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ON MERRIFIELD–SIMMONS INDEX OF MOLECULAR GRAPHS

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ABSTRACT. The Merrifield–Simmons index $\sigma = \sigma(G)$ of a graph G is the number of independent vertex sets of G. This index can be calculated recursively and expressed in terms of Fibonacci numbers. We determine the molecular graphs for which σ can be recursively calculated in a single step.

1 Introduction: The Merrifield–Simmons index

In a series of articles [1–5], published in the 1970s and 1980s, Richard Merrifield and Howard Simmons elaborated a mathematically oriented theory of molecular structure, based on set topology. Eventually, this theory was outlined in the book [6]. Today, more than 30 years later, we see that this theory fall into oblivion and is not pursued

by any contemporary scholar. The only surviving feature of this theory is a quantity that nowadays is referred to as the *Merrifield–Simmons index*.

Let G be a graph with vertex set $\mathbf{V}(G) = \{v_1, v_2, \ldots, v_n\}$. An *independent vertex set* of G is a subset of $\mathbf{V}(G)$, such that no two vertices in it are adjacent. The number of distinct k-element independent vertex sets is denoted by $n(G, k)$. By definition, $n(G, 0) = 1$ for all graphs, and $n(G, 1) = n$.

The Merrifield–Simmons index is then defined as

$$\sigma = \sigma(G) = \sum_{k \geq 0} n(G, k)$$

i.e., it is just the total number of independent vertex sets of the underlying graph G [7].

The name "Merrifield–Simmons index" for the graph invariant σ was first time used by one of the present authors [8]. Nowadays, in mathematical chemistry and mathematics this name is commonly accepted. For details of the theory of the Merrifield–Simmons index see the review [9], the recent papers [10–14], and the references cited therein.

For the present consideration we need the following recurrence relations [6, 9].

If a graph G consists of disconnected components $H_1, H_2, \ldots, H_p$, then

$$\sigma(G) = \prod_{i=1}^{p} \sigma(H_i) \,. \tag{1}$$

Let v be a vertex of the graph G, and let N_v be the set consisting of the vertex v and its first neighbors. Then

$$\sigma(G) = \sigma(G - v) + \sigma(G - N_v) \,. \tag{2}$$

The Fibonacci numbers F_n , $n \geq 0$ are defined recursively as

$$F_n = F_{n-1} + F_{n-2}$$

with initial conditions $F_0 = F_1 = 1$. Thus

$$F_2 = 2 \ , \ F_3 = 3 \ , \ F_4 = 5 \ , \ F_5 = 8 \ , \ F_6 = 13 \ , \ F_7 = 21 \ , \ F_8 = 34$$

etc.

When formula (2) is applied to the terminal vertex of the n-vertex path P_n, we get

$$\sigma(P_n) = \sigma(P_{n-1}) + \sigma(P_{n-2}) \tag{3}$$

a relation that has the same form as the recurrence relation for the Fibonacci numbers. By direct calculation, we can check that $\sigma(P_1) = 2$ and $\sigma(P_2) = 3$, from which, by using Eq. (3), it follows step-by-step

$$\sigma(P_3) = 5 \ , \ \sigma(P_4) = 8 \ , \ \sigma(P_5) = 13 \ , \ \sigma(P_6) = 21 \ , \ \sigma(P_7) = 34$$

etc. We thus conclude that the Merrifield–Simmons index of the path is simply related with the Fibonacci numbers as

$$\sigma(P_n) = F_{n+1} \quad \text{for} \ \ n = 1, 2, 3, \ldots \ . \tag{4}$$

Identity (4) is also known for a long time.

2 Calculating the Merrifield–Simmons index

Combining the recursion relations (1), (2), and the identity (4), it is possible to express the Merrifield–Simmons index of any (molecular) graph in terms of Fibonacci numbers. We illustrate this fact on the example of triphenylene.

