D_{1,4}-D_{1,2}] =$$
$$= (G_{uu'}G_{vv'}-GG_{uu',vv'})H_{t't}J_{w'w}$$
$$(G_{uu'}G_{vv'}^{u'}-G^{u'}G_{uu',vv'})H_{t't}^{s'}J_{w'w}$$
$$- (G_{uu'}^{v'}G_{vv'}-G^{v'}G_{uu',vv'})H_{t't}J_{w'w}^{y'} +$$
$$+ (G_{uu'}^{v'}G_{vv'}^{u'}-G^{u'v'}G_{uu',vv'})H_{t't}^{s'}J_{w'w}^{y'} . \qquad (46)$$

With eq. (25) an intermediate result for $(C^{af}-C^{ae})$ has been given in the case where C agrees with the structure shown in Figure 3. The r.h.s. of eq. (25) is the sum of the r.h.s. of the eqs. (32), (36), and (40)-(46). Several terms of this sum may be contracted if eq. (33) and related equalities, also generated by the isomorphism of H and J, are taken into consideration. But as a very careful treatment of the resulting expression has shown that a quadratic form for $(C^{af}-C^{ae})$ cannot be achieved by any means. This situation is changed neither by the assumption that G be symmetric in accord to eq. (35) nor by taking t = 0 which would restrict the consideration to acyclic polynomials only. Thus, one has to state:

Result 3: If a pair of topologically related isomers is constructed according to Scheme 1 and the structure of the central subunit, C, is represented as in Figure 3, the appearance of inversions within the TEMO pattern of these isomers cannot be excluded.

Certainly the numerous cyclic contributions to $(C^{af}-C^{ae})$ make it more difficult to achieve a quadratic form; but the impossibility of transforming even the r.h.s. of eq. (32) into a square indicates that the difficulties do not arise only from the cyclic contributions.

4. Structure III.

In order to achieve a quadratic form, in the case of structure I it was essential to reduce the cardinality of the vertex set $\{v_\mu\}$ to 1. Such a reduction has the effect that the generation of cycles localized in F(G) is prevented when $C^{af}(C^{ae})$ is partitioned at the vertex e(f). This observation suggests the reduction of the number of additional linking edges. This is implemented in Structure III as shown by Figure 5.

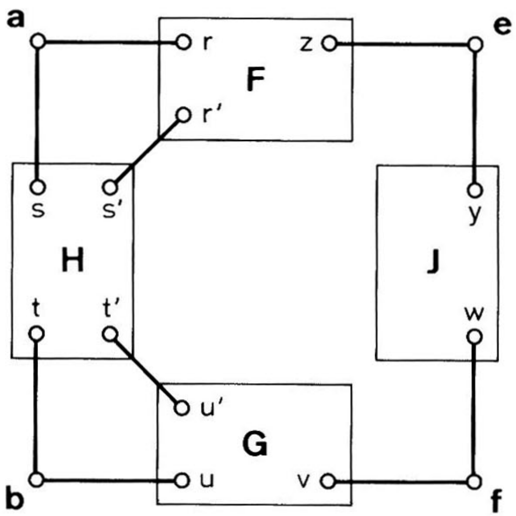


Figure 5: General Structure III

The treatment of Structure III does not differ in principle from that of Structure II; it is noticeably simpler and involves only a few terms. Therefore, the final result only is given:

$$(C^{af}-C^{ae}) =$$

$$= (G^2_{uv}H + G^2_{u'v}(H^{s't}-H^{t't})-2G_{uv}G^{u'}_{uv}H^{s'} + (G^{u'}_{uv})^2H^{s't'} + \qquad (47)$$

$$+ 2t(G_{uv}G_{u'v}H_{tt'} - G^{u'}_{uv}G_{u'v}H^{s'}_{tt'}))J.$$

Obviously, this expression cannot be transformed directly into a sequare; in order to make this feasible some requirements must be satisfied, for instance (HJ) as well as $[H^{s't}-H^{t't})J]$ must be squares. Obviously this will be the case only if all the different factors, H, $(H^{s't}-H^{t't})$, and J, are squares on their own. This would be realized for J if its graph is either an even membered Möbius cycle or a disconnected graph which consists of a pair of isomorphic components, say $J = \bar{J} \cup \tilde{J}$, $\bar{J} = \tilde{J}$. In the case of H the requirement that H and $(H^{s't} - H^{t't})$ are squares on their own can be realized only if the graph H consists of a pair isomorphic components, $H = \bar{H} \cup \tilde{H}$, $\bar{H} = \tilde{H}$, where $\bar{H}$ be connected with F, i.e. $s,s' \in \bar{H}$, and $\tilde{H}$ with G, i.e. $t,t' \in \tilde{H}$. Under this conditions $(H^{s't}-H^{t't})$ would indeed be a square:

$$H^{s't} - H^{t't} = \bar{H}^{s'}\tilde{H}^{t} - \bar{H}\tilde{H}^{t't} = \tilde{H}^2_{t't}$$

because $\bar{H}^{s'} = \tilde{H}^{t'}$ and $\bar{H} = \tilde{H}$. After having treated the other terms of eq. (47) in an analogous manner one obtains

$$C^{af}-C^{ae} = ([G_{uv}\tilde{H} - G^{u'}_{uv}\tilde{H}^{t'} + G_{u'v}\tilde{H}_{t't}]J)^2 \geq 0. \tag{48}$$

Unfortunately due to the assumption that H and J are disconnected, Structure III loses an essential characteristic, namely its connectivity. As a consequence, the structure corresponding to eq. (48) cannot be identified with Structure III but with the one shown in Figure 6. In this Structure IIIa $\bar{H}$ and $\tilde{H}$ are considered as parts of F and G, respectively, hence, they are not indicated in Figure 6. An essential feature of Structure IIIa is that the vertices e and f are connected by only one edge with F and G, respectively. In the case of Structure IIIa eq. (48) takes the following simple form

$$C^{af} - C^{ae} = (\tilde{J} \sum_{u} G_{uv})^2 \quad . \qquad (48')$$

The results of this section may be summarized as follows:

Result 4: If a pair of topologically related isomers is constructed according to Scheme 1 and the central subunit, C, exhibits a structure which agrees with the one shown in Figure 5, the non-appearance of inversions within the TEMO pattern cannot be concluded but if C agrees with the structure shown in Figure 6 TEMO without inversions result.

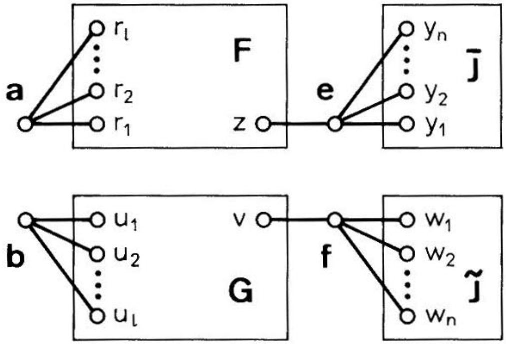


Figure 6: General structure IIIa for the central subunit C (the same result, eq. (48), is obtained if the vertices a and b and/or e and f are connected by an edge)

5. Structures IV and V

The result of the last section seems to indicate that a definite conclusion for TEMO without inversions is precluded, if in C the subunits F, G, H, and J are not only connected via the vertices a, b, e, and f, but there are additional connections either between F and G or between H and J. In order to prove these possibilities the Structures IV and V, depicted in Figure 7, are taken into consideration; in IV the subunits F and G, in V the subunits H and J are connected via an additional subunit, K. For convenience it is assumed that the vertices a, b, e, and f are of degree 2 in C.

We now consider the structure IV. Due to the symmetry of C, as expressed by eqs. (4-6), in case of IV there are the following relations in addition to eqs. (4)-(6):

$$PK = K,\ Pj = m,\ Pk = l,\ Pl = k,\ Pm = j. \tag{49}$$

For the sake of simplicity let L denote that partial graph of C which consists of F, G, K and the edges which connect them

$$L = F \cup G \cup K \cup \{\{jk\},\{lm\}\}. \tag{50}$$

After the partition of C^{af} and C^{ae} at the vertices b, e, and f, respectively, by means of eq. (7) one obtains

$$(C^{af}-C^{ae}) = HJ[L^{uz}-L^{uv}]. \tag{51}$$

Assuming $HJ = [h(x)]^2$ as in the case of structure I, the conclusion as to whether $(C^{af}-C^{ae}) \gtreqless 0$ depends only on $(L^{uz}-L^{uv}) \gtreqless 0$. Thus, the original problem concerning C is converted into a similar one which concerns L; the only difference is: the neighbourhoods of the vertices a, b, e, and f in C are of course arbitrary but defined while the neighbourhoods of u, v, and z in L are undefined.

