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MOLECULAR TOPOLOGY.9. COMPOSITION RULES FOR SOME TOPOLOGICAL INDICES +

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Abstract. Composition rules for the Zagreb, M_1 [75Gut], Randić, χ [75Ran], Wiener, W [47Wie], Bertz, B [88Ber] and Y [90Diu] indices, and recursive relations for the last two in some particular classes of graphs, are presented and discussed.

1. Introduction. The fragmentation of a molecular graph and fragmental topological indices were developed in connection with QSAR studies [76Kie, 84Bal, 88Diu, 88Mek] and a theoretical fundament for the fragmental invariants is given by Mekenyan, Bonchev and Balaban in [88Mek].

Thus, the general rule for the fragmentation, stated in [88Mek]:

$$EF.I(F) = I(G) - \left[IF.I(F) + \sum_c IF.I(G - F)_c\right] \qquad (1)$$

defines the external fragment index, EF.I(F), as the difference in value between the global index, I(G) and the internal fragment indices for both the fragment, IF.I(F), and the remainder of the graph, $\sum_c IF.I(G-F)_c$, which can be a connected (c = 1) or a disconnected (c>1) one.

Conversely, the "synthesis" (computer assisted) of a molecule from precursors would be interested in the composition of the topological indices.

Let $H_1(V_1,E_1)$ and $H_2(V_2,E_2)$ be two precursor graphs which join together to give a graph G(V,E) with $V = V_1 \cup V_2$ and $E = E_1 \cup E_2 \cup NE$, where NE stands for the newly formed edges.

+ M.T.S. Centricities in Molecular Graphs. The MOLCEN Algorithm, M. V. Diudea et al. (manuscript in preparation)

The general rule for the composition of topological indices :

$$I(G) = I(H_1) + I(H_2) + E.I(H_1,H_2) \qquad (2)$$

requires the external interaction between the two precursors, $E.I(H_1,H_2)$, to be anticipated. Since the summation of more than two graph indices $I(H_1) + I(H_2) + \ldots + I(H_k)$ can be subsequently made as : $[I(H_1) + I(H_2)] + \ldots + I(H_k)$, we limit here to the two precursor scheme (eq.2).

In this paper, composition rules for some topological indices, for which the external interaction $E.I(G_1,G_2)$ was derived by us or taken from [88Mek, 88Ber], as well as recursive relations in some particular classes of graphs, are presented and discussed. Many examples refer to the graphs G_1 - G_4 whose "synthesis" is shown in fig.1.

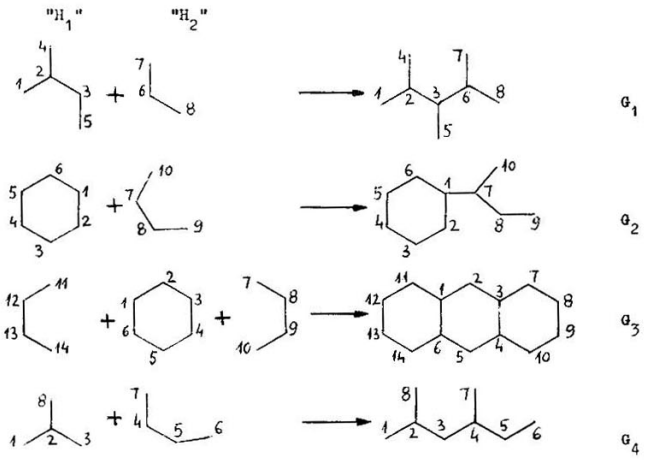

Fig.1. The "synthesis" of four molecular graphs

The numbering in G_1 - G_3 is maintained as in [88Mek] with the aim to facilitate the comparison between the two symmetric operations : fragmentation and composition of the topological indices.

