

**ON TOPOLOGICAL INDICES INDICATING BRANCHING.
PART 2. THE SUITABILITY OF SOME PHYSICOCHEMICAL PROPERTIES
OF ALKANES AS REFERENCES TO ASSESS BRANCHING**

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Received 31-05-2000

Abstract

The susceptibility for branching, $S_{i,j}$, the difference-normalised difference of data for octanes, Δnorm_i , as well as a number of additional criteria are used to judge the suitability of 24 physicochemical properties of alkanes as references for branching. The most appropriate as primary references for branching regarding these criteria seem to be $\Delta\text{Hf}^\circ\text{g}$, Tc/Pc, and BP/Tc. They are to be used simultaneously. The following properties, Tc^2/Pc , ω , and C are considered less appropriate. The other tested physicochemical properties are considered inappropriate measures of branching. From the data of $\Delta\text{Hf}^\circ\text{g}$, Tc/Pc, and BP/Tc, reference values for branching indices are constructed, obeying the Methane-based definition as well as for those indices obeying the *n*-Alkane-based definition of molecular branching.

Introduction

In the previous paper,¹ the suitability of topological indices (further on: indices) J, W, Z, D, MTI, Xu, ID, χ , $\lambda\lambda_1$, EA_{max} , and λ_1 as branching indices, as well as of physicochemical properties (further on: properties) MON, BP, d, Vi, Vm, Vc, Tc, Pc, dc, Zc, αc , ΔHv , A, B, C, n_{D} , MR, a_0 , b_0 , $\Delta\text{Hf}^\circ\text{g}$, $\Delta\text{Gf}^\circ\text{g}$, S, R^2 , and ω , as reference properties for branching of alkanes was tested by means of the Principal Component Analysis. It has been observed that most of the properties and indices correlate highly with the carbon number of alkanes, although they are influenced also by branching. Of the influences of branching, assessed separately by the properties and by the indices, the most important is the number of branches, followed by the type of branched structure, i.e. whether the branch bearing carbon is tertiary or quaternary, by the position of branches, i.e. whether they are central or peripheral, distant or adjacent, and the least important is the shape of branched molecules, i.e. whether they are spherical, flat or elongated, as well as symmetric or asymmetric. The properties have been divided into intrinsic and

interaction-dependent ones and it has been explained why the latter ones are not suitable as primary references for branching. Two definitions of branching have been presented, the *Methane-based* definition as a general definition and the *n-Alkane-based* definition as a special definition more familiar to chemists. In the present paper we discuss additional criteria, which might enable us to assess branching better, in particular criteria to assess the suitability of physicochemical properties as references for branching indices.

Data

The data for the boiling point (BP) and the quadratic mean radius (R^2) were taken from Ren². The data for the melting point (MP), density (d), the critical data T_c , P_c , V_c , Z_c , α_c , and d_c , as well as the standard enthalpy of formation for the ideal gas (ΔH_f°), the standard Gibbs energy of formation for the ideal gas (ΔG_f°), the enthalpy of vaporisation (ΔH_v), the Antoine constants A, B, and C as well as the Pitzer's acentric factor (ω) and the refractive index (n_D) were taken from CRC Handbook³ or from Lange's Handbook⁴. The data of vapour pressure (log VP) were taken from Goll and Jurs⁵. The data for the liquid molar volume (V_m), the intrinsic molar volume (V_i), the van der Waals parameters a_0 and b_0 , and the molar refraction (MR) were calculated from data presented in the handbooks. After the first step of analysis, the ratios T_c^2/P_c and T_c/P_c are used instead of the van der Waals parameters a_0 and b_0 , which are derived from these ratios. Besides them also BP/ T_c is included.

Methods

The structures of alkanes are presented in shorthand, e.g. 223M5 is 2,2,3-trimethyl pentane or 3Et2M5 is 3-ethyl-2-methyl pentane. Other terms are explained on 2,3- and 2,5-dimethyl hexane (23M6 and 25M6) as examples. The branches (tertiary carbons) in 23M6 are adjacent and those in 25M6 are distant. The branches on carbons No. 2 and 5 are peripheral, that on carbon No. 3 is central (as far as it is possible in this case). 25M6 is symmetric, whereas 23M6 is not.

The susceptibility of properties for branching is used as the Method No. 1 to assess the suitability of properties as reference for branching indices. It is defined as the normalised difference of the properties' values, Eq. 1,

$$S_{i,j} = P_i/P_j - 1 \quad (1)$$

where $S_{i,j}$ is the susceptibility to branching, P is a property, i refers to the more branched structure and j refers to the less branched structure. Which one is more branched is concluded by intuition as presented in ref.⁶ as well as by the Methane-based definition and the n -Alkane-based definition¹.

Two groups of $S_{i,j}$ data are used. In the first group, i refers to the structures having the same number and type of branches as j , but one carbon more. For example, in $S_{\text{octane,heptane}}$ octane means any octane having the same number and type of branches as a heptane. In $S_{\text{Oct,Hp}}$ i refers to n -octane (Oct) and j to n -heptane (Hp), or in $S_{2M7,2M6}$ to 2-methyl heptane (2M7) and 2-methyl hexane (2M6), etc. In the second group of $S_{i,j}$ data, i and j refer to alkanes of the same carbon number; for example, $S_{i,\text{Oct}}$ refers to any octane and n -octane, $S_{2M7,\text{Oct}}$ refers to 2-methyl heptane and n -octane.

To assess the data, the following criterion is applied as the criterion No. 1: A property might be useful as reference, if the sign of all $S_{\text{octane,heptane}}$ values is the same and that of all $S_{i,\text{Oct}}$ values is the same as well. It is not useful if the sign among members within each group differs. The two groups of sign may or may not be equal.

As the Method No. 2, the difference-normalised difference of the properties' values for octanes is used, Eq. 2,

$$\Delta \text{norm}_i = (P_i - P_{\text{Oct}})/(P_{2233M4} - P_{\text{Oct}}) \quad (2)$$

Criterion No. 2: A property is suitable as reference if all $0 < \Delta \text{norm}_i < 1$, and not suitable if any $\Delta \text{norm}_i < 0$ or $\Delta \text{norm}_i > 1$.

The criteria No. 1 and 2 serve to eliminate the properties, which are the most inappropriate references for branching. The other criteria presented below serve to rank the remaining properties.

As the Method No. 3 we use the dependence of properties on carbon number expressed in different ways:

- The $S_{\text{octane,heptane}}$ compared to the corresponding S-values derived from data for carbon number, N_C ,
- The correlation coefficient with N_C , the r_{N_C} .

Criterion No. 3: No clear-cut criterion could be set in this case.