The molecular graph of triphenylene G_0 is depicted in Fig. 1. The vertex to which relation (2) will be applied is indicated by a heavy dot. This yields

$$\sigma(G_0) = \sigma(G_1) + \sigma(G_2) \, .$$

The recurrence relation (2) needs now to be applied to the subgraphs G_1 and G_2 (again to the vertices indicated by heavy dots, see Fig. 1), resulting in:

$$\begin{aligned} \sigma(G_1) &= \sigma(G_3) + \sigma(G_4) \\ \sigma(G_2) &= \sigma(G_5) + \sigma(G_6) \, . \end{aligned}$$

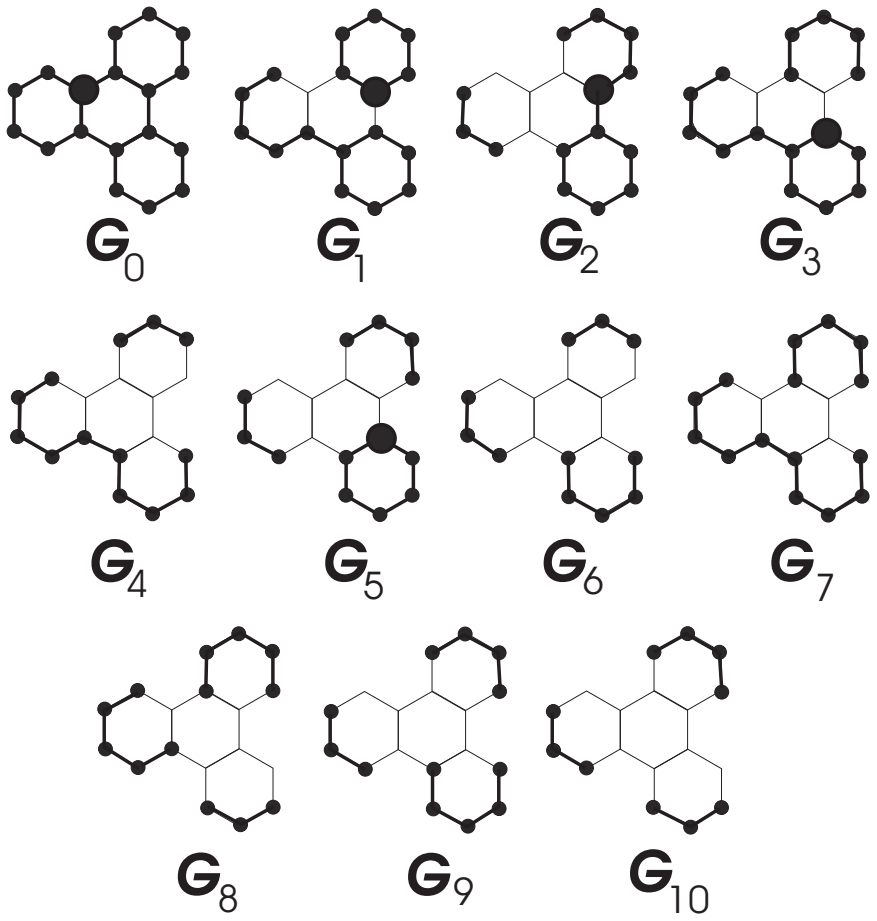

Fig. 1. The molecular graph of triphenylene (G_0) and its subgraphs needed for the calculation of the Merrifield–Simmons index $\sigma(G_0)$.

The subgraph G_4 consists of two components, both being paths. The subgraph G_6 consists of three components, all three being paths. Therefore, applying (1) and (4), we get

$$\begin{aligned} \sigma(G_4) &= \sigma(P_{10})\,\sigma(P_3) = F_{11}\,F_4 = 144 \cdot 5 = 720 \\ \sigma(G_6) &= \sigma(P_5)\,\sigma(P_3)\,\sigma(P_3) = F_6\,F_4\,F_4 = 13 \cdot 5 \cdot 5 = 325\,. \end{aligned}$$