2. Composition rules for some topological indices

2.1. Composition of the Zagreb index M_1 [75Gut]

$$M_1(G) = \sum_{i \in V} d_i^2$$

$$E.M_1(H_1,H_2) = 2 \sum_{(ij) \in NE} (d_{i \in H_1} + d_{j \in H_2} + 1) \qquad [88Mek] \quad (3)$$

$$M_1(G) = M_1(H_1) + M_1(H_2) + E.M_1(H_1,H_2)$$

The global external relation, $E.M_1(H_1,H_2)$ can be presented as a sum of "external action" of a precursor over the other one and viceversa, in the construction of M_1 index :

$$E.M_1(H_1,H_2) = E.M_1(H_1/H_2) + E.M_1(H_2/H_1) \qquad (4)$$

and subsequently (see [88Ber])

$$\begin{aligned} E.M_1(H_1/H_2) &= d_{G_i}^2 - d_{i \in H_1}^2 \\ E.M_1(H_2/H_1) &= d_{G_j}^2 - d_{j \in H_2}^2 \end{aligned} \qquad (5)$$

where d_{G_i}, d_{G_j} are the degrees of the affixing points after the bond $(ij) \in NE$ is achieved. Since $d_{G_i} = d_i + 1$, from eq.(4) and (5) one obtains the eq.(3) for the global external relation. The composition rule (3) is examplified on the graphs $G_1 - G_3$ [88Mek] :

G	$M_1(H_1)$	$M_1(H_2)$	$E.M_1(H_1,H_2)$	$M_1(G)$
1	16	6	10	32
2	24	10	10	44
3	10+10	24	32	76

2.2. Composition of the Randic index χ [75Ran]

$$\chi(G) = \sum_{(ij) \in E} (d_i \times d_j)^{-1/2}$$

$$E.\chi(H_1,H_2) = \sum_{(ij)\in NE}\left\{\left[(d_i + 1)(d_j + 1)\right]^{-1/2} + \sum_{a,i\in H_1}\left[\left[(d_i + 1) \times d_a\right]^{-1/2} - (d_i \times d_a)^{-1/2}\right] + \sum_{a,j\in H_2}\left[\left[(d_j + 1) \times d_a\right]^{-1/2} - (d_j \times d_a)^{-1/2}\right]\right\} \qquad [88Mek] \qquad (6)$$

$$\chi(G) = \chi(H_1) + \chi(H_2) + E.\chi(H_1,H_2)$$

where **a** represents vertexes adjacent to the affixing points $i\in H_1$ and $j\in H_2$. The rule (6) is exemplified on $G_1 - G_3$ [88Mek] :

G	$\chi(H_1)$	$\chi(H_2)$	$E.\chi(H_1,H_2)$	$\chi(G)$
1	2.27006	1.41421	-0.13085	3.553420
2	3.00000	1.91421	-0.07168	4.842535
3	3.82843	3.00000	0.10422	6.932653

Notice the identity between $E.\chi(H_1,H_2)$ and $EF.\chi(F)$ in [88Mek].

2.3. Composition of the Wiener index W [47Wie]

$$W(G) = 1/2 \sum_{(ij)\in V} d(ij)$$

$$E.W(H_1,H_2) = \sum_{j\in H_1}\sum_{j\in H_2}\left[d_{kj\in H_1} + d_{lj\in H_2} + 1\right] \quad (k,l)\in NE \quad (7)$$

$$W(G) = W(H_1) + W(H_2) + E.W(H_1,H_2)$$

where k\l are the affixing points and $d_{kj\in H_1} \setminus d_{lj\in H_2}$ represent the topological distance vs. the affixing points, in $H_1 \setminus H_2$. The cyclization processes produce supplemental complications, so that we limit here graphs to trees. For G_1 and G_2 one obtains :

G	$W(H_1)$	$W(H_2)$	$E.W(H_1,H_2)$	W(G)
1	18	4	43	65
2	27	10	84	121

2.4. Composition of the Bertz index B [88Ber]

$$B(G) = \sum_{i \in V} \binom{d_i}{2}$$

$$E.B(H_1,H_2) = \sum_{(ij) \in NE} (d_i + d_j) \qquad [88Ber] \qquad (8)$$

$$B(G) = B(H_1) + B(H_2) + E.B(H_1,H_2)$$

For G_1 - G_3 one obtains :

G	$B(H_1)$	$B(H_2)$	$E.B(H_1,H_2)$	B(G)
1	4	1	2 + 2	9
2	6	2	2 + 2	12
3	2 + 2	6	4 + 1 + 2	22

Notice that the Bertz index, B, is identical with the index or edge adjacencies [64Gor].

