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Papers

Equiseparable molecules and molecular graphs

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By deleting an edge e_i from the molecular graph G of an acyclic molecule, it decomposes into two fragments, with $n_1(e_i|G)$ and $n_2(e_i|G)$ vertices, $n_1(e_i|G) \leq n_2(e_i|G)$, $i=1,2,...,m$. If the edges of the graphs G' and G'', representing two isomeric acyclic molecules, can be chosen so that $n_1(e_i|G') = n_1(e_i|G'')$ holds for all $i=1,2,...,m$, then G' and G'' are said to be equiseparable. The respective two isomeric molecules are also said to be equiseparable. The main (known) physico-chemical consequences of equiseparability are pointed out. A general method for designing pairs of equiseparable molecular graphs is described, by which large sets of equiseparable species can be constructed.

Recent studies[1-13] of distance-based molecular-structure-descriptors revealed the chemical importance of the graph invariants $n_1(e_i|G)$ and $n_2(e_i|G)$, associated with the edge e_i of the graph G. These invariants were first precisely defined by one of the present authors[14], although they are encountered already in Harold Wiener's seminal paper[15].

Let G be an acyclic (molecular) graph and let e_1, $e_2,...,e_m$ be its edges. By removing the edge e_i from G, it decomposes into two fragments, with $n_1(e_i|G)$ and $n_2(e_i|G)$ vertices. In other words, $n_1(e_i|G)$ and $n_2(e_i|G)$ vertices lie on the two sides of the edge e_i of the graph G. Conventionally, the smaller of these two numbers is denoted by $n_1(e_i|G)$, i. e., we assume that $n_1(e_i|G) \leq n_2(e_i|G)$.

If the graph G possesses n vertices, then it possesses $n-1$ edges ($m=n-1$), and the equality $n_1(e_i|G) + n_2(e_i|G) = n$ holds for all $i=1, 2,...,m$.

The definition of the quantities $n_1(e_i|G)$ and $n_2(e_i|G)$ in the case of cycle-containing graphs is somewhat more complicated[14]; details on this matter are found in the review[16].

As early as in 1947, Wiener noticed[15] that the structure-descriptor $W(G)$ (the sum of distances between all pairs of vertices of the molecular graph G, now called "Wiener index") can be computed by means of the formula:

$$W(G) = \sum_{i=1}^{m} n_1(e_i \mid G)\, n_2(e_i \mid G) \qquad \ldots (1)$$

Few years ago, Eq. (1) served as a motivation for defining[4] the "modified Wiener index":

$${}^{m}W(G) = \sum_{i=1}^{m} [n_1(e_i \mid G)\, n_2(e_i \mid G)]^{-1} \qquad \ldots (2)$$

and, soon after that[7,13], of the "variable Wiener index":

$$W_\lambda(G) = \sum_{i=1}^{m} [n_1(e_i \mid G)\, n_2(e_i \mid G)]^{\lambda} \qquad \ldots (3)$$

where λ is an adjustable real-valued parameter. Clearly, for $\lambda=1$ and $\lambda=-1$ the variable Wiener index reduces to the ordinary and to the modified Wiener index, respectively. In some recent applications[11] $\lambda \approx -0.5$ was found to be the optimal choice.

Independently of these researches, Zenkevich[1,2] conceived a quantity U which can be expressed as[6]:

$$U(G) = (gn + 2h)^{1/2} \sum_{i=1}^{m} \{[gn_1(e_i \mid G + h)][gn_2(e_i \mid G) + h]\}^{-1/2} \qquad \ldots (4)$$

where $g \approx 14$ and $h \approx 1$ are the relative masses of the CH_2-group and of the hydrogen atom, respectively. It is worthnoting that U provides a good approximation for the internal energy of the corresponding alkane[1-3,6,11].

Examining the above mentioned molecular-structure-descriptors, we discovered[12] that there exist pairs of molecular graphs, say G' and G'', pertaining to isomers, whose edges can be chosen so that the equalities:

$$n_1(e_i|G') = n_1(e_i|G'')$$

are obeyed for all $i=1,2,...,m$. Such pairs of graphs are said to be equiseparable. In Fig. 1 is depicted the smallest pair of equiseparable chemical trees, with appropriately labelled edges.

From Eqs (1)-(4) it is evident that if two graphs are equiseparable, then their variable Wiener indices coincide for any value of λ, and also their Zenkevich indices coincide. This has the consequence that whenever some physico-chemical property of a class of compounds can be modelled by either W or ${}^{m}W$ or W_λ or U, equiseparable species are predicted to have nearly equal values of this property. A few examples corroborating this topological regularity have been reported elsewhere[11,12]; a detailed study thereof is in preparation.