In order to compute $\sigma(G_3)$ and $\sigma(G_5)$, one needs to apply (1), (2) and (4) once again. Thus,

$$\begin{aligned}\sigma(G_3) &= \sigma(G_7) + \sigma(G_8) \\ &= \sigma(P_{10})\,\sigma(P_5) + \sigma(P_5)\,\sigma(P_5)\,\sigma(P_3) \\ &= F_{11}\,F_6 + F_6\,F_6\,F_4 = 144 \cdot 13 + 13 \cdot 13 \cdot 5 = 1872 + 845 = 2717\end{aligned}$$

and

$$\begin{aligned}\sigma(G_5) &= \sigma(G_9) + \sigma(G_{10}) \\ &= \sigma(P_5)\,\sigma(P_4)\,\sigma(P_3) + \sigma(P_4)\,\sigma(P_3)\,\sigma(P_3) \\ &= F_6\,F_5\,F_4 + F_5\,F_4\,F_4 = 13 \cdot 8 \cdot 5 + 8 \cdot 5 \cdot 5 = 520 + 200 = 720\,.\end{aligned}$$

This now gives

$$\begin{aligned}\sigma(G_1) &= 2717 + 720 = 3437 \\ \sigma(G_2) &= 720 + 325 = 1045\end{aligned}$$

which finally yields

$$\sigma(G_0) = 3437 + 1045 = 4482\,.$$

By means of this example we see how the Merrifield–Simmons index of any (molecular) graph can be expressed in terms of Fibonacci numbers. In the general case, in order to achieve this goal, we must apply Eqs. (1), (2), and (4) several times. This requires the examination of a large number of vertex–deleted subgraphs, making the calculations complicated and error prone.

However, there exists large classes of molecular graphs in which the above described calculation can be accomplished in a single step. In the subsequent sections we describe these classes.

3 Simple calculation of the Merrifield–Simmons index of some acyclic molecular graphs

Example 3.1. *Consider the molecular graph T_0 of 3-ethyl-5-methyloctane, depicted in Fig. 2. When Eqs. (1), (2), and (4) are applied to its vertex labeled by v, then*

$$T_0 - v = P_5 \cup P_5 \qquad \textit{and} \qquad T_0 - N_v = P_1 \cup P_2 \cup P_2 \cup P_3$$

implying

$$\begin{aligned}\sigma(T_0) &= \sigma(P_5)\,\sigma(P_5) + \sigma(P_1)\,\sigma(P_2)\,\sigma(P_2)\,\sigma(P_3) \\ &= F_6\,F_6 + F_2\,F_3\,F_3\,F_4 = 13 \cdot 13 + 2 \cdot 3 \cdot 3 \cdot 5 = 259\,.\end{aligned}$$

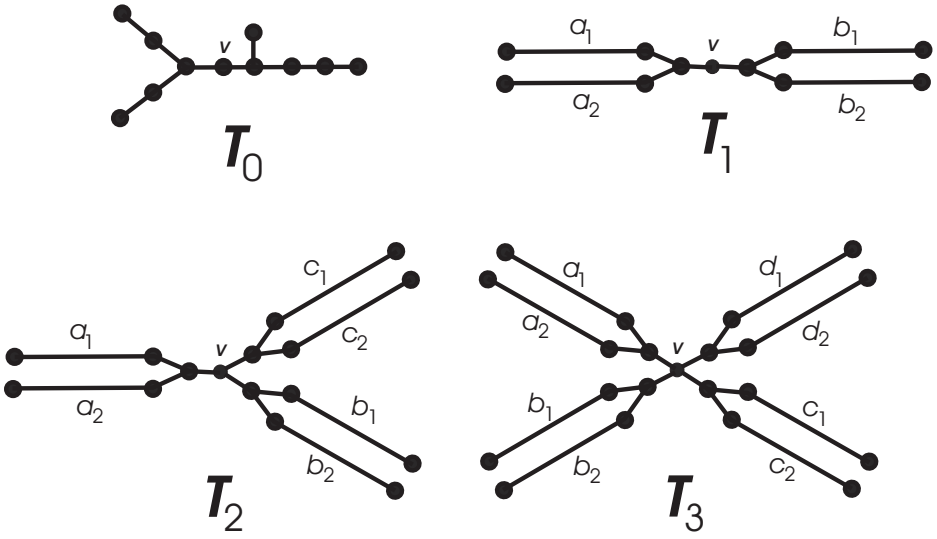

Fig. 2. Acyclic molecular graphs for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step.