2.5. Composition or the Y - index [90Diu$_1$]

$$Y(G) = \sum_{i,d(ij) \in G} b_{(i,d(ij))} \times 10^{-d(ij)}$$

$$E.Y(H_1,H_2) = \sum_{d(lj) \in H_2} \left[1.1 + \sum_{d(kj) \in H_1} b_{(k,d(kj))} \times 10^{-(d(kj)+1)} \right] \times$$

$$\times 10^{-d(lj)} + \sum_{d(kj) \in H_1} \left[1.1 + \sum_{d(lj) \in H_2} b_{(l,d(lj))} \times \right.$$

$$\left. \times 10^{-(d(lj)+1)} \right] \times 10^{-d(kj)} \qquad (9)$$

$$Y(G) = Y(H_1) + Y(H_2) + E.Y(H_1,H_2)$$

where :

$$b_{(i,d(ij))} = \sum_{j:d(ij)=const} d_j \; ; \; i,j \in G \; ; \; d(ij) = \begin{cases} 0, & i=j \\ 0 < d(ij) \leqslant d(G) \end{cases}$$

and stands for the entries in the B (branch) - matrix (the layer matrix of vertex degrees) [90Diu$_1$]

$b_{(k,d(kj))} \backslash b_{(l,d(lj))}$ and $d(kj) \backslash d(lj)$ are the entries (in the B

and D matrices of precursors, respectively) corresponding to the affixing point ($k \in H_1 \setminus l \in H_2$) rows.

d(G) is the diameter of graph

For trees, the external (global) interaction of precursors, $E.Y(T_1,T_2)$ is double of the external (partial) interaction of precursors, on each other (the same, in this case) :

$$E.Y(T_1,T_2) = 2\ E.Y(T_2/T_1) = 2\ E.Y(T_1/T_2)$$

so that the global external relation, $E.Y(H_1,H_2)$ becomes :

$$E.Y(T_1,T_2) = 2 \sum_{d(lj)\in T_2} \left(\sum_{d(kj)\in T_1} 1.1 \times 10^{-d(kj)} \right) \times 10^{-d(lj)} =$$

$$= 2 \sum_{d(kj)\in T_1} \left(\sum_{d(lj)\in T_2} 1.1 \times 10^{-d(lj)} \right) \times 10^{-d(kj)} \qquad (10)$$

Notice that in eq.(10) the rows $b_{k,d(kj)} \setminus b_{l,d(lj)}$ are no more involved; only the distance rows, $d(lj) \setminus d(kj)$ are needed and only one term from (9) is to be calculated (by virtue of the operational symmetry). However, if one of the trees, H_1 and H_2 is bonded to a cycle, the relation (10) loses its validity and the calculation must be made according to eq.(9). The cyclization processes complicate so much the composition of Y invariants, that computations become cumbersone. Fig.2 provides four examples of the Y - composition :

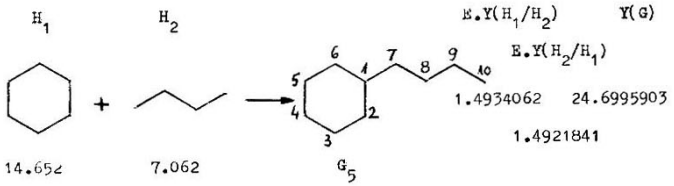

Fig.2. Composition of Y - indices [90Diu1]

