Equiseparable chemical trees

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Abstract: Let $n_1(e|T)$ and $n_2(e|T)$ denote the number of vertices of a tree T, lying on the two sides of the edge e. Let T_1 and T_2 be two trees with equal number of vertices, let e be an edge of T_1 and f an edge of T_2. Then e and f are said to be equiseparable if either $n_1(e|T_1) = n_1(f|T_2)$ or $n_1(e|T_1) = n_2(f|T_2)$. If all edges of T_1 and T_2 can be chosen so as to form equiseparable pairs, then T_1 and T_2 are equiseparable trees. A number of molecular structure-descriptors of equiseparable chemical trees coincide, implying that the corresponding alkane isomers must have similar physico-chemical properties. It is shown how equiseparable chemical trees can be constructed in a systematic manner.

Keywords: Wiener index, variable Wiener index, chemical trees, alkanes, equiseparability.

INTRODUCTION

As early as 1947 Wiener[1] discovered the formula

$$W = \sum_{e} n_1\,(e|T)\,n_2(e|T) \tag{1}$$

by means of which the molecular structures descriptor W (nowadays known under the name *"Wiener index"*) can be computed in the case of alkanes; more details on the Wiener index are found eslewhere.[2,3] In Eq. (1) T stands for a chemical tree (= the molecular graph[2] of the alkane to which W pertains), e is an edge of T, whereas $n_1(e|T)$ and $n_2(e|T)$ are the number of vertices of T, lying on the two sides of e. The summation on the right-hand side of (1) goes over all edges of the tree T.

The numbers $n_1(e|T)$ and $n_2(e|T)$ may be viewed as the count of the vertices of the two fragments, obtained by deleting the edge e from T. In other words, the edge e separates T into two fragments, with $n_1(e|T)$ and $n_2(e|T)$ vertices. Clearly, if the tree T has n vertices, then for all of its edges,

$$n_1(e|T) + n_2(e|T) = n \tag{2}$$

A few years ago, formula (1) was used for the definition of another structure-descriptor, named *"modified Wiener index"*:[4]

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$$W_m = \sum_\varepsilon \left[\nu_1(\varepsilon|T) \, \nu_2(\varepsilon|T) \right]^{-1}$$

which then served as a motivation for introducing a whole class of *"variable Wiener indices"*:[5]

$$W_m(\lambda) = \sum_\varepsilon \left[\nu_1(\varepsilon|T) \, \nu_2(\varepsilon|T) \right]^{-\lambda} \tag{3}$$

Recently, several mathematical[5–8] and chemical[9,10] properties of $W_m(\lambda)$ were established.

In the work[5] it was noticed that there exist pairs of isomeric alkanes whose variable Wiener indices coincide for all values of the parameter λ. The simplest such pair are the molecular graphs of 2,2-dimethylpentane and 2,3-dimethylpentane, *cf.* Fig. 1. These observations lead to the definition of *equiseparable trees*.

Definition 1. Let T_1 and T_2 be two trees with equal number of vertices. Let e be an edge of T_1 and f and edge of T_2. The edges e and f are said to be *equiseparable*, $e \approx f$, if by deleting e from T_1 and by deleting f from T_2 fragments are obtained with equal number of vertices.

More formally, $e \approx f$ if either $n_1(e|T_1) = n_1(f|T_2)$ [which because of relation (2) is tantamount to $n_2(e|T_1) = n_2(f|T_2)$], or $n_1(e|T_1) = n_2(f|T_2)$ [which is tantamount to $n_2(e|T_1) = n_1(f|T_2)$].

Definition 2. Let T_1 and T_2 be two trees with equal number of vertices. The trees T_1 and T_2 are said to be *equiseparable*, $T_1 \approx T_2$, if all their edges can be chosen so as to form equiseparable pairs.

More formally, if $e_1, e_2, ..., e_m$ are the edges of T_1 and $f_1, f_2, ..., f_m$ the edges of T_2, then $T_1 \approx T_2$ if one can label the edges so that $e_i \approx f_i$ holds for all $i = 1, 2, ..., m$.