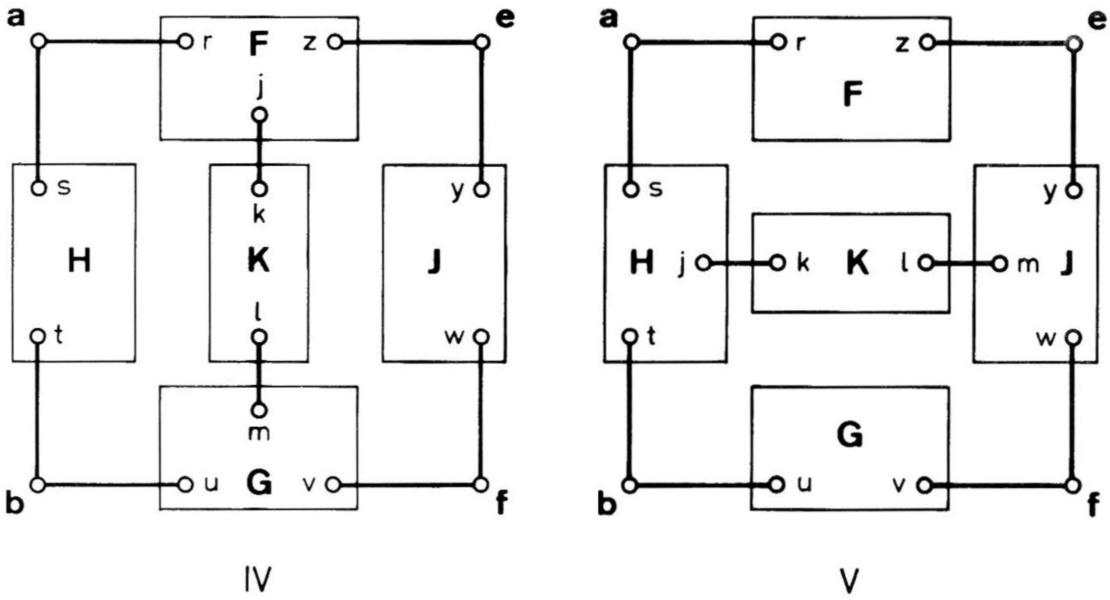


Figure 7: General Structures IV and V.

Having removed the edges {jk} and {lm} from the partial graphs of L and using the equalities of certain polynomials of F, G, and K due to the symmetry presumed one obtains

$$(L^{uz} - L^{uv}) = KG^2_{uv} - 2 K^k G_{uv} G^m_{uv} + K^{kl}(G^m_{uv})^2 \qquad (52)$$

This would be a perfect square if K, K^k, and K^{kl} would satisfy the condition

$$K = \alpha^2,\ K^k = \alpha\beta,\ k^{kl} = \beta^2, \qquad (53)$$

where α and β denote appropriate real polynomials. This demand is satisfied in a trivial manner if K would consist of two isomorphic components; such a situation has been discussed above in connection with eq. (47). But in this case, F and G would not be connected via K, i.e. Structure IV would have lost an essential characteristic and would have been converted into a variant of Structure I.

But eq. (53) can be satisfied also in a non-trivial manner if for K an even membered Möbius cycle is assumed, in which the vertices k and l are located at opposite positions. This may be proved as follows:

(1) The zeros of a 2n-membered Möbius cycle are given [12] by

$$x_\kappa = 2\cos(2\kappa-1)(\pi/2n),\ 1 \leqq \kappa \leqq 2n;$$

they are pairwise degenerate, hence,

$$K = \{\prod_{\kappa=1}^{n} [x-2\cos(2\kappa-1)(\pi/2n)]\}^2,$$

(2) K^{kl} consists of two isomorphic path graphs, P_{n-1}, which consists of (n-1) vertices each. The zeros of P_{n-1} are

$$x_\lambda = 2\cos(\lambda\pi/n), \quad 1 \leqq \lambda \leqq (n-1).$$

Due to the relation of the graphs, $K^{kl} = P_{n-1} \cup P_{n-1}$, each zero of P_{n-1} is a double root of K^{kl}; hence:

$$K^{kl} = \{\prod_{\lambda=1}^{n-1} [x-2\cos(\lambda\pi/n)]\}^2.$$

(3) The graphs $K^k = K^l$ are isomorphic with P_{2n-1}. The zeros of P_{2n-1} are

$$x_\mu = 2\cos(\mu\pi/2n), \quad 1 \leqq \mu \leqq (2n-1).$$

Within this set the index μ takes n times an even value and an odd value (n-1) times which may be described by $\mu = 2\lambda$, $1 \leqq \lambda \leqq (n-1)$ and $\mu = 2\kappa-1$, $1 \leqq \kappa \leqq n$, respectively. Thus the polynomials $K^k = K^l = P_{2n-1}$ may be expressed as follows:

$$K^k = \{\prod_{\kappa=1}^{n} [x-2\cos(2\kappa-1)(\pi/2n)]\}\{\prod_{\lambda=1}^{n-1} [x-2\cos(\lambda\pi/n)]\}.$$