As the Method No. 4 we use the dependence of properties on branching. As a general dependence it is expressed by the $S_{i,\text{Oct}}$ data as well as by the ratio $S_{i,\text{Oct}}/S_{\text{octane,heptane}}$. As special indicators we use the following ratios: $S_{234M5,\text{Oct}}/S_{2233M4,\text{Oct}}$, $S_{25M6,\text{Oct}}/S_{22M6,\text{Oct}}$, and $S_{34M6,\text{Oct}}/S_{33M6,\text{Oct}}$ compare the susceptibility of a property for the presence of tertiary carbons vs. that of quaternary ones in octanes. The ratio $S_{25M6,\text{Oct}}/S_{34M6,\text{Oct}}$ indicates whether a property is more susceptible to peripheral or central position of branches.

Criterion No. 4 could not be clearly defined yet, but some useful information is given by this method.

As the Method No. 5 we use the comparison of the sequences of octanes having the same number of branches and the extent of information that can be derived thereby.

Criterion No. 5: As a reference is better the property having the sequences closer to those expected by intuition as well as that one presenting more information on structural details.

As the Method No. 6 we use the evenness of Δnorm_i data. It is assessed visually in Fig. 1 and 2, by the differences of Δnorm_i , i.e. $\Delta(\Delta\text{norm}_i)_{\text{max}}$, $\Delta(\Delta\text{norm}_i)_{\text{min}}$, as well as by their relative standard deviation (RSD). Besides the evenness as such, from these data can be deduced also the influence of the number of branches, of the (mutual) position of branches, and of the symmetry of molecules among octanes on the properties considered potentially useful as reference properties.

Criterion No. 6: As a reference is better the property having more evenly distributed Δnorm_i data.

As the Method No. 7 we use the estimate of the linearity of the increase of the values for n-alkanes with carbon number.

Criterion No. 7: A property is the better reference the closer to linearity is its increase in n-alkanes with carbon number.

Results and discussion

A selection of topological indices and physicochemical properties of alkanes from methane to octanes was studied by means of the Principal Component Analysis¹. Most of the properties and indices were found to correlate highly with the carbon number of alkanes and the influence of branching on them seemed to be lower. Of the influences of branching, the most important was the number of branches, followed by the type of branched structure, i.e. whether the branch bearing carbon is tertiary or quaternary, the position of branches, i.e. whether they are central or peripheral, distant or neighbouring, and the least important was the shape of branched molecules, i.e. whether they are spherical, flat or elongated, as well as symmetric or asymmetric.

The suitability of topological indices as branching indices is usually tested with physicochemical properties of alkanes. This test is performed by binary correlations. Different properties indicate different agreements with indices, so the first question is which of the properties are suitable as references for branching. The answer to this question is approached here in several steps. First, the sign of $S_{i,j}$ as a criterion enables elimination of some properties which are not appropriate as references. In the second step, the remaining properties are tested with Δnorm_i as a criterion and several of them are eliminated. In the additional steps the properties remaining after the second step are tested with additional methods to rank them for their suitability to serve as references.

The methods for the selection of physicochemical properties as references for branching of alkanes

Method No. 1: The sign of the susceptibility of a property for branching, $S_{i,j}$

In the previous paper the Principal Component Analysis was used to study the physicochemical properties of alkanes for their suitability as references for branching¹. As another possibility to assess the data we suggest here the susceptibility of properties for branching, $S_{i,j}$, defined as the normalised difference of the properties' values.

The reason to apply $S_{i,j}$ as a criterion is as follows. An index is expected to behave consistently, i.e. to increase with carbon number and either to increase or decrease with branching but not to have mixed behaviour. The same must be expected from a physicochemical property, which should serve as a reference property. On increasing carbon number at the same type of branching, the value of a property should in all cases either increase or decrease, so the $S_{i,j}$ data should be either all positive or all negative. On increasing branching, the same should hold true. If a property gives rise in either case to a mixed result, i.e. if the values for some isomers increase with carbon number or branching whereas those for other isomers decrease, then such a property is considered inappropriate as a reference for branching. These suppositions were tested with $S_{\text{octane,heptane}}$ for the increase of carbon number from 7 to 8, i.e. from *n*-heptane to *n*-octane, from 2M6 to 2M7, from 3M6 to 3M7, from 3Et5 to 3Et6, from 22M5 to 22M6, from 23M5 to 23M6 and 34M6, from 24M5 to 24M6 and 25M6, from 33M5 to 33M6, and from 223M4 to 223M5, as well as with $S_{i,\text{Oct}}$ for the increase of branching from *n*-octane to all other octanes for which the data were available. Table 1 presents the grouping of alkanes' properties regarding the sign of $S_{i,j}$.

Table 1. Grouping of 24 physicochemical properties of octanes regarding the sign of their susceptibility to branching.

$S_{\text{octane,heptane}}$	$S_{i,\text{Oct}}$	Physicochemical property
All +	All +	$\Delta H_f^\circ g$
All +	0	Mw, V_i
All +	All -	ω , BP, BP/Tc, V_c , α_c , ΔH_v , A, B, a_0 , b_0
All -	All +	C, VP
All -	All -	-
Some +, some -	All +	dc
Some +, some -	All -	-
All +	Some +, some -	d, Vm, Tc, n_D , MR, $\Delta G_f^\circ g$
All -	Some +, some -	Pc*
Some +, some -	Some +, some -	Zc
Pc* : $S_{2M7,\text{Oct}}$ is negative, $S_{25M6,\text{Oct}}$ is 0.		- : none found

According to Table 1, among the intrinsic molecular data considered here, only the susceptibility to branching of $\Delta H_f^\circ g$ is positive and increases both with carbon number

and branching. This is a serious reason to consider it a better primary reference for branching than other properties. Molar weight and the intrinsic molar volume, V_i , increase with carbon number and do not depend on branching. The values of ω increase with carbon number and decrease on branching.

Among the properties dependent on intermolecular interactions, the values of $S_{i,j}$ of BP, BP/Tc, Vc, α_c , ΔH_v , A, B, a_0 , and b_0 are positive on increasing the carbon number and negative on increasing branching. The values of $S_{i,j}$ of C and VP decrease with carbon number and increase with branching. No property gives rise to only negative values of $S_{i,j}$, i.e. no one decreases with increasing carbon number and branching. The properties Tc, Pc, dc, d, V_m , n_D , MR, and especially Zc give rise in the first and/or the second $S_{i,j}$ group to some positive as well as to some negative values and for this reason they seem to be the most inappropriate references for branching among the tested properties. Therefore, they are not considered further.

The $S_{\text{octane,heptane}}$ values of C decrease and those of ΔH_f° , BP/Tc, Vc, ω , α_c , a_0 , and b_0 increase on insertion of a secondary carbon. The decrease and the increase, respectively, are higher if the insertion is adjacent to an existing secondary carbon. BP and B increase more if the inserted secondary carbon is not adjacent to an existing one.

It might be worth mentioning that a_0 and b_0 are in fact derived from Tc and Pc considered here as inappropriate references for branching. It seems that Tc and Pc contain the information of the influence of branching as well as of packing. In the derivation of the secondary data a_0 and b_0 the information of packing seems to be cancelled out to an appreciable extent. To stress where they are derived from, the data and designations Tc^2/Pc and Tc/Pc are used from this point on instead of a_0 and b_0 .