It can be easily recognized that T_0 is a special case of the molecular graph T_1, in which the parameters a_1, a_2, b_1, b_2 are non-negative integers. Thus, for T_0, $a_1 = a_2 = 2$, $b_1 = 1$, $b_2 = 3$.

Bearing in mind that

$$T_1 - v = P_{a_1+a_2+1} \cup P_{b_1+b_2+1} \qquad \text{and} \qquad T_1 - N_v = P_{a_1} \cup P_{a_2} \cup P_{b_1} \cup P_{b_2}$$

by applying Eqs. (1), (2), and (4) we get:

$$\begin{aligned}\sigma(T_1) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{b_1+b_2+1}) + \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{b_1})\,\sigma(P_{b_2}) \\ &= F_{a_1+a_2+2}\,F_{b_1+b_2+2} + F_{a_1+1}\,F_{a_2+1}\,F_{b_1+1}\,F_{b_2+1}\,.\end{aligned}$$

Extending this argument, we arrive at the chemical trees T_2 and T_3. By fully analogous calculation, we have:

$$\begin{aligned}\sigma(T_2) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{b_1+b_2+1})\,\sigma(P_{c_1+c_2+1}) \\ &+ \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{b_1})\,\sigma(P_{b_2})\,\sigma(P_{c_1})\,\sigma(P_{c_2})\end{aligned}$$

and

$$\begin{aligned}\sigma(T_3) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{b_1+b_2+1})\,\sigma(P_{c_1+c_2+1})\,\sigma(P_{d_1+d_2+1}) \\ &+ \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{b_1})\,\sigma(P_{b_2})\,\sigma(P_{c_1})\,\sigma(P_{c_2})\,\sigma(P_{d_1})\,\sigma(P_{d_2})\,.\end{aligned}$$

The series T_1, T_2, T_3 cannot be continued because in the case of molecular graphs the vertex degree must not be greater than 4 (see [15]). Thus T_1, T_2, T_3 form a complete set of acyclic molecular graphs for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step.

4 Simple calculation of the Merrifield–Simmons index of some unicyclic molecular graphs

Example 4.1. *Consider the molecular graph U_0 of isopropyl-cyclopentane, depicted in Fig. 3. When Eqs. (1), (2), and (4) are applied to its vertex labeled by v, then*

$$U_0 - v = P_3 \cup P_4 \qquad \textit{and} \qquad T_0 - N_v = P_1 \cup P_1 \cup P_2$$

implying

$$\begin{aligned}\sigma(U_0) &= \sigma(P_3)\,\sigma(P_4) + \sigma(P_1)\,\sigma(P_1)\,\sigma(P_2) \\ &= F_4\,F_5 + F_2\,F_2\,F_3 = 5 \cdot 8 + 2 \cdot 2 \cdot 3 = 52\,.\end{aligned}$$

The molecular graph U_0 is a special case of U_1, in which the parameters a_1, a_2 are non-negative integers whereas r is the size of the (unique) cycle, $r \geq 3$. In particular, for U_0, $a_1 = a_2 = 1$, $r = 5$.