Obviously, if K represents an even membered Möbius cycle, eq. (53) is satisfied; then $(L^{uz}-L^{uv}) \geqq 0$ and consequently under the condition $HJ = [h(x)]^2$ there is also $(C^{af}-C^{ae}) \geqq 0$. All this together allows one to state:

Results 5: For a pair of topologically related isomers constructed within Scheme 1 a TEMO pattern without inversion will result, if A and B are isomorphic and the central subunit C agrees with Structure IV shown in Figure 7 wherein H and I are either a) isomorphic or b) cospectral or c) two even (odd) membered Hückel-(Möbius)-cycles and K represents an even membered Möbius cycle in which k and l are located at opposite positions.

One may suppose that by modifying even membered Möbius cycles a series of graphs K could be generated which satisfy eq. (53). No attempts have been made in this direction because there is some doubt that such structures could really be used in the construction of pairs of topologically related isomers which have a thermodynamic stability such that they may be also synthesized and investigated experimentally.

We now turn to Structure V. Here, in contrast to eq. (50), the symmetry of C as expressed by eqs. (4)-(6) requires

$$PK = K,\ Pj = j,\ Pk = k,\ Pl = l,\ Pm = m. \tag{54}$$

Analogous to L the inner part of Structure V will be denoted by M and is defined as follows:

$$M = H \cup J \cup K \cup \{(jk), (lm)\}. \tag{55}$$

The partitioning of C^{af} and C^{ae} at the vertices b, e, and f, respectively, by means of eq. (7) results in

$$(C^{af} - C^{ae}) = M \cdot G_{uv}^{2}. \tag{56}$$

Obviously, $(C^{af} - C^{ae}) \gtreqless 0$ depends on $M \gtreqless 0$.

After the removal of the edges {jk} and {lm} the polynomial M is expressed as follows

$$M = HJK - H^{j}JK^{k} - HJ^{m}K^{l} + H^{j}J^{m}K^{kl}. \tag{57}$$

In order to transform the r.h.s. of eq. (57) into a square, K must satisfy eq. (53); further, H and J need to agree with

$$H = J, \; H^{j} = J^{m}.$$

This is realized simply if H and J are isomorphic; the assumption of cospectrality is insufficient here.

Under these conditions with regard to eq. (53) M takes the form

$$M = (\alpha H - \beta H^{j})^{2} \gtreqless 0.$$

Thus, in case of Structure V one may state:

<u>Results 6:</u> For a pair of topologically related isomers constructed within Scheme 1 a TEMO pattern without inversions will result, if A and B are isomorphic and the central subunit C agrees with Structure V shown in Figure 7 wherein H and J

are isomorphic and K represents an even membered Möbius cycle in which k and l are located at opposite positions.

The results 5 and 6 differs only slightly in the requirements concerning H and J.

It should be noted, that eqs. (51) and (56) may be applied to any graphs L and M, respectively, provided that they exhibit the symmetry presumed.

6. Some concrete structures for C

In the course of the research reported here some concrete structures of C have been considered to clear up or to prove some details in question. Apart from VI and VII (see Figure 8) they might be part of some polycyclic aromatic hydrocarbons. All these examples are presented in Table 1 which is completed by incorporating some earlier results [2].