In the discussion of the measures of branching in molecules several questions may be raised in spite of the thorough treatment of the problem performed until now⁶⁻⁸. The first question is which of the known measures of branching is better. It is a general opinion that the best way to describe something is to do it in a simple and straightforward way in direct relationship to the problem in question. A reverse relationship is acceptable only if a direct one is lacking. The most appropriate reference for branching is in this respects ΔH_f° , whereas ω , BP, BP/Tc, Vc, α_c , ΔH_v , A, B, Tc^2/Pc , Tc/Pc , and C may be

considered in that order as secondary ones, to be used only in those cases when ΔH_f° does not indicate an unequivocal answer.

Method No. 2: The difference-normalised difference, $\Delta norm_i$

The 12 properties ΔH_f° , ω , BP, BP/Tc, Vc, α_c , ΔH_v , A, B, Tc²/Pc, Tc/Pc, and C, giving, according to Table 1, the same sign in the same group of susceptibilities for branching, were tested also with the second criterion presented here, the $\Delta norm_i$. VP could not be included since its value for the 2233M4 was not available. The least branched octane, the *n*-octane, has the value of $\Delta norm_i$ equal to 0 and the most branched octane, the 2233M4 has the value of $\Delta norm_i$ equal to 1 by definition (Eq. 2). Any property having for any octane $\Delta norm_i < 0$ or $\Delta norm_i > 1$ is considered inappropriate as a reference for judging the indices, since in the former case, it presents the octane in question to be less branched than the *n*-octane and, in the latter case, as more branched than the 2233M4, which is obviously not the fact. The results of this analysis are presented in Table 2.

Table 2. The grouping of 13 properties regarding the criterion $0 < \Delta norm_i < 1$.

$0 < \Delta norm_i < 1$	$\Delta norm_i > 1$ *
ΔH_f° , ω , C, BP/Tc, Tc ² /Pc, Tc/Pc	BP (1), ΔH_v (1), R ² (3), Vc (7), A (11), B (12), α_c (15)

* In parenthesis the number of cases out of the 16 possible is given, when $\Delta norm_i > 1$.

According to this criterion, the properties ΔH_f° , ω , C, BP/Tc, Tc²/Pc, and Tc/Pc seem to be suitable as reference properties. BP, ΔH_v , R², Vc, A, B, and especially α_c , on the other hand, are not suitable as references. In most of the unsuitable properties the data indicate that 2,2,4-trimethyl pentane (224M5) is more branched than 2,2,3,3-tetramethyl butane (2233M4). This is not surprising if we recall that 224M5 in the liquid state has the highest intermolecular "free" space¹, i.e. the loosest packing, whereas 2233M4 is packed the most densely of all octanes. The data of 224M5 might serve as a good indicator of whether a property is suitable as a reference of branching or not.

Ranking of the 6 remaining properties by a series of additional criteria

Method No.3: The dependence on carbon number

The properties, which seemed suitable as references to evaluate branching indices, i.e. $\Delta H_f^\circ g$, ω , C, BP/Tc, Tc^2/Pc , and Tc/Pc, were additionally tested using several criteria. Their dependence on carbon number is presented on the one hand by the mean and the maximum $S_{\text{octane,heptane}}$, Table 3. As a reference value, $S_{\text{octane,heptane}}$ for carbon number, N_C , is included.

Table 3. Susceptibilities of properties to the increase in carbon number.

	$S_{\text{octane,heptane}}$
Mean	$0.25 > Tc^2/Pc > \omega \sim Tc/Pc > N_C = 0.14 > \Delta H_f^\circ g > BP/Tc > 0 > C > -0.04$
Max.	$0.25 > Tc^2/Pc > \omega > Tc/Pc > N_C > \Delta H_f^\circ g > BP/Tc > 0 > C > -0.05$
RSD	$0.2 > C > \Delta H_f^\circ g > \omega > BP/Tc > 0.1 > Tc/Pc > Tc^2/Pc > N_C = 0$
r_{NC}	$1.000 > Tc/Pc > Tc^2/Pc > \Delta H_f^\circ g > BP/Tc > 0.95 > \omega > 0.90 >>> -0.95 > C$

According to Table 3, ω , Tc^2/Pc , and Tc/Pc are more susceptible to the increase in carbon number than the carbon number itself, whereas $\Delta H_f^\circ g$, C, and BP/Tc are less susceptible. On the other hand, the dependence on carbon number can also be presented by r_{NC} . The properties tested here correlate well with carbon number.

Method No.4: The dependence on branching

As another means to assess the properties, the susceptibility to branching at the same carbon number is presented by the mean and the maximum $S_{i,\text{Oct}}$, Table 4. $\Delta H_f^\circ g$ and C increase on branching, whereas ω , Tc/Pc, Tc^2/Pc , and BP/Tc decrease on branching. The ranking according to the absolute value of the mean susceptibility to branching is $\omega > 0.17 > Tc^2/Pc > Tc/Pc > 0.05 > \Delta H_f^\circ g > C > 0.02 > BP/Tc$. The most susceptible to branching at the same carbon number are ω , Tc^2/Pc , and Tc/Pc.

As the next means, the comparison of the susceptibilities to branching vs. that to the increase of carbon number is presented by the ratio of mean $S_{i,\text{Oct}}/S_{\text{octane,heptane}}$ in Table 4.

The absolute values of this ratio indicate that only ω is somewhat more susceptible to branching than to the increase of the carbon number, C and BP/Tc are slightly less susceptible, whereas $\Delta H_f^\circ g$, Tc/Pc, and Tc²/Pc are more than two times more susceptible to the increase in carbon number than to branching.

Table 4. Mean and maximum susceptibilities of properties to the branching.

	$S_{i,Oct}$
Mean	0.05 > $\Delta H_f^\circ g$ > C > 0 > BP/Tc > Tc/Pc > Tc ² /Pc > ω > -0.2
Max.	0.1 > $\Delta H_f^\circ g$ ~ C > 0 > BP/Tc > Tc/Pc ~ Tc ² /Pc > ω > -0.4
RSD	0.7 > BP/Tc > $\Delta H_f^\circ g$ > C ~ ω ~ Tc/Pc > Tc ² /Pc > 0.4
	$S_{i,Oct}/S_{octane,heptane}$
Mean	0.5 > $\Delta H_f^\circ g$ >>> -0.3 > Tc ² /Pc > Tc/Pc > -0.5 > BP/Tc > C > -1 > ω
RSD - Relative standard deviation of the influence of branching.	

Besides the mean and maximum $S_{i,j}$ values, also the value of the most branched octane, $S_{2233M4,Oct}$, as well as the ratios of the values of some typical octane structures, e.g. $S_{234M5,Oct}/S_{2233M4,Oct}$, $S_{25M6,Oct}/S_{22M6,Oct}$, and $S_{34M6,Oct}/S_{33M6,Oct}$ can present some additional information about the remaining properties.

Table 5. The ranking of properties regarding some susceptibilities to branching and their ratios.

