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Research Notes on the Topological Effect on Molecular Orbitals (TEMO); 6*.

Some Bicyclic C-Moieties for TEMO Model 3.

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Some bicyclic C-moieties for TEMO model 3 are derived from a general graph. The corresponding polynomials $\Delta C = C^{af} - C^{ae}$ are given.

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* For Part 5 see ref. [1].

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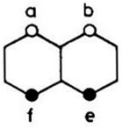
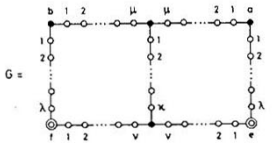
In the preceding note [1] of this series a procedure for a systematic generation of the central moiety C of a particular variant of TEMO model 3 was presented. This procedure has been termed C-formation. A kit of structures $\{F_j\}$ useful for this procedure was also given in [1]. The individual members F_j have been either derived from a general structure G_0 or generated from these by C-formation. At the end of this note it was mentioned that the following C-moiety

C = 

$$C^{af} - C^{ae} = 3(x^2-1) \qquad (1)$$

cannot be derived from the general graph G_0, neither directly nor by means of C-formation.

The C-moiety given above is obviously homeomorphic with the bicyclic graph G shown below and is obtained from G by taking $\kappa = \mu = \nu = 0$ and $\lambda = 2$. For the reasons discussed in some details in [1] we have been interested in whether some additional moieties, perhaps useful for C-formation, could be derived from G.

G = 

In order to test these possibilities we expand $G^{af} - G^{ae}$ in terms of P_n where P_n denotes the characteristic polynomial of a path con-

sisting of n vertices; in the expansion n is some integer formed from the structural parameters κ,λ,μ, and ν. The result of this is as follows

$$G^{af}-G^{ae} = \{2P_{\lambda}+[P_{\kappa+2}P_{\mu}P_{\nu}-2P_{\kappa+1}(P_{\mu}P_{\nu-1}+P_{\mu-1}P_{\nu})+4P_{\kappa}P_{\mu-1}P_{\nu-1}]\}P_{\mu}P_{\nu} \quad .(2)$$

Although eq. (2) is obtained in a straightforward calculation, its derivation is given in the Appendix because some transformations involved are not obvious.

From G some C-moieties are derived; they are collected in Table 1. Since $\kappa > 0$ would cause the non-planarity of any unsaturated hydrocarbon corresponding to G, $\kappa = 0$ is assumed for all moieties shown in Table 1. As seen from eq. (2) this expression is invariant in regard of an interchange of μ and ν; thus without any loss of generality and completeness for the structures given in Table 1 $\mu \geq \nu$ is assumed. It might be noted by the way that an interchange of μ and ν transforms any moiety into its side-inverted form [1].

As seen from Table 1 only one structure, G_1, exhibits the desirable property $\Delta G_1 \geq 0$. Obviously, $\Delta C = C^{af} - C^{ae} \geq 0$ is achieved if the C-moiety is produced by C-formation [1] according to $C = G_j \circledcirc \bar{G}_j$ or $C = G_j \circledcirc G_j$ or $C = \bar{G}_j \circledcirc \bar{G}_j$ where $\bar{G}_j$ denotes the side-inverted form of G_j. However, the moieties obtained in that manner correspond to common organic structures only if $\nu = 0$ in G_j. Thus, the value of the kit represented by Table 1 seems to be limited in comparison to that given in [1].

Table 1: Some C-moieties derived from G

(for all examples $\kappa = 0$ is assumed).