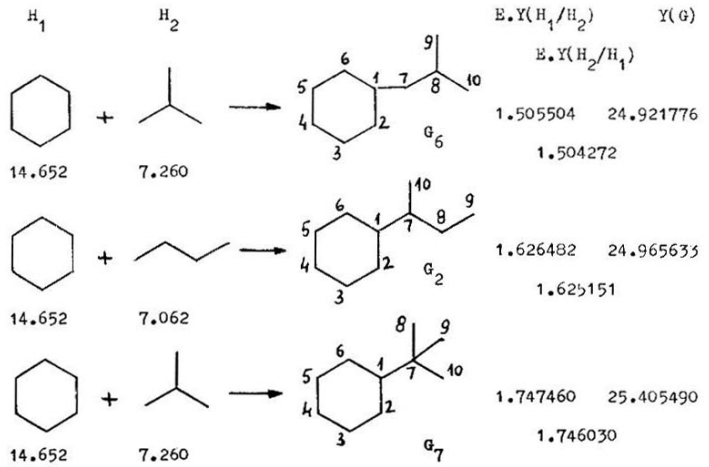

Fig.2. Composition of Y - indices [90Diu$_1$] (continued)

3. Composition rules in the construction "point by point" of trees

3.1. General relations

It is of interest to follow the construction of trees in adding vertex by vertex and the corresponding construction of the discussed topological indices. Thus, by adding a point, P_1 (path of single vertex) to a point, P_1 (which can by labeled as a star, $K_{1,0}$ - or zero edges), one obtains the $P_2 \backslash K_{1,1}$ tree.

The next added point leads to $P_3 \backslash K_{1,2}$ and hence the new point can be affixed either to a vertex of degree 1 (to give P_4) or to one of degree 2 (when $K_{1,3}$ is obtained).

By continuing the procedure of "point by point" construction the more and more complex trees can be generated, as shown in fig.3 (taken from [88Ber]).

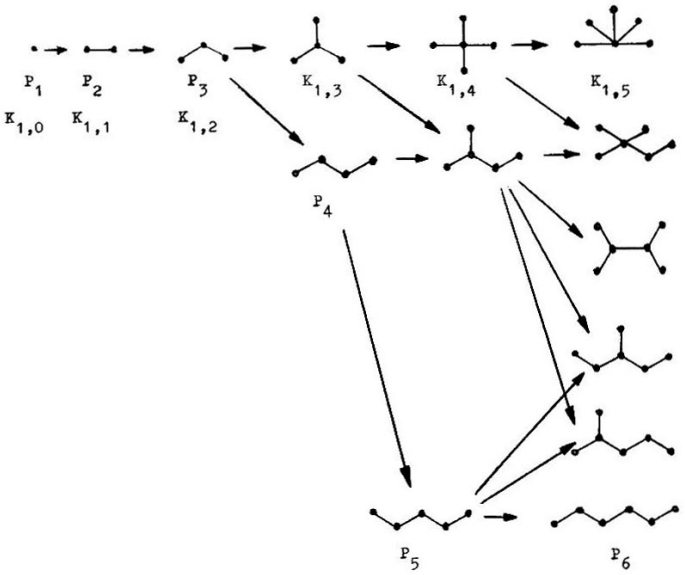

Fig.3. The generation of trees (from [88Ber])

Next, by keeping in mind that for an isolated point (e.g. P_1), the degree intrinsic distance and $I(P_1)$ are zero, the above composition rules eq. (3), (6) - (10) can be drastically simplified :

$$I(T_{v+1}) = I(T_v) + E.I(T_v,P_1) \qquad (11)$$

$$E.M_1(T_v,P_1) = 2\,(d_i + 1) \qquad (12)$$

$$E.\chi(T_v,P_1) = (d_i + 1)^{-1/2} + \sum_a \left[\left[(d_i + 1) \times d_a\right]^{-1/2} - (d_i \times d_a)^{-1/2}\right] \qquad (13)$$

$$E.B(T_v,P_1) = d_i \qquad (14)$$

$$E.W(T_v,P_1) = \sum_{j \in T} (d(ij) + 1) \qquad (15)$$

$$E.Y(T_v,P_1) = 2 \sum_{d(ij) \in T} 1.1 \times 10^{-d(ij)} \qquad (16)$$

where i denotes the affixing point and a (eq.(13)) are its adjacent points.