Criterion	Ranking
$S_{2233M4,Oct}$	0.1 > $\Delta H_f^\circ g$ > C > 0 > BP/Tc > -0.1 > Tc/Pc > Tc ² /Pc > -0.2 > ω > -0.4
$ S_{2233M4,Oct} $	0.4 > ω > 0.2 > Tc ² /Pc > Tc/Pc > 0.1 > $\Delta H_f^\circ g$ > C > 0.05 > BP/Tc
$S_{234M5,Oct}/S_{2233M4,Oct}$	Tc ² /Pc > 0.7 > Tc/Pc > BP/Tc > ω > $\Delta H_f^\circ g$ > 0.5 > C
$S_{25M6,Oct}/S_{22M6,Oct}$	0.9 > C > Tc ² /Pc > $\Delta H_f^\circ g$ > 0.8 > Tc/Pc > ω > BP/Tc > 0.6
$S_{34M6,Oct}/S_{33M6,Oct}$	Tc/Pc > 1 > Tc ² /Pc > BP/Tc > ω > 0.7 > C > 0.5 > $\Delta H_f^\circ g$ > 0.3
$S_{25M6,Oct}/S_{34M6,Oct}$	3.2 > $\Delta H_f^\circ g$ > 1 > C > Tc ² /Pc > ω = 0.7 > BP/Tc > Tc/Pc > 0.4

The rankings of the properties are presented in Table 5. According to $S_{2233M4,Oct}$, among the tested properties only $\Delta H_f^\circ g$ and C increase with branching, whereas the most susceptible to branching is ω , followed by Tc²/Pc.

The branches are placed in alkanes on tertiary and/or quaternary carbons. The ability to distinguish between the presence of tertiary and quaternary carbons in the structure of alkanes is presented here as the ratio of susceptibilities to branching, $S_{234M5,Oct}/S_{2233M4,Oct}$, $S_{25M6,Oct}/S_{22M6,Oct}$, and $S_{34M6,Oct}/S_{33M6,Oct}$. This ability depends on the position of branches. If the branches are central, as presented by $S_{34M6,Oct}/S_{33M6,Oct}$, then the most susceptible to the presence of tertiary carbons is Tc/Pc and to that of quaternary ones it is $\Delta H_f^\circ g$. If the branches are peripheral, as presented by $S_{25M6,Oct}/S_{22M6,Oct}$, then the property most susceptible to the presence of tertiary structures is C and to quaternary structures it is BP/Tc. This relationship is thus quite complex.

The ratio $S_{25M6,Oct}/S_{34M6,Oct}$ indicates that in symmetric structures, $\Delta H_f^\circ g$ is more susceptible to peripheral substitution whereas C, Tc^2/Pc , ω , BP/Tc, and Tc/Pc are more susceptible to central substitution. Other ratios like this contain information of several features at once, such as the symmetry of substitution, the adjacency of branches, and their position from the centre of the molecule, so they are more difficult to interpret unequivocally and therefore they are not presented.

Method No.5: The influence of branching of octanes on their properties

Since among the influences expressed by branching on properties and indices, the most important is the number of branches, followed by the type of branched structure, i.e. whether the branch bearing carbon is tertiary or quaternary, the position of branches (central or peripheral), (distant or adjacent), and the least important is the shape of branched molecules (spherical, flat or elongated), (symmetric or asymmetric), the properties $\Delta H_f^\circ g$, BP/Tc, C, ω , Tc/Pc, and Tc^2/Pc were tested in this respect, too, Table 6-11.

The most consistent is the dependence on branching of the intrinsic property $\Delta H_f^\circ g$, as well as of the property Tc/Pc, which is derived from interaction dependent properties Tc and Pc.

At each number of branches they give the same ranking of the influence of particular characteristics of the branches and the highest number of these characteristics.

In this respect they are followed by Tc²/Pc and BP/Tc, whereas ω and C present the least information.

Table 6. The influence of branching on ΔHf^og of octanes.

<i>N_{br}</i>	Series	Result
1	3Et < 4M < 3M < 2M	Et < M, <i>centr.</i> < <i>periph.</i> , <i>sym.</i> < <i>asym.</i>
2	3Et2M < 34M < 23M < 3Et3M < 24M < 33M < 25M < 22M	<i>t</i> < <i>q</i>
<i>t</i>	3Et2M < 34M < 23M < 24M < 25M	Et < M, <i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>
<i>q</i>	3Et3M < 33M < 22M	Et < M, <i>centr.</i> < <i>periph.</i>
3	233M < 234M < 223M < 224M	<i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>

Abbreviations: *N_{br}* - number of branches; *centr.* - central; *periph.* - peripheral; *sym.* - symmetric; *asym.* - asymmetric; *adj.* - adjacent; *dist.* - distant (not adjacent); *q* - quaternary carbon. *t* - tertiary carbon.

Table 7. The influence of branching on the ratio Tc/Pc (van der Waals constant b₀) of octanes. Abbreviations: see Table 6.

<i>N_{br}</i>	Series	Result
1	3Et < 4M < 3M < 2M	Et < M, <i>centr.</i> < <i>periph.</i> , <i>sym.</i> < <i>asym.</i>
2	3Et3M < 3Et2M < 34M < 33M < 23M < 24M < 22M < 25M	<i>q</i> < <i>t</i>
<i>t</i>	3Et2M < 34M < 23M < 24M < 25M	M < Et, <i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>
<i>q</i>	3Et3M < 33M < 22M	Et < M, <i>centr.</i> < <i>periph.</i>
3	233M < 223M < 234M < 224M	<i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>

Table 8. The influence of branching on the reduced boiling point BP/Tc of octanes. Abbreviations: see Table 6.

<i>N_{br}</i>	Series	Result
1	3Et < 3M < 4M < 2M	Et < M
2	3Et3M < 33M < 3Et2M < 34M < 23M < 22M < 24M < 25M	<i>q</i> < <i>t</i>
<i>t</i>	3Et2M < 34M < 23M < 24M < 25M	Et < M, <i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>
<i>q</i>	3Et3M < 33M < 22M	Et < M, <i>centr.</i> < <i>periph.</i>
3	233M < 223M < 234M < 224M	<i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>

Table 9. The influence of branching on the Pitzer acentric factor (ω) of octanes. Abbreviations: see Table 6.

N_{br}	Series	Result
1	3Et < 3M < 4M < 2M	Et < M
2	3Et3M < 33M < 3Et2M < 22M = 34M < 24M < 23M < 25M	$q < t$
t	3Et2M < 34M < 24M < 23M < 25M	Et < M, <i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>
q	3Et3M < 33M < 22M	Et < M, <i>centr.</i> < <i>periph.</i> ,
3	233M < 223M < 224M < 234M	$q < t$, <i>centr.</i> < <i>periph.</i> , <i>adj.</i> < <i>dist.</i>

Table 10. The influence of branching on the ratio Tc^2/Pc (van der Waals constant a_0) of octanes. Abbreviations: see Table 6.