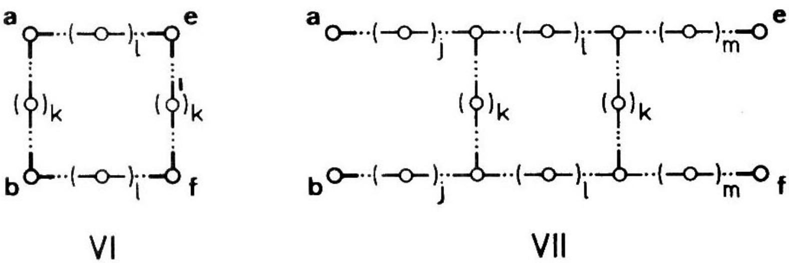
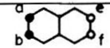
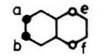
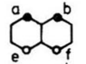
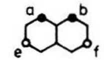
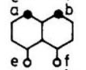
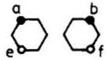
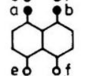
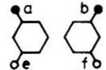
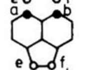
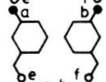
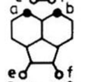
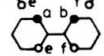
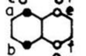
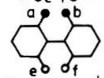
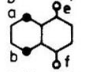
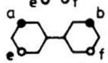
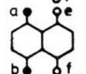
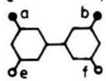
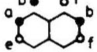


Figure 8: Structure VI and VII.

Table 1: Some concrete examples for C and $(C^{af}-C^{ae})$

No	C	$(C^{af}-C^{ae})$		No	C	$(C^{af}-C^{ae})$	
1	VI	P_k^2	a) c)	12		1	a)
2	VII	P_k^2	a) c)	13		(x^2-1)	b)
3		$3(x^2-1)$	b) [2]	14		$x^2(x^2-1)$	b)
4		$3(x^2-1)$	b)	15		$x^2(x^2-1)^2$	a) [2]
5		$3(x^2-1)$	b)	16		$x^2(x^2-1)^2$	a)
6		$3(x^2-1)$	b) [2]	17		$x^2(x^2-1)^2$	a)
7		$3(x^2-1)$	b) [2]	18		$x^2(x^2-1)^2-1$	b) [2]
8		$(x^2-1)^2$	a)	19		$x^2(x^2-1)^2-1$	b)
9		$(x^2-1)^2$	a)	20		$x^2(x^4-3x^2+1)$	b)
10		$(x^2-1)^2$	a)	21		$x^2(x^4-3x^2+1)$	b)
11		$x^2(x^2-2)(x^2-3)$	b)				

a) TEMO without inversions is anticipated; b) inversions are not excluded;
c) P_k denotes the polynomial of a path graph of k vertices

The examples 1 and 15-17 represent realisations of Structure I with H and J isomorphic and empty, respectively, while the examples 8, 12, and 13 verify Structure IV for H and J isomorphic (8,12) and different (13). As is to be expected, $(C^{af}-C^{ae}) \geqq 0$ is realized in case of 1, 8, 12, and 15-17.

With the examples 3, 8, and 11-14 all the possible distributions of the vertices a, b, e, and f upon the secondary carbon atoms of the skeleton of naphthalene are realized. Due to the symmetry of C expressed by eqs. (4)-(6) a and b as well as e and f must occupy equivalent positions. Disregarding the trivalent vertices of the naphthalene skeleton there are two classes of equivalent vertices assigned by α and β positions in chemistry (a vertex in α position is adjacent to a trivalent vertex). The pairs (a,b) and (e,f) may belong either to the same or to different equivalence classes; further, the vertices of a pair may be members either of the same or different six-membered rings. In this manner the six combinations listed above are generated. As seen from the Table, $(C^{af}-C^{ae})$ takes different expressions in the different cases. Such behaviour should be anticipated as, for instance, the application of eq. (51) to 8, 12, and 13 shows.

The Table contains some series of examples within which $(C^{af}-C^{ae})$ does not alter; such series are: (1,2), (3-7), (8-10), (15-17), (18,19), and (20,21). In each member of a given series a certain "kernel structure" is present which seems to determine the analytical form of $(C^{af}-C^{ae})$. Obviously, the kernel structure of 1(=VI) is a (2k+4) membered cycle in which a and e as well as b and f are adjacent and a and b as well as e and f are separated by k vertices. 1 is generated from its kernel structure by replacing the edges {ae} and {bf} by paths of the length (l+1). From the cycle 1(=VI) the example 2(=VII) is produced by transporting simultaneously the vertices which are related by the symmetry supposed (i.e.: {a,b} and {e,f}, respectively) along paths of the length (j+1) and (m+1), respectively, which originate from those vertices of the cycle 1 which were the original locations of the vertices {a,b} and {e,f}, respectively; j and m may be any natural number or zero. It seems that the members of the other series are related in a similar manner; as the examples 6 and 7 show, beside the route described above for the generation of 2 from 1, several modes for the derivation of structures from a given kernel structure seem to exist. Although all these points seem to reflect an interesting problem, no further investigation have been carried out.