3.2. Recursive relations

The general relation (11) which calculates a topological index on the basis of the precedent term, can be explicitly formulated for some types of graphs (trees and cycles).

In this respect we developed recursive relations for the indices B and Y as follows :

B - index

Paths : $B(P_{v+1}) = B(P_v) + 1$ (17)

Stars : $B(K_{1,v'+1}) = B(K_{1,v'}) + v' \; ; \; v'=v-1$ (18)

Cycles : $B(C_{v+1}) = B(C_v) + 1$ (19)

Complete graphs : $B(K_{v+1}) = B(K_v) \times \left(\frac{v+1}{v-2}\right)$ (20)

Y - index

Paths : $Y(P_{v+1}) = Y(P_v) + 2\,(1 + 2\sum_{j=2}^{v} 10^{1-j} + 10^{-v})$ (21)

Stars : $Y(K_{1,v'+1}) = Y(K_{1,v'}) + 2\,(1.1 + 0.11 \times v')$ (22)

Cycles : $Y(C_{2k}) = \left(\frac{2k}{2k-1}\right) \times Y(C_{2k-1}) + 2 \times (2k) \times 10^{-k}$ (23)

$Y(C_{2k+1}) = \left(\frac{2k+1}{2k}\right) \times Y(C_{2k}) + 2 \times (2k+1) \times 10^{-k}$ (24)

Complete graphs : $Y(K_{v+1}) = Y(K_v) + v \times (0.3 \times v + 1.9)$ (25)

The recursive relations (21 - 25) can be used in connection with the relationships that we had presented in [90Diu$_2$] :

Paths : $Y(P_v) = 2\,(v-1) + \sum_{j=2}^{v} 4\,(v-j) + 2 \times 10^{1-j}$ (26)

Stars : $Y(K_{1,v'}) = v'\left[2 + 0.1\,(v'+1) + 0.01\,(v'-1)\right]$ (27)

Cycles : $$Y(2k) = 4k \times (1 + 2 \sum_{j=2}^{k} 10^{1-j} + 10^{-k}) \quad (28)$$

$$Y(2k+1) = 2 \times (2k + 1) \times (1 + 2 \sum_{j=2}^{k+1} 10^{1-j}) \quad (29)$$

Complete graphs : $$Y(K_v) = v \times (v - 1) \times (0.9 + 0.1 \times v) \quad (30)$$

4. Discussion

As stated in [88Mek], an external fragment invariant EF.I(F) (actually, the external interaction invariant, $E.I(H_1,H_2)$) must reflect the topology of the fragment in the same manner as the corresponding global invariant (topological index) does for the whole graph.

The property we tested was the molecular branching and, from fig. 2, it is obvious that the external interaction invariants, E.Y, follow the trend of global invariants, Y(G). However, this parallelism is perturbed both by the type of precursors and the location of mutual affixing points. The last term also involves two aspects: the vertex degree and its distance vs. the local center (s) of complexity. The degree of the affixing points seems to be decisive in this respect.

Thus in a variant of the "synthesis" of heptane isomers (fig.4), the C_2 fragment can be affixed to show the following E.Y values : 3.1702 ; 2.9524 and 2.7346 (entries 2; 6; 3) as the degree of its affixing point decreases from 3 to 1, irrespectively of the intrinsic complexity of its "reaction partner".

Similarly for the fragment C_3 : when affixed by a vertex of degree 1, it shows 2.95482 ; 2.73504 and 2.71306 (entries 7 - 9) whereas when affixed by the vertex of degree 2 the external values are 3.4320 ; 3.1944 and 2.9568 (entries 1,4 and 5).