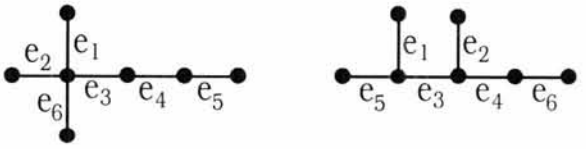

Fig. 1—The molecular graphs of 1,1-dimethylpentane and 1,2-dimethylpentane are equiseparable: for i=1, 2,...,6, by deleting the edges labelled by e_i both graphs decompose into components with equal number of vertices. These are the smallest equiseparable graphs.

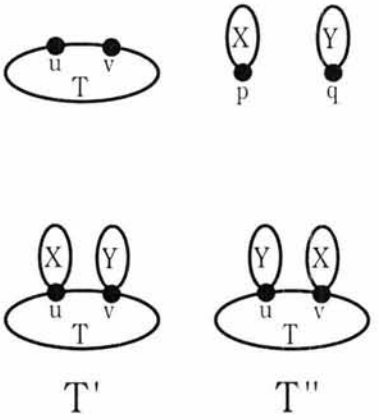

Fig. 2—Construction of trees T' and T''. These are equiseparable if the fragments X and Y possess equal number of vertices.

Constructing equiseparable chemical trees

A connected acyclic graph is called a tree. A tree in which no vertex has degree (number of first neighbours) greater than four is called a chemical tree. Chemical trees are the graph representations of alkanes.

In this section, we describe a general method for constructing equiseparable trees and chemical trees.

Let T, X and Y be arbitrary trees, each with more than two vertices. Let u and v be two vertices of T, p a vertex of X and q a vertex of Y. Let the tree T' be obtained from T, X and Y by identifying the vertices u and p, and by identifying the vertices v and q. Let T'' be obtained from T, X and Y by identifying the vertices u and q and by identifying the vertices v and p. In order that T' differ from T'', the fragments X and Y (when attached via the vertices p and q) are required to be different.

The structure of the trees T' and T'' is depicted in Fig. 2.

Theorem 1. If X and Y have equal number of vertices, then the trees T' and T'' are equiseparable.

Proof. Denote the number of vertices of T, X and Y by $|T|$, $|X|$, and $|Y|$, respectively. We have to distinguish between four different types of edges in T' and T'':

(i) edge e, belonging to T, lying between the vertices u and v;
(ii) edge f, belonging to T, such that both u & v lie on one of its sides;
(iii) edge x, belonging to X; and
(iv) edge y, belonging to Y.

Case (i): By inspection of Fig. 2 we see that

$$n_1(e|T')=n_1(e|T)+|X|-1;\ n_2(e|T')=n_2(e|T)+|Y|-1$$
$$n_1(e|T'')=n_1(e|T)+|Y|-1;\ n_2(e|T'')=n_2(e|T)+|X|-1$$

Thus $n_1(e|T') = n_1(e|T'')$ will hold for any edge of type (i) if, and only if, $|X|=|Y|$.

Case (ii): We now have

$$n_1(f|T') = n_1(f|T) + |X|+|Y|-2;\ n_2(f|T') = n_2(f|T)$$
$$n_1(f|T'') = n_1(f|T) + |X|+|Y|-2;\ n_2(f|T'') = n_2(f|T)$$

and thus equality $n_1(f|T') = n_1(f|T'')$ holds for all edges of the type f, irrespective of the number of vertices of X and Y.

Case (iii):

$$n_1(x|T') = n_1(x|X) + |T| + |Y| - 2;\ n_2(x|T') = n_2(x|X)$$
$$n_1(x|T'') = n_1(x|X) + |T| + |Y| - 2;\ n_2(x|T'') = n_2(x|X)$$

and, again, equality $n_1(x|T') = n_1(x|T'')$ is always satisfied.

Case (iv) is fully analogous to case (iii).

Thus we see that if $|X|=|Y|$, then the equality $n_1(e_i|T') = n_1(e_i|T'')$ is obeyed by all edges of the trees T' and T''.

In Theorem 1 it is not required that the vertices u & v of the tree T be symmetry-non-equivalent. However, if these vertices are symmetry-equivalent, then T' and T'' are identical trees and thus the claim of Theorem 1 is trivial. Therefore, in what follows, we will additionally require that the vertices u and v be symmetry non-equivalent.

By means of Theorem 1 we can easily design arbitrarily many pairs of equiseparable trees and chemical trees. The smallest example of this kind is obtained when both T, X and Y are 3-vertex trees, and when the vertices u, v, p and q are chosen as indicated in Fig. 3. For additional examples see Figs 4 and 5.

Large families of equiseparable chemical trees

A direct extension of Theorem 1 makes it possible to obtain families of equiseparable trees or chemical trees, of arbitrary large size.