It is evident from Eq. (3) that equiseparable trees have the same variable Wiener indices, for any value of the parameter λ. This implies that any physico-chemical property that correlates with $W_m(\lambda)$, must have similar values for all members of an equiseparable family of alkanes. An example supporting this conclusion is found in Fig. 4. More interestingly, equiseparable alkanes have nearly equal internal energies[9] and nearly equal frequencies of the stretching carbon–carbon vibrations.[11,12]

In what follows it will be shown how families of equiseparable chemical trees can be constructed.

AN EXAMPLE: EQUISEPARABLE DIMETHYL ALKANES

The smallest pair of equiseparable molecular graphs, pertaining to 2,2-dimethyl- and 2,3-dimethylpentane, is depicted in Fig. 1.

Examining this pair one can arrive at the following generalization: a pair of isomeric dimethyl alkanes with n carbon atoms, one possessing two methyl groups in position i, the other possessing a methyl group in position i and another in position j, $j > i$, see Fig. 1.

Now the condition that the parameters i, j, and n must satisfy, in order that the respective chemical trees T_1 and T_2 be equiseparable is established.

In order to simplify the formalism, the edge of T_1, connecting the vertices u and v, is denoted by e_{uv}. The analogous edge of T_2 will be denoted by f_{uv}. The labeling of the verti-
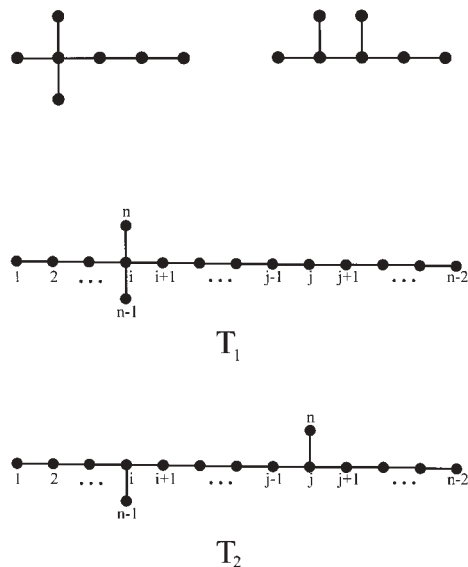
Fig. 1. The two smallest equiseparable trees and their generalizations T_1 and T_2. The trees T_1 and T_2 are found to be equiseparable whenever $i + j = n - 2$, *e.g.*, for $n = 7$, $i = 2$, $j = 3$.

ces of T_1 and T_2 is indicated in Fig. 1.

The edges lying left from vertex i and right from vertex j are obviously equiseparable, namely: $e_{t,t+1} \approx f_{t,t+1}$ for $t = 1, 2, ..., i-1$ and $t = j, j+1, ..., n-3$. Also, $e_{i,n-1} \approx f_{i,n-1}$ and $e_{i,n} \approx f_{j,n}$. What remains to be examined are the edges lying between the vertices i and j.

Because the molecules pertaining to T_1 and T_2 have one and two methyl groups in position i respectively, it follow that

$$e_{i,i+1} \approx f_{i+1,i+2}$$
$$e_{i+1,i+2} \approx f_{i+2,i+3}$$
$$... \qquad ...$$
$$e_{j-2,j-1} \approx f_{j-1,j}$$

The only two edges that remain to be examined are $e_{j-1,j}$ and $f_{i,i+1}$. Now, by inspecting Fig. 1, if can be seen that: $n_1(e_{j-1,j}|T_1) = j + 1$, $n_2(e_{j-1,j}|T_1) = n - j - 1$, $n_1(f_{i,i+1}|T_2) = i + 1$, $n_2(e_{i,i+1}|T_2) = n - i - 1$. It cannot be $n_1(e_{j-1,j}|T_1) = n_1(f_{i,i+1}|T_2)$. Therefore, in order that $T_1 \approx T_2$, it must be that $n_1(e_{j-1,j}|T_1) = n_2(f_{i,i+1}|T_2)$, *i.e.*, $j + 1 = n - i - 1$, *i.e.*, $i + j = n - 2$.

Thus the following has been proved:

Rule 1. The molecular graphs of the (i,i)-dimethyl alkane and (i,j)-dimethyl alkane with n carbon atoms are equiseparable if $i + j = n - 2$.