N_{br}	Series	Result
1	3Et < 4M < 3M < 2M	Et < M, <i>centr.</i> < <i>periph.</i> , <i>sym.</i> < <i>asym.</i>
2	3Et3M < 33M < 3Et2M < 24M < 34M < 22M < 23M < 25M	$q < t$
t	3Et2M < 24M < 34M < 23M < 25M	Et < M
q	3Et3M < 33M < 22M	Et < M, <i>centr.</i> < <i>periph.</i>
3	224M < 223M < 233M < 234M	$q < t$, <i>periph.</i> < <i>centr.</i> , <i>dist.</i> < <i>adj.</i>

Table 11. The influence of branching of octanes on the Antoine constant C. Abbreviations: see Table 6.

N_{br}	Series	Result
1	3M < 4M < 3Et < 2M	M < Et
2	23M < 25M < 24M < 34M < 22M < 3Et2M < 33M < 3Et3M	$t < q$
t	23M < 25M < 24M < 34M < 3Et2M	M < Et, <i>periph.</i> < <i>centr.</i>
q	22M < 33M < 3Et3M	M < Et, <i>periph.</i> < <i>centr.</i>
3	234M < 223M < 233M < 224M	$t < q$, <i>adj.</i> < <i>dist.</i>

Method No.6: The evenness of the $\Delta norm_i$ data

Another criterion might be the uniformity (evenness) of $\Delta norm_i$ data, Table 12. It can be assessed with the highest and the lowest differences of sorted $\Delta norm_i$ data as well as of their standard deviation. The lower the $\Delta(\Delta norm_i)_{max}$, the higher $\Delta(\Delta norm_i)_{min}$, and the lower their relative standard deviation, RSD, the better suited might be the property as a reference. In this respect, Tc/Pc seems to be the best, followed by $\Delta Hf^\circ g$, and C seems to be the worst reference.

Table 12. The sequence of properties regarding the evenness of the $\Delta norm_i$ data.

Evenness	Sequence
$\Delta(\Delta norm_i)_{max}$	$C > \omega > BP/Tc > Tc^2/Pc > Tc/Pc > \Delta Hf^\circ g$
$\Delta(\Delta norm_i)_{min}$	$Tc/Pc > Tc^2/Pc > BP/Tc > \Delta Hf^\circ g, C, \omega$

 RSD $C > \omega > BP/Tc > Tc^2/Pc > Tc/Pc > \Delta H_f^\circ g$

To illustrate the series presented in Table 12, Fig. 1 presents the $\Delta n_{norm, i}$ data for octanes of properties $\Delta H_f^\circ g$, Tc/Pc, and Tc^2/Pc , whereas Fig. 2 presents those of C, ω , and BP/Tc. The data points are arranged according to the number of branches. Using only data of octanes, the influence of carbon number is excluded. In Table 13 compilation of the content of Fig. 1 and 2 is presented in shorthand.

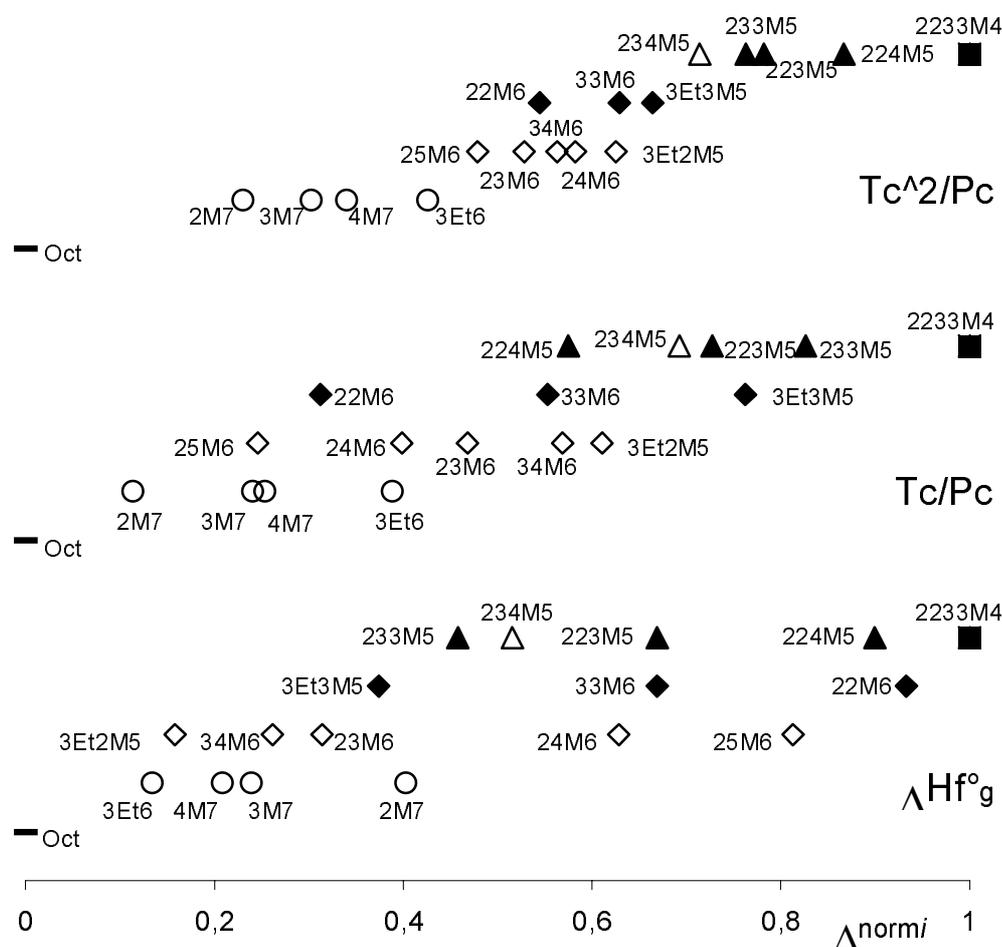


Figure 1: The distribution of octanes by $\Delta n_{norm, i}$ of $\Delta H_f^\circ g$, Tc/Pc, and Tc^2/Pc . Empty symbols indicate the presence of tertiary carbons, filled symbols indicate the presence of (also) quaternary carbons in the structure of octanes.

According to Fig. 1 and 2, the values of particular alkanes are the most evenly distributed by $\Delta H_f^\circ g$, Tc/Pc, and BP/Tc. Regarding the distribution in Fig. 1 and 2 which is compiled in Table 13, the properties to serve best as a reference for branching would be $\Delta H_f^\circ g$ and Tc/Pc, followed by BP/Tc, whereas Tc^2/Pc , ω , and especially C seem to be

less suitable. For Tc^2/Pc it seems that the distortion due to the influence of packing contained in Tc as well as in Pc is still contained to a noticeable degree, whereas in Tc/Pc it seems to be well compensated. The influence of packing might be contained in C to an appreciable extent. The reason for the worse performance of ω is not clear at the moment.