Let T be a tree and $v_1, v_2,...,v_{2k}$ its vertices which are mutually symmetry-nonequivalent. Let X and Y be two trees with equal number of vertices, p a vertex of X and q a vertex of Y.

Construct a set of graphs $ES(T,X,Y)$ as follows. Each element of $ES(T,X,Y)$ is obtained from a copy of T, k copies of X and k copies of Y, so that fragments X are attached (via their vertices p) to k among the vertices $v_1, v_2,...,v_{2k}$ of T, whereas fragments Y are attached (via their vertices q) to the remaining k vertices $v_1, v_2,...,v_{2k}$ of T. Again, we require that the fragments X and Y (when attached via the vertices p and q) be different.

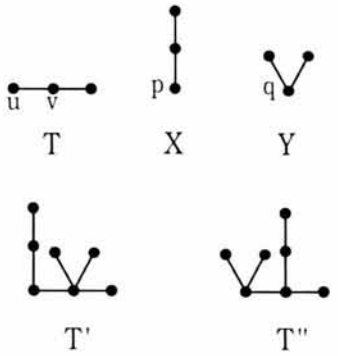

Fig. 3—The smallest pair of equiseparable trees, constructed by means of Theorem 1. The trees T' and T'' coincide with those depicted in Fig. 1.

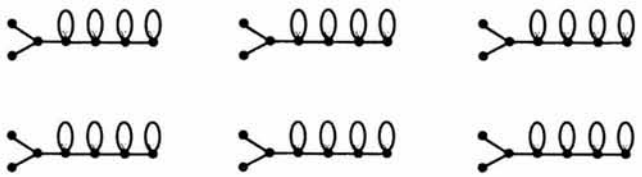

Fig. 4—A family of 6 mutually equiseparable trees.

Theorem 2. (a) The set $ES(T,X,Y)$ consists of $\binom{2k}{k}$ mutually distinct trees. (b) If X and Y have equal number of vertices, then all elements of $ES(T,X,Y)$ are mutually equiseparable.

At this point it is useful to note that for k=1,2,3,4,5,6,... the binomial coefficient $\binom{2k}{k}$ is equal to 2, 6, 20, 70, 252, 924,... , respectively.

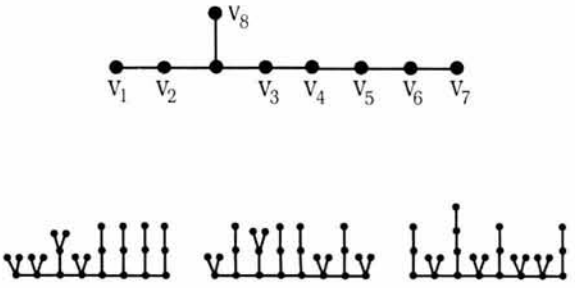

Fig. 5—Three equiseparable chemical trees, obtained from the molecular graph of 3-methyloctane, by attaching to the vertices v_1, $v_2,...,v_8$ the same 3-vertex fragments X and Y as in Fig. 3. The complete construction leads to a 20-membered family of such equiseparable chemical trees (each with 25 vertices).

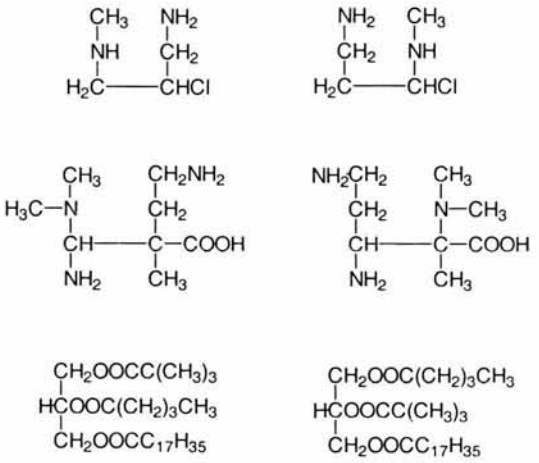

Fig. 6—Examples of pairs of equiseparable molecules which are not hydrocarbons. Their construction follows from Theorem 1 because it remains valid if the graphs T, X & Y possess weighted edges and/or self-loops.

In Fig. 4 are depicted the 6 distinct equiseparable trees obtained when T is the molecular graph of 2-methylheptane, whereas in Fig. 5 are shown three (from the 20 possible) mutually equiseparable molecular graphs derived from 3-methyloctane, choosing for X and Y the same 3-vertex trees as in Fig. 3.

Equiseparable molecules different from alkanes

The graphs encountered in Theorems 1 and 2 may possess weighted edges and/or self-loops, which means that these may represent molecules possessing heteroatoms and/or functional groups. Bearing this observation in mind we easily arrive at pairs (or larger families) of equiseparable molecules different from alkanes. Some typical examples are depicted in Fig. 6.

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