The examples 18-21 may be derived from 15 and 16 by connecting the two components of C in a different manner; due to this interference the behaviour with regard to TEMO is changed.

7. Conclusions

If a pair of topologically related isomers is constructed according to Scheme 1 (this means: the terminal moieties A and B are isomorphic and the central moiety C is consistent either with Structure I, IV or V, satisfying the conditions listed in the Results 1, 5, and 6, respectively) then the union of the eigenvalue spectra of these isomers will present a perfect TEMO pattern without inversions.

The interest in TEMO patterns without inversions is quite natural: Because TEMO results solely from pure topology [13] it must be classified as a formalism from which, a priori, one does not know to what extent it is realized in nature. Fortunately, photo electron (PE) spectroscopy offers a possibility to prove the validity of the TEMO theorem experimentically. But this proof does not consist of the "topological predictions" of ionization potentials with any accuracy, but rather it consists of the prediction of the relative locations of the ionization potentials of the topologically related isomers. If TEMO without inversions is anticipated but the union of the PE spectra of the isomers exhibits some inversions, then these inversions indicate that among all the factors which determine the location of the ionization potentials the topological one does not dominate (it is interesting to see the reasons for that [14]). Because such a conclusion could not be drawn in the case where inversions are not definitely excluded from the TEMO pattern, the interest in topological models which guarantee TEMO without inversions is explained. It also explains the motivation for carrying out the cumbersome but very necessary work presented in the first three notes of the series.

8. Acknowledgement

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9. References and Annotations

[1] O.E. Polansky, Match, this issue, preceeding paper (Part 1 of this series).

[2] A. Graovac, O.E. Polansky, Croat. Chem. Acta, in press.

[3] O.E. Polansky, "Die Entwicklung des My-Polynoms...", Match, this issue.

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

[5] I. Gutman, Z. Naturforsch. 36a, 1112 (1981).

[6] O.E. Polansky, Match, this issue, subsequent paper (Part 3 of this series).

[7] See for example eq. (56) in [4].

[8] This is easily understood if each edge of a simple graph is considered as a pair of arcs which have opposite directions. Thus, any non-zero off-diagonal element, $(\Delta)_{rs}$, corresponds to the arc pointing from r to s. If the row r and the column s are struck out, the minor $\Delta_{r,s}$ does not contain any element corresponding to arcs which have either the vertex r as starting point or the vertex s as end point; hence any path P_{rs} is directed from s to r.

[9] I. Gutman, O.E. Polansky, Theoret. Chim. Acta 60, 203 (1981).

[10] see subsection 3.1 in [1].

[11] The remaining terms given in the round brackets of eq. (29e) cannot be transformed completely. With regard to the definitions given in [1] this expression is written in terms of μ-polynomials [9] as follows

$$[\sum\mu(G-u-P_{u'v'})][\sum\mu(G-v-P_{u'v'})]-[\sum\mu(G-P_{u'v'})][\sum\mu(G-u-v-P_{u'v'})]$$

where in each factor the summation runs independently over the set $\{P_{u'v'}\}$. Let this set be denoted by $\{P^j|1,2,\ldots,j,k,\ldots\} = \{P_{u'v'}\}$, then the expression above takes the form

$$\sum_{jk}\sum[\mu(G-u-P^j)\mu(G-v-P^k)-\mu(G-P^j)\mu(G-u-v-P^k)]$$

where j and k are independent, i.e. $j \lesseqgtr k$. If j = k, eq. (13) can be applied because $(G-P^j)$ may be understood as an individual graph; but the terms for which $j \neq k$ cannot be transformed in any way.

[12] E. Heilbronner, Tetrahedr. Letts. 1964, 1923;
H.E. Zimmerman, Tetrahedr. 38, 753 (1982);
R.A. Harris, Chem. Phys. Letts. 95, 256 (1983);
O.E. Polansky, Match 14, 47 (1983).

[13] O.E. Polansky, M. Zander, J. Mol. Struct. 84, 361 (1982);
O.E. Polansky, J. Mol. Struct. 113, 281 (1984);
M. Zander, O.E. Polansky, Naturwiss., in press.

[14] I. Motoc, J.N. Silverman, O.E. Polansky, Phys. Rev. A, 28, 3673 (1983);
I. Motoc, J.N. Silverman, O.E. Polansky Chem. Phys. Letts. 103, 285 (1984);
I. Motoc, J.N. Silverman, O.E. Polansky, G. Olbrich, Theor. Chim. Acta, in press.