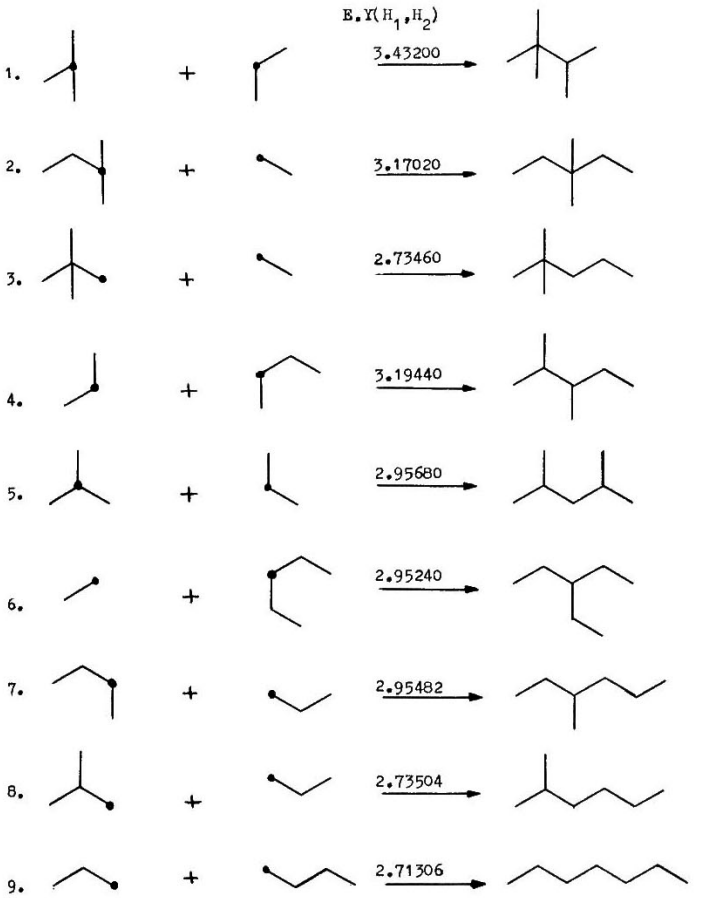

Fig.4. Construction of heptane isomers

When one of the precursors reduces to a point, similar regularities can be found. In fig.5 we designed the construction of heptane isomers by adding a point, in hexane precursors, either to a vertex with minimal degree (path (i)) or to one with maximal degree (path (ii)), to give one and the same heptane. The external interactions, in Y index, corresponding to

fig.5, are listed in Table 1.