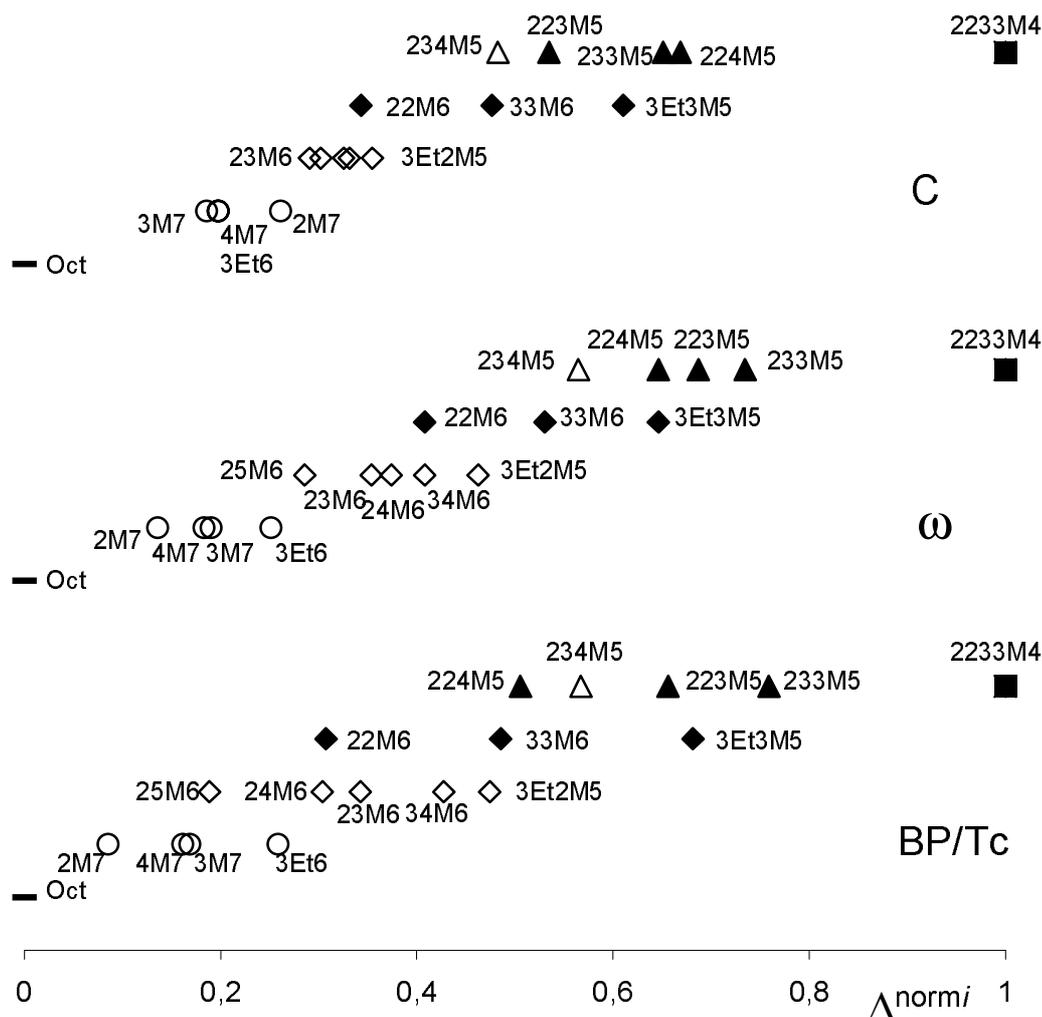


Figure 2: The distribution of octanes by Δ_{norm_i} of BP/Tc, ω , and C. Empty symbols indicate the presence of tertiary carbons, filled symbols indicate the presence of (also) quaternary carbons in the structure of octanes.

In addition to preceding findings, from the Δ_{norm_i} data, cf. Fig. 1 and 2 and Tables 6-11, one can also deduce the influence of the number of branches, N_{br} , of the type of branched structure, i.e. the influence of tertiary and quaternary carbons, t/q , of the position of branches, i.e. whether they are central or peripheral, *centr./periph.*, adjacent

or distant, *adj./dist.*, as well as of the symmetry of octanes, *sym./asym.*, on the considered properties. The conclusions made here must be viewed with caution, since except for the influence of the number of branches, where 9 pairs of data were available, they are derived from only 4 pairs of data each. The presented conclusions are to be checked with data of nonanes and decanes when they become available. The results are collected in Table 14 as a ranking of properties regarding the extent of influence of particular structural details, and in Table 15 as a ranking of importance of particular structural details for individual properties.

Table 13. The sequences according to $\Delta n o r m_i$ of octanes having the same number of branches. Given is the position of branches. If not marked Et for ethyl, the branch is methyl.

Nbr	Sequence	Property
1(<i>t</i>)	2, 3, 4, 3Et 2, 4, 3, 3Et 3, 4, 3Et, 2	$\Delta H_f^\circ g$, Tc/Pc, and Tc ² /Pc BP/Tc, ω C
2(<i>t</i>)	25, 24, 23, 34, 3Et2 25, 23, 34, 24, 3Et2 25, 23, 24, 34, 3Et2 23, 25, 24, 34, 3Et2	$\Delta H_f^\circ g$, Tc/Pc, and BP/Tc Tc ² /Pc ω C
2(<i>q</i>)	22, 33, 3Et3	All
3(<i>t, q</i>)	224, 223, 234, 233 224, 234, 223, 233 234, 233, 223, 224 234, 224, 223, 233 234, 223, 233, 224	$\Delta H_f^\circ g$ Tc/Pc, BP/Tc Tc ² /Pc ω C

t - tertiary; *q* - quaternary

$\Delta H_f^\circ g$ differs in this respect markedly from other properties, since it is the least of all dependent on the number of branches. This fact is in contrast also to the previous observation on all 24 tested properties as a group¹ that the number of branches is the most important feature next to carbon number. Low dependence on the number of branches seems to be a peculiarity of $\Delta H_f^\circ g$, making it less appropriate as a reference

property than it would be expected with regard to its other characteristics. For the interaction dependent properties as well as for ω , the number of branches is more important than the other influences tested here. Among the other structural details tested here, it is important where the branches are placed, in the centre or on peripheral positions of molecules. The adjacency of branches, as well as the symmetry of molecules, which have a similar degree of influence, seems to be less important than where the branches are placed.

Table 14. The influence of the number of branches, of the (mutual) position of branches, and of the symmetry of molecules on $\Delta H_f^\circ g$, Tc/Pc, BP/Tc, Tc²/Pc, ω , and C of octanes.

Influence of	The series of decreasing influence
N_{br}	Tc ² /Pc ~ Tc/Pc > ω ~ BP/Tc > C ~ $\Delta H_f^\circ g$
t/q	$\Delta H_f^\circ g$ > C > ω > Tc/Pc > Tc ² /Pc > BP/Tc
<i>centr./periph.</i>	$\Delta H_f^\circ g$ > Tc/Pc > BP/Tc > Tc ² /Pc ~ ω > C
<i>adj./dist.</i>	$\Delta H_f^\circ g$ > Tc/Pc > BP/Tc > Tc ² /Pc > C ~ ω ,
<i>sym./asym.</i>	$\Delta H_f^\circ g$ > Tc/Pc > BP/Tc > C ~ ω ~ Tc ² /Pc

Table 15. The contribution of the following structural details: the number of branches, the (mutual) position of branches, and the symmetry of molecules on $\Delta H_f^\circ g$, Tc/Pc, BP/Tc, Tc²/Pc, ω , and C of octanes.