Bearing in mind that

$$U_1 - v = P_{a_1+a_2+1} \cup P_{r-1} \qquad \text{and} \qquad U_1 - N_v = P_{a_1} \cup P_{a_2} \cup P_{r-3}$$

by applying Eqs. (1), (2), and (4) we get:

$$\begin{aligned}\sigma(U_1) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{r-1}) + \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{r-3}) \\ &= F_{a_1+a_2+2}\,F_r + F_{a_1+1}\,F_{a_2+1}\,F_{r-2}\,.\end{aligned}$$

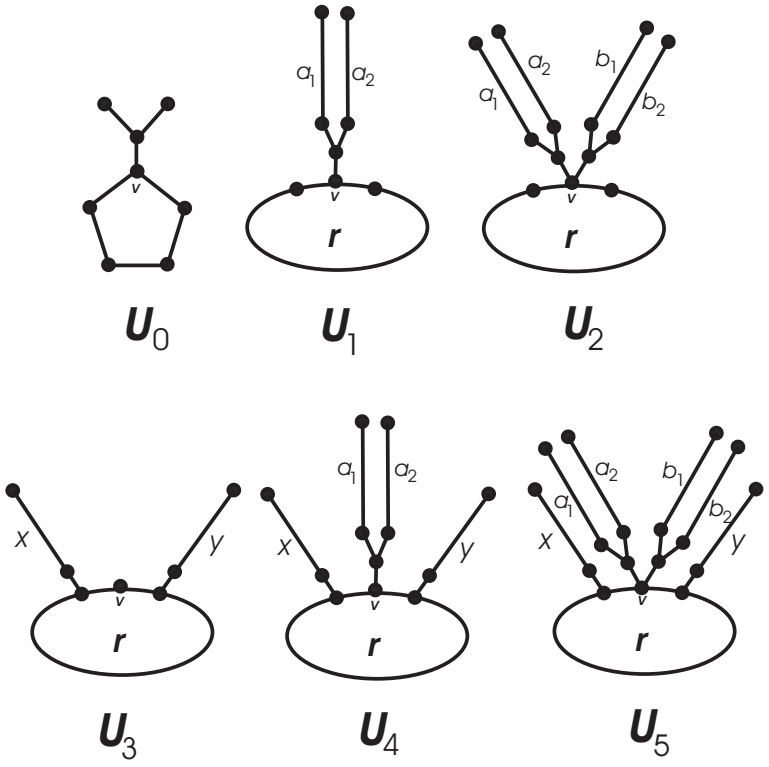

Fig. 3. Unicyclic molecular graphs for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step.

By attaching two branches to the vertex v we obtain the molecular graph U_2. Note that two is the maximal number of branches that may be attached. Then, in full analogy to the previous case, we have:

$$\sigma(U_2) = \sigma(P_{a_1+a_2+1})\,\sigma(P_{b_1+b_2+1})\,\sigma(P_{r-1}) + \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{b_1})\,\sigma(P_{b_2})\,\sigma(P_{r-3})\,.$$

Another class of unicyclic molecular graphs with the required property is represented by U_3, cf. Fig. 3. In this graph, two path fragments with x and y vertices are

attached to the first neighbors of the vertex v. Recall that if $x = y = 0$, then U_3 is just the cycle of size r. For this molecular graph,

$$U_3 - v = P_{x+y+r-1} \qquad \text{and} \qquad U_3 - N_v = P_x \cup P_y \cup P_{r-3}$$

which directly yields

$$\sigma(U_3) = \sigma(P_{x+y+r-1}) + \sigma(P_x)\,\sigma(P_y)\,\sigma(P_{r-3})\,.$$

Also the combination of the above described two types of molecular graphs, namely U_4 and U_5 possess the needed property. By calculation fully analogous to what was described above, we get:

$$\begin{aligned}
\sigma(U_4) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{x+y+r-1}) + \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_x)\,\sigma(P_y)\,\sigma(P_{r-3}) \\
\sigma(U_5) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{b_1+b_2+1})\,\sigma(P_{x+y+r-1}) \\
&+ \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{b_1})\,\sigma(P_{b_2})\,\sigma(P_x)\,\sigma(P_y)\,\sigma(P_{r-3})\,.
\end{aligned}$$

The molecular graphs U_1, U_2, U_3, U_4, U_5 with parameters $a_1, a_2, b_1, b_2, x, y, \geq 0$ and $r \geq 3$ are the only unicyclic species for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step.