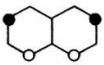
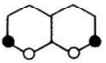
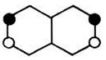
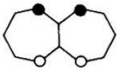
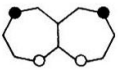
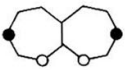
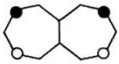
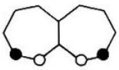
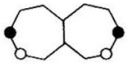
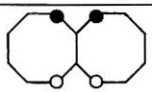
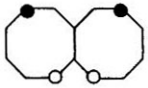
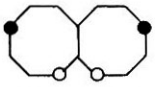
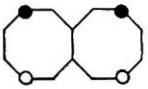
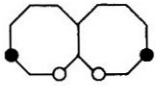
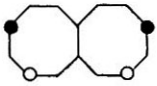
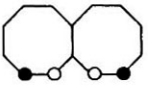
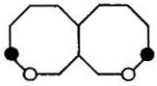
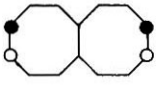
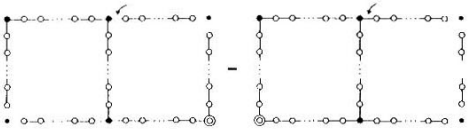
j	λ μ ν	G_j	$\Delta G_j = G_j^{af} - G_j^{ae}$
1	0 0 0		$(x^2+1) \geqq 0$
2	1 0 0		$(x+1)^2 - 2$
3	0 1 0		$x(x-1)^2(x+2)$
4	2 0 0		$3(x^2-1)$
5	1 1 0		$x^2(x^2-1)$
6	0 2 0		$(x^2-1)^2(x^2-3)$
7	0 1 1		$x^2(x^2-2)(x^2-3)$
8	3 0 0		$2x(x^2-2)+(x^2-1)$
9	2 1 0		$x(x^3+2x^2-3x-2)$
10	1 2 0		$(x+1)(x-1)^2[(x+1)^2(x-1)-2x]$
11	1 1 1		$x^2[(x^2-1)(x^2-4)+2x]$
12	0 3 0		$x(x^2-2)[x(x^2-1)(x^2-4)+2]$
13	0 2 1		$x(x^2-1)[x(x^4-6x^2+7)+2]$

Table 1 (cont.)

14	4	0	0		$2x^4-5x^2+1$
15	3	1	0		$x^2(3x^2-7)$
16	2	2	0		$(x^2-1)[(x^2-1)^2-2]$
17	2	1	1		$x^2(x^2-1)(x^2-2)$
18	1	3	0		$x^2(x^2-2)^2(x^2-3)$
19	1	2	1		$x^2(x^2-1)(x^2-3)^2$
20	0	4	0		$(x^4-3x^2+1)[x^2(x^2-2)(x^2-4)+1]$
21	0	3	1		$x^2(x^2-2)(x^6-7x^4+12x^2-2)$
22	0	2	2		$(x^2-1)^2(x^6-7x^4+11x^2+1)$

Appendix

Here eq. (2) is derived. The polynomial $\Delta G = G^{af} - G^{ae}$ is the difference of two characteristic polynomials, namely G^{af} and G^{ae}, which are uniquely determined by the corresponding graphs; thus, we use these graphs in order to represent the polynomial ΔG as follows:

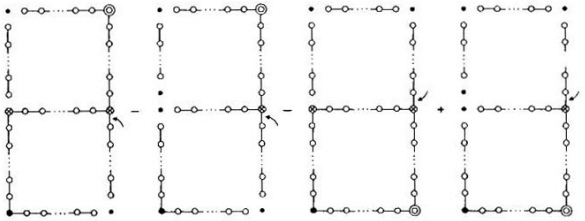
$\Delta G = G^{af} - G^{ae} =$  $-$

The vertices, which have been removed (i.e.: {a,f} and {a,e}, respectively) are indicated by dots.

In the first step the graphs are partitioned at the edges indicated by arrows. Since these edges are bridges Heilbronner's formula may be applied:

$$\phi(G,x) = \phi(G-e,x) - \phi(G-u-v,x) \qquad (3)$$

where $e = (u,v)$ is an edge of G incident with the vertices u and v and $\phi(G,x)$, $\phi(G-e,x)$, and $\phi(G-u-v,x)$ are the characteristic polynomials of the graph G and those graphs which are derived from G by removing the edge e and the vertices u and v, respectively. Thus one obtains:



In the next step the graphs are partitioned at the bridges marked by arrows. Partitioning the third graph from the left, one has an N-membered cycle, $N = \kappa + \lambda + \mu + \nu + 4$ for which one inserts

$$C_N = P_N - P_{N-2} - 2 \quad . \tag{4}$$

Thus, in this step one obtains:

$$\begin{aligned}
\Delta G = {} & [P_{\kappa-2\lambda+\mu+\nu+4} P_\mu P_\nu - P_{\kappa+\lambda+\mu+2} P_{\lambda+\nu+1} P_\mu P_{\nu-1}] - \\
& - [P_{\kappa+\lambda+\nu+2} P_{\lambda+\mu+1} P_{\mu-1} P_\nu - P_\kappa P_{\lambda+\mu+1} P_{\lambda+\nu+1} P_{\mu-1} P_{\mu-1}] - \\
& - [(P_{\kappa+\lambda+\mu+\nu+4} - P_{\kappa+\lambda+\mu+\nu+2} - 2) P_\lambda P_\mu P_\nu - P_{\kappa+\lambda+\mu+\nu+3} P_\lambda P_\mu P_{\nu-1}] + \\
& + [P_{\kappa+\lambda+\mu+\nu+3} P_\lambda P_{\mu-1} P_\nu - P_\kappa P_\lambda P_{\lambda+\mu+\nu+2} P_{\mu-1} P_{\nu-1}] \quad .
\end{aligned}$$

These ten terms are combined as follows:

$$
\begin{aligned}
\Delta G = {} & 2P_\lambda P_\mu P_\nu + \\
& + [P_{\kappa+\lambda+\mu+\nu+2}P_\lambda + (P_{\kappa+2\lambda+\mu+\nu+4} - P_{\kappa+\lambda+\mu+\nu+4}P_\lambda)]P_\mu P_\nu - \\
& - [P_{\kappa+\lambda+\nu+2}P_{\lambda+\mu+1} - P_{\kappa+\lambda+\mu+\nu+3}P_\lambda]P_{\mu-1}P_\nu - \\
& - [P_{\kappa+\lambda+\mu+2}P_{\lambda+\nu+1} - P_{\kappa+\lambda+\mu+\nu+3}P_\lambda]P_\mu P_{\nu-1} + \\
& + P_\kappa[P_{\lambda+\mu+1}P_{\lambda+\nu+1} - P_{\lambda+\mu+\nu+2}P_\lambda]P_{\mu-1}P_{\nu-1} \quad .
\end{aligned}
\tag{5}
$$

The terms of eq. (5) are transformed by means of the following equalities:

$$P_{k+\ell} = P_k P_\ell - P_{k-1}P_{\ell-1} \quad , \tag{6}$$

$$P_{k+\ell} - P_k P_\ell = -P_{k-1}P_{\ell-1} \quad , \tag{7}$$

$$P_k P_\ell - P_{k+a}P_{\ell-a} = P_{a-1}P_{k-\ell+a-1} \quad . \tag{8}$$

Eq. (6) is obtained by applying eq. (3) to a path with $k+\ell$ vertices. Eq. (7) follows from eq. (6). Eq. (8) is verified in a straightforward calculation after inserting $P_k = \sin(k+1)\delta/\sin\delta$ etc.

The first term of eq. (5) will be left unchanged. The square brackets of the last three terms of eq. (5) are transformed according to eq. (8). The second term is treated as follows: At first eq. (7) is applied to the round brackets of this term, then eq. (8) to the square brackets; so one obtains

$$
\begin{aligned}
& [P_{\kappa+\lambda+\mu+\nu+2}P_\lambda + (P_{\kappa+2\lambda+\mu+\nu+4} - P_{\kappa+\lambda+\mu+\nu+4}P_\lambda)] = \\
& = P_{\kappa+\lambda+\mu+\nu+2}P_\lambda - P_{\kappa+\lambda+\mu+\nu+3}P_{\lambda-1} = P_{\kappa+\mu+\nu+2} \quad .
\end{aligned}
$$

All these operations transform eq. (5) into the following expression:

$$\Delta G = [2P_{\lambda} + P_{\kappa+\mu+\nu+2} - P_{\kappa+\mu+1}P_{\nu-1} - P_{\kappa+\nu+1}P_{\mu-1} + P_{\kappa}P_{\mu-1}P_{\nu-1}]P_{\mu}P_{\nu} \quad (9)$$

From this expression eq. (2) is obtained by means of eq. (6).

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References

[1] J. Kruszewski, O.E. Polansky, Match (Math.Chem.), this issue, preceding paper