The contribution to	Ranking of importance of structural details
$\Delta H_f^\circ g$	t/q ~ <i>centr./periph.</i> > <i>adj./dist.</i> > <i>sym./asym.</i> > N_{br}
Tc/Pc	N_{br} > <i>centr./periph.</i> > <i>sym./asym.</i> ~ <i>adj./dist.</i> > t/q
BP/Tc	N_{br} > <i>centr./periph.</i> > <i>adj./dist.</i> ~ <i>sym./asym.</i> > t/q
ω	N_{br} > t/q > <i>centr./periph.</i> > <i>sym./asym.</i> ~ <i>adj./dist.</i>
Tc ² /Pc	N_{br} > <i>centr./periph.</i> > t/q > <i>adj./dist.</i> > <i>sym./asym.</i>
C	N_{br} > t/q > <i>centr./periph.</i> ~ <i>sym./asym.</i> ~ <i>adj./dist.</i>

Method No. 7: The increase of the values for n-alkanes with carbon number

The next question is how $\Delta H_f^\circ g$, Tc/Pc, and BP/Tc increase with the increase of carbon number in *n*-alkanes. According to the Methane-based definition¹, a linear increase would be expected. To see whether this is true, the difference-normalised data of *n*-alkanes from C₁ to C₁₈ are presented in Fig. 3.

According to Fig. 3, $\Delta H_f^\circ g$ increases from ethane on linearly with carbon number. Such an increase is expected according to the Methane-based definition of branching, since the insertion of an additional CH_2 group into an n -alkane presents the same contribution in any case. $\Delta H_f^\circ g$ might be in this respect, as well as due to its increase with branching, a prototype reference property to test whether a topological index obeys the Methane-based definition of branching.

The sign of tabulated data of $\Delta H_f^\circ g$ of alkanes^{3,4}, which is by definition negative in exothermic reactions, is not related to branching. This sign indicates only the direction of heat flow during the reaction. Therefore, absolute values of $\Delta H_f^\circ g$ are to be used when branching of molecules is considered.

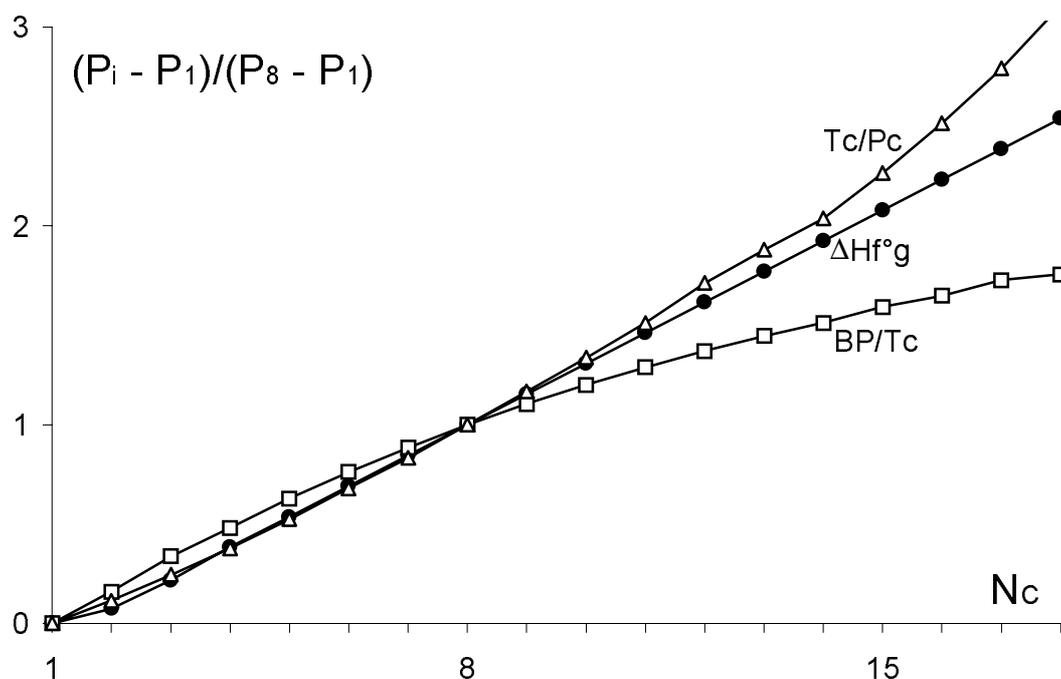


Figure 3. The increase of $\Delta H_f^\circ g$, Tc/Pc, and BP/Tc with carbon number (N_c) in n -alkanes (the data are normalised at n -octane).

Tc/Pc, on the other hand, increases slightly faster than carbon number, whereas BP/Tc increases slower than carbon number but faster than BP and Tc. In this respect, BP/Tc and especially Tc/Pc might be useful references for branching at particular carbon numbers.

Reference data for judging the branching indices

In the preceding parts of this paper has been found that the properties that seem to be the best reference ones for judging the branching indices are ΔH_f° and Tc/Pc, followed by BP/Tc. Each of them has some peculiarities, which diminish its ability to serve as the single best one. One of the strengths of ΔH_f° is its linear increase with carbon number in *n*-alkanes as well as its increase with branching. This behaviour is in accordance with the Methane-based definition of branching and it would be desired that other reference data share it. Its weakness is the low dependence on the number of branches. With Tc/Pc and BP/Tc, the situation is reversed. They do not increase linearly with carbon number but they seem to have an appropriate dependence on the number of branches. Thus, all these properties, ΔH_f° , Tc/Pc, and BP/Tc are to be used simultaneously as references.

Another possibility is to take the best of the reference properties and to construct one or more quasi-ideal references. For example, the principle of linear increase with carbon number is taken from ΔH_f° and its values are rearranged to serve as reference values. The data for methane is an outlier in the trend of ΔH_f° values for *n*-alkanes. In spite of that, the reference values ($RV_{\Delta H_f^\circ}$) can be based on data for ΔH_f° of other *n*-alkanes setting for $RV_{\Delta H_f^\circ}$ of *n*-alkanes the value $N_C - 1$ by definition to obtain for methane the reference value of 0. The $RV_{\Delta H_f^\circ}$ are then calculated as follows, Eq. 3:

$$RV_{\Delta H_f^\circ} = (N_C - 1) * \Delta H_f^\circ_i / \Delta H_f^\circ_n \quad (3)$$

where *i* stands for any alkane of the same carbon number and *n* stands for *n*-alkane of the same carbon number. They are presented in Table 16.