5 Simple calculation of the Merrifield–Simmons index of some bicyclic molecular graphs

Example 5.1. *Consider the molecular graph B_0 of 1,8-diethyl-naphthalene, depicted in Fig. 4. When Eqs. (1), (2), and (4) are applied to its vertex labeled by v, then*

$$B_0 - v = P_{13} \qquad \textit{and} \qquad B_0 - N_v = P_2 \cup P_2 \cup P_3 \cup P_3$$

implying

$$\begin{aligned}
\sigma(B_0) &= \sigma(P_{13}) + \sigma(P_2)\,\sigma(P_2)\,\sigma(P_3)\,\sigma(P_3) \\
&= F_{14} + F_3\,F_3\,F_4\,F_4 = 610 + 3 \cdot 3 \cdot 5 \cdot 5 = 835\,.
\end{aligned}$$

As easily seen, the bicyclic molecular graph B_0 is a special case of B_1, in which the parameters x, y are non-negative integers whereas r and s are the sizes of the two cycle, $r, s \geq 3$. In particular, for B_0, $x = y = 2$, $r, s = 6$.

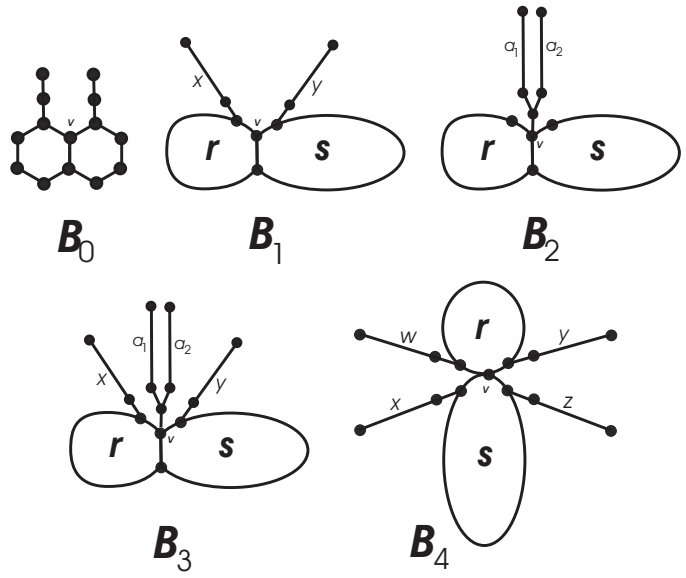

Fig. 4. Bicyclic molecular graphs for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step.

Using the same reasoning as in the cases of acyclic and unicyclic graphs, we immediately arrive at the molecular graphs B_2 and B_3 depicted in Fig. 4. In addition to these, we have one more bicyclic system, represented by B_4 in which the parameters w, x, y, z are non-negative integers. By direct calculation we arrive at the following expressions:

$$\begin{aligned}
\sigma(B_1) &= \sigma(P_{x+y+r+s-3}) + \sigma(P_x)\,\sigma(P_y)\,\sigma(P_{r-3})\,\sigma(P_{s-3}) \\
\sigma(B_2) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{r+s-3}) + \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_{r-3})\,\sigma(P_{s-3}) \\
\sigma(B_3) &= \sigma(P_{a_1+a_2+1})\,\sigma(P_{x+y+r+s-3}) + \sigma(P_{a_1})\,\sigma(P_{a_2})\,\sigma(P_x)\,\sigma(P_y)\,\sigma(P_{r-3})\,\sigma(P_{s-3}) \\
\sigma(B_4) &= \sigma(P_{w+y+r-1})\,\sigma(P_{x+z+s-1}) + \sigma(P_w)\,\sigma(P_x)\,\sigma(P_y)\,\sigma(P_z)\,\sigma(P_{r-3})\,\sigma(P_{s-3})\,.
\end{aligned}$$