THE METHYL-SHIFT RULE

When deducing Rule 1, it should be noticed that the edges lying left from vertex i and right from vertex j play no role in determining the conditions for equiseparability of T_1 and

T_2. The same is true for edges lying between i and j, except the edge of T_1 incident to vertex j, and edge of T_2 incident to vertex i. Bearing this in mind the general case depicted in Fig. 2 may be considered.
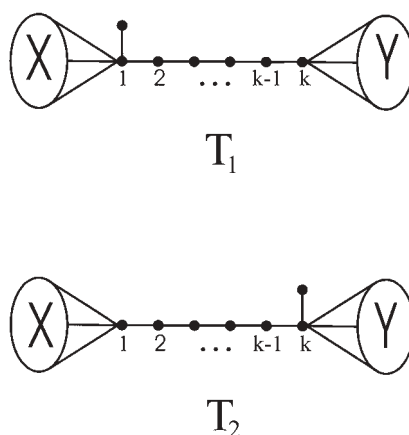

$$T_1$$

$$T_2$$

Fig. 2. The chemical trees T_1 and T_2 correspond to alkane molecules differing in the position of a single methyl group. Hence the transformation $T_1 \rightarrow T_2$ corresponds to the shift of a methyl group from position 1 to position k. The trees T_1 and T_2 are equiseparable if the fragments X and Y have equal number of vertices; otherwise the structure of X and Y may be arbitrary and the parameter k may assume any value greater than unity.

As before

$$e_{1,2} \approx f_{2,3}$$
$$e_{2,3} \approx f_{4,5}$$
$$\ldots \qquad \ldots$$
$$e_{k-2,k-1} \approx f_{k-1,k}$$

Consequently, $T_1 \approx T_2$ will be if $e_{k-1,k} \approx f_{12}$.

Denote the number of vertices of X and Y by x and y, respectively. Then the edge $e_{k-1,k-1}$ separates T_1 into fragments with $x + k$ and y vertices, whereas the edge $f_{1,2}$ separates T_2 into fragments with x and $y + k$ vertices. In order to have $e_{k-1,k} \approx f_{12}$ either $x + k = x$ must be (which is impossible), or $x + k = y + k$ (which implies $x = y$). Thus the following is arrived at:

Rule 2. (*Methyl-Shift*) The chemical trees T_1 and T_2 depicted in Fig. 2 are equiseparable if the fragments X and Y have equal number of vetices. The parameter k may be any integer greater than unity.

MORE EQUISEPARABLE CHEMICAL TREES

In an analogous, but significantly more complicated way Rule 3 can be deduced:

Rule 3. (*Ethyl-Shift*) Let T_1 and T_2 be chemical tree analogous to those depicted in Fig. 2, but differing in the position of an ethyl group. T_1 and T_2 are equiseparable if the fragments X and Y have equal number of vertices, for any value of the parameter $k \geq 2$.

Both the methyl- and ethyl-shift rules are special cases of a more general results, that can be formulated as:

Rule 4. The chemical trees T_1 and T_2 depicted in Fig. 3 are equiseparable if the fragments X and Y have equal number of vertices. The parameter k may be any integer greater than unity and the fragment Z may be arbitrary.
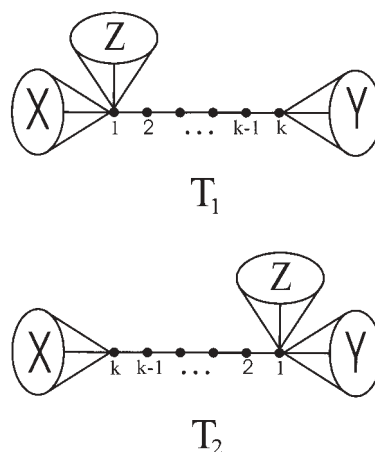

$$T_1$$

$$T_2$$

Fig. 3. The chemical trees used in the formulation of Rule 4. These are equiseparable if X and Y have equal number of vertices, irrespective of the value of $k \geq 2$ and the nature of the substituent Z.

Suprisingly, the proof of Rule 4 is quite simple.

Again, only the edges lying between vertices 1 and k need to be considered. Bearing in mind the structure of the trees T_1 and T_2, shown in Fig. 3, and the way in which their vertices are labeled, the results shown in Table I are obtained . The number of vertices of the fragment Z is denoted by z.