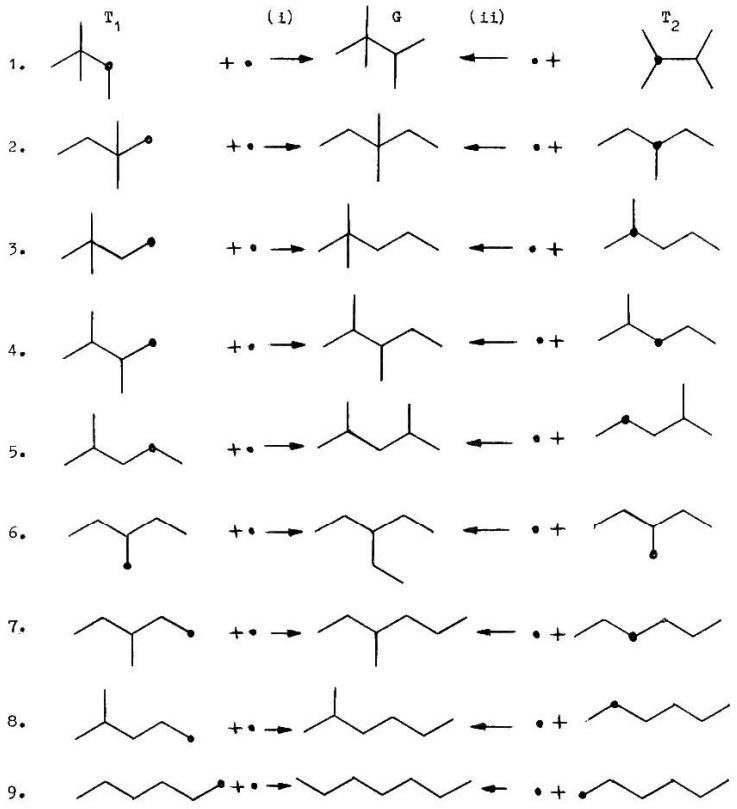

Fig.5. Construction of heptane isomers by affixing a vertex to (i) a vertex with minimal degree, and (ii) a vertex with maximal degree in hexane precursors.

Table 1. Minimal and maximal values of $E.Y(T,P_1)$ in the composition of $Y(G)$ in heptane isomers

No	$E.Y(T_1,P_1)_{min}$	$Y(T_1)$	$Y(G)$	$Y(T_2)$	$E.Y(T_2,P_1)_{max}$
1	2.70600	12.60600	15.31200	12.40800	2.90400

Table 1. (continued)

2	2.48820	12.60600	15.09420	12.19020	2.90400
3	2.44860	12.60600	15.05460	12.17040	2.88420
4	2.46840	12.40800	14.87640	12.17040	2.70600
5	2.66640	12.17040	14.83680	12.17040	2.66640
6	2.46840	12.19020	14.65860	12.19020	2.46840
7	2.44662	12.19020	14.63682	11.95062	2.68620
8	2.44464	12.17040	14.61504	11.95062	2.66442
9	2.44444	11.95062	14.39506	11.95062	2.44444

One can see that path (i) leads to minimal external interactions, whereas path (ii) gives maximal values of $E.Y(T,P_1)$. The interaction of the newly added point with one and the same precursor (e.g. entries 1-3) is differentiated by the degree of the affixing point and its distance vs. the local branching center. These differences we present (for all five topological indices herein discussed) in fig.6 and Table 2.

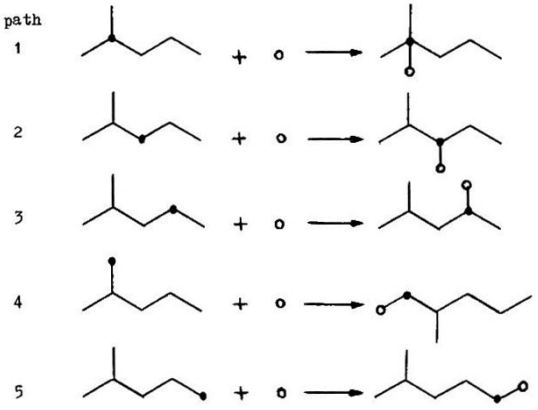

Fig.6. Construction of heptane isomers by affixing a vertex in various paths to 2 Me-pentane.

Table 2. E.I(T,P_1) and I(G) in the construction of heptane isomers starting from 2 me-pentane.

I(T)	path	M_1		χ		B		W		Y	
		EI	I(G)	EI	I(G)	EI	I(G)	EI	I(G)	EI	I(G)
M_1=20	1	8	28	0.29060	3.06066	3	8	14	46	2.88420	15.05460
χ=2.77006	2	6	26	0.41068	3.18074	2	7	14	46	2.70600	14.87640
B=5	3	6	26	0.35584	3.12590	2	7	16	48	2.66640	14.83680
W=32	4	4	24	0.53800	3.30806	1	6	18	50	2.46642	14.63682
Y=12.1704	5	4	24	0.50000	3.27006	1	6	20	52	2.44464	14.61504

In all these indices, EI parallels I, but only the EY ordering suggests the increasing of activation energy in going from a sterically nonhindered reaction center to a more hindered one (entries 5 to 1).

Conclusion

The composition of topological indices of a large graph (molecule) from the indices of its possible precursors is a practical question which in addition to the fragmentation [88Mek] enriches the theoretical and practical tools of molecular topology.

Acknowledgements

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