6 Simple calculation of the Merrifield–Simmons index of some tricyclic molecular graphs

Example 6.1. *Consider the molecular graph D_0 of dicyclobutano[1,2;2,3]cyclohexane, depicted in Fig. 5. When Eqs. (1), (2), and (4) are applied to its vertex labeled by v, then*

$$D_0 - v = P_9 \qquad \textit{and} \qquad D_0 - N_v = P_1 \cup P_1 \cup P_3$$

implying

$$\begin{aligned}\sigma(D_0) &= \sigma(P_9) + \sigma(P_1)\,\sigma(P_1)\,\sigma(P_3) \\ &= F_{10} + F_2\,F_2\,F_4 = 89 + 2 \cdot 2 \cdot 5 = 109\,.\end{aligned}$$

The tricyclic molecular graph D_0 is a special case of D_1, in which the parameters r, s, t are integers greater than or equal to 3. In particular, for B_0, $r = s = 4$, $t = 6$.

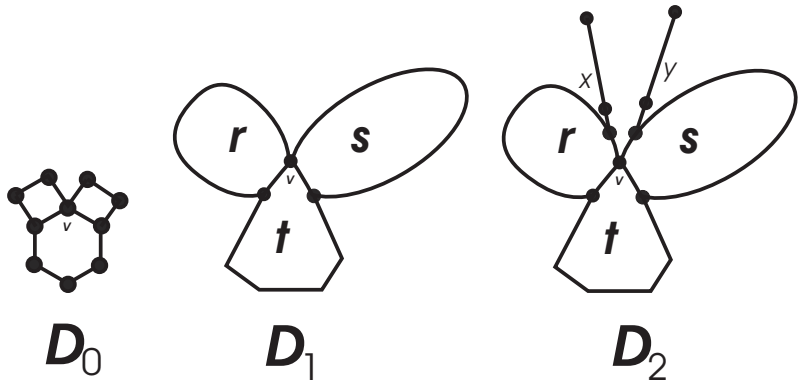

Fig. 5. Tricyclic molecular graphs for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step.

From the diagram depicted in Fig. 5 we see that

$$D_1 - v = P_{r+s+t-5} \qquad \text{and} \qquad D_1 - N_v = P_{r-3} \cup P_{s-3} \cup P_{t-3}$$

and therefore

$$\begin{aligned}\sigma(D_1) &= \sigma(P_{r+s+t-5}) + \sigma(P_{r-3})\,\sigma(P_{s-3})\,\sigma(P_{t-3}) \\ &= F_{r+s+t-4} + F_{r-2}\,F_{s-2}\,F_{t-2}\,.\end{aligned}$$

In the same way as in the acyclic, unicyclic, and bicyclic molecular graphs, the case D_1 can be generalized into D_2, with parameters $x, y \geq 0$. The respective expression reads:

$$\begin{aligned}\sigma(D_2) &= \sigma(P_{r+s+t+x+y-5}) + \sigma(P_{r-3})\,\sigma(P_{s-3})\,\sigma(P_{t-3})\,\sigma(P_x)\,\sigma(P_y) \\ &= F_{r+s+t+x+y-4} + F_{r-2}\,F_{s-2}\,F_{t-2}\,F_{x+1}\,F_{y+1}\,.\end{aligned}$$

7 Concluding remarks

In view of the fact that the vertex degrees in molecular graphs (provided these represent organic compounds) must not exceed 4 [15], the acyclic graphs T_1, T_2, T_3, unicyclic graphs U_1, U_2, U_3, U_4, U_5, bicyclic graphs B_1, B_2, B_3, B_4, and tricyclic graphs D_1, D_2 (depicted in Figs. 2–5) with parameters $a_1, a_2, b_1, b_2, c_1, c_2, d_1, d_2, x, y, z, w \geq 0$ and $r, s, t \geq 3$ seem to be the only species for which the recursive calculation of the Merrifield–Simmons index can be achieved in a single step. For the same reason, it seems that tetracyclic and higher–cyclic molecular graphs of this kind do not exist. Therefore, the graphs presented in this work appear to be the only possible of this kind.

It would be interesting to have a formal mathematical verification of the above claim.

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