TABLE I. Data needed for the proof of Rule 4

t	#1 $n_1(e_{t,t+1}\|T_1$	#2 $n_2(e_{t,t+1}\|T_1)$	#3 $n_1(f_{t,t+1}\|T_2)$	#4 $n_1(f_{t,t+1}\|T_2)$
1	$x+z+1$	$y+k-1$	$x+k-1$	$y+z+1$
2	$x+z+2$	$y+k-2$	$x+k-2$	$y+z+2$
3	$x+z+3$	$y+k-3$	$x+k-3$	$y+z+3$
...	...	...	...	...
t	$x+z+t$	$y+k-t$	$x+k-t$	$y+z+t$
...	...	...	...	...
$k-2$	$x+z+k-2$	$y+2$	$x+2$	$y+z+k-2$
$k-1$	$x+z+k-1$	$y+1$	$x+1$	$y+z+k-1$

The conditions under which $e_{t,t+1} \approx f_{t,t+1}$ will hold for all $t = 1, 2, ..., k-1$ have to be found.

The numbers in column #1 in Table I increase, whereas those in column #3 decrease with increasing t. Therefore, it is not possible to establish equality between them, that would hold for all t. On the other hand, the numbers in column #4 also increase and the entire column #4 will become equal to column #1 if $x = y$. Under the very same conditions, column #2 will become equal to column #3.
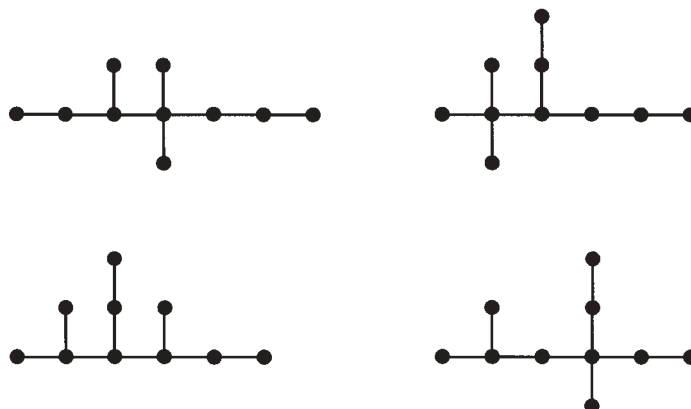
Rule 4 follows.

Fig. 4. A family of equiseparable chemical trees: 3,4,4-trimethylheptane, 3-ethyl-2,2-dimethylhexane, 3-ethyl-2,4-dimethylhexane, and 4-ethyl-2,4-dimethylhexane. Their boiling points (at standard atmospheric pressure) are 434, 429, 433, and 434 K, respectively. Their heats of evaporation (at 298 K) are 46.7, 45.6, 46.5, 45.2 kJ/mol, their standard heats of formation (in the gaseous state, at 298 K) are –257.1, –252.5, –246.3, and –256.4 kJ/mol, their standard entropies (in the gaseous state, at 298 K) are 501.8, 503.8, 516.7, and 497.6 J/(K mol), their heat capacities (in the gaseous state, at 298 K) are 234.2, 226.5, 230.0, and 233.6 J/(K mol), respectively.

By means of a systematic search many more equiseparable families of chemical trees were discovered, many of which cannot be rationalized by means of Rule 4 (or by its species cases, Rules 1–3). A characteristic example is shown in Fig. 4.

ИЗВОД

ЕКВИСЕПАРАБИЛНА ХЕМИЈСКА СТАБЛА

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Нека $n_1(e|T)$ и $n_2(e|T)$ означавају број чворова стабла T, који леже са две стране гране e. Нека су T_1 и T_2 два стабла са истим бројем чворова, нека је e грана стабла T_1, а f грана стабла T_2. Тада за e и f кажемо да су еквисепарабилни ако важи $n_1(e|T_1) = n_1(f|T_2)$ или $n_1(e|T_1) = n_2(f|T_2)$. Ако се све гране стабала T_1 и T_2 могу изабрати тако да образују еквисепарабилне парове, тада су T_1 и T_2 еквисепарабилна стабла. Већи број молекулских структурних дескриптора имају исте вредности за еквисепарабилна хемијска стабла, из чега следи да одговарајући изомерни алкани морају имати сличне физичко-хемијске особине. Показано је како се еквисепарабилна хемијска стабла могу систематски конструисати.

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