In a similar manner the reference values based on Tc/Pc or BP/Tc are constructed, forcing them to align to the linear increase of the values for *n*-alkanes and setting the value of 0 for methane, Eq. 4:

$$RV_X = (N_C - 1) * X_n / X_i \quad (4)$$

where X is Tc/Pc or BP/Tc and N_C is the carbon number (number of vertices in the graph). These reference values are presented in Table 17. The value of $RV_{Tc/Pc}$ for 2M3 is an outlier. To correct it, better data for Tc and Pc of *n*-butane and 2-methyl propane are needed.

Table 16. Reference values for branching indices, derived from ΔH_f° , obeying the Methane-based definition ($RV_{\Delta H_f^\circ}$).

CxHy	$RV_{\Delta H_f^\circ}$	CxHy	$RV_{\Delta H_f^\circ}$	CxHy	$RV_{\Delta H_f^\circ}$
				3Et6	7.0787
M	0	Hp	6	22M6	7.5466
Et	1	2M6	6.2286	23M6	7.1841
Pr	2	3M6	6.1444	24M6	7.3681
Bu	3	3Et5	6.0602	25M6	7.4763
2M3	3.1990	22M5	6.5869	33M6	7.3920
Pe	4	23M5	6.3663	34M6	7.1532
2M4	4.2194	24M5	6.4545	3Et2M5	7.0927
22M3	4.5337	33M5	6.4398	3Et3M5	7.2192
Hx	5	223M4	6.54418	223M5	7.3920
2M5	5.2127	Oct	7	224M5	7.5269
3M5	5.1326	2M7	7.2361	233M5	7.2684
22M4	5.5493	3M7	7.1405	234M5	7.3021
23M4	5.3166	4M7	7.1222	2233M4	7.5859

The correlation coefficients of $RV_{\Delta H_f^\circ}$, $RV_{Tc/Pc}$, and $RV_{BP/Tc}$ are: $r_{\Delta H_f^\circ, Tc/Pc} = 0.993$, $r_{\Delta H_f^\circ, BP/Tc} = 0.996$, and $r_{Tc/Pc, BP/Tc} = 0.997$. A good branching index obeying the Methane-based definition seems to have to fall within this range.

Table 17. Reference values for branching indices, derived from Tc/Pc and BP/Tc, obeying the Methane-based definition ($RV_{Tc/Pc}$ and $RV_{BP/Tc}$).

CxHy	$RV_{Tc/Pc}$	$RV_{BP/Tc}$	CxHy	$RV_{Tc/Pc}$	$RV_{BP/Tc}$	CxHy	$RV_{Tc/Pc}$	$RV_{BP/Tc}$
						3Et6	7.3669	7.0854
M	0	0	Hp	6	6	22M6	7.3464	7.1017
Et	1	1	2M6	6.0632	6.0265	23M6	7.4498	7.1135

Pr	2	2	3M6	6.1835	6.0520	24M6	7.3752	7.1005
Bu	3	3	3Et5	6.2892	6.0858	25M6	7.2218	7.0621
2M3	2.9999	3.0035	22M5	6.2667	6.0966	33M6	7.5422	7.1620
Pe	4	4	23M5	6.3651	6.1104	34M6	7.5784	7.1423
2M4	4.1011	4.0282	24M5	6.1936	6.0658	3Et2M5	7.6053	7.1582
22M3	4.1159	4.0415	33M5	6.4603	6.1627	3Et3M5	7.7792	7.2295
Hx	5	5	223M4	6.5412	6.1920	223M5	7.7389	7.2207
2M5	5.1360	5.0270	Oct	7	7	224M5	7.5406	7.1688
3M5	5.2256	5.0511	2M7	7.0894	7.0280	233M5	7.8533	7.2565
22M4	5.3314	5.0999	3M7	7.2148	7.0556	234M5	7.6979	7.1900
23M4	5.2811	5.0869	4M7	7.2278	7.0533	2233M4	8.0742	7.3420

From the conclusion made above, that a reference value should be equal to $(N_C - 1)$ for *n*-alkanes, as well as from the fact that the tested properties are dependent not only on carbon number but also on the number of branches, the type of branched structure, the position of branches, and the symmetry of molecules¹, it follows that to compose a branching index obeying the Methane-based definition (BI_M), the following general equation is to be used, Eq. 5:

$$BI_M = (N_C - 1) + f(N_{br}, t/q, centr./periph., adj./dist., sym./asym.) \quad (5)$$

where $f(N_{br}, t/q, centr./periph., adj./dist., sym./asym.)$ is nothing but the *n*-Alkane-based definition of branching¹ obeying branching index (BI_A). Thus, Eq. 6 presents this relation:

$$BI_M = (N_C - 1) + BI_A \quad (6)$$

The reference values to assess BI_A can be derived from the reference properties ΔH_f° , Tc/Pc, or BP/Tc. From the data tabulated in Tables 16 and 17 we can derive the reference values useful for assessing BI_A by subtracting from them $N_C - 1$, i.e. the value set for the *n*-alkane.

Based on the findings made in a previous¹ and the present work, a general equation (Eq. 7 or 7a) presenting the dependence of physicochemical properties on branching can be set, too:

$$P = f(N_C) + f(N_{br}, t/q, centr./periph., sym./asym., adj./dist.) + f(\text{packing}) \quad (7)$$

or,

$$P = f(N_C) + BI_A + f(\text{packing}) \quad (7a)$$

In the case of reference values for branching indices, $f(N_C) = N_C - 1$.

For $f(\text{packing})$, $f(V_m)$, e.g. in the form of $f(V_m - V_i)$, might be representative as a reference (cf. the discussion of the density of alkanes in the previous paper¹).

Conclusions

Summing up this analysis, the suitability of the studied alkanes' properties to serve as references to judge the branching indices is as follows:

- Regarding the criterion No. 1, the sign of $S_{i,j}$, the following properties might be appropriate: ΔH_f° , ω , BP, V_c , α_c , ΔH_V , A, B, C, T_c^2/P_c , T_c/P_c , and BP/T_c .
- Regarding the criterion No. 2, $0 < \Delta n_{orm_i} < 1$, the following ones might be appropriate: ΔH_f° , ω , C, T_c/P_c , T_c^2/P_c , and BP/T_c .
- Regarding their mean dependence on carbon number, they are ranked $T_c^2/P_c > \omega > T_c/P_c > \Delta H_f^\circ > BP/T_c > C$.
- Their correlation coefficient with carbon number, r_{NC} , is > 0.95 , except for ω .
- Their susceptibility for branching is $\omega > T_c^2/P_c > T_c/P_c > \Delta H_f^\circ > C > BP/T_c$.
- Regarding the criterion No. 5, they are ranked ΔH_f° , $T_c/P_c > T_c^2/P_c$, $BP/T_c > \omega$, C.
- Regarding the criterion No. 6, the evenness of Δn_{orm_i} data, they are ranked as follows: By the relative standard deviation of Δn_{orm_i} these properties would be ranked: $\Delta H_f^\circ > T_c/P_c > T_c^2/P_c > BP/T_c > \omega > C$ (> stands for "better than"). Regarding the $\Delta \Delta n_{orm_i \max}$ they would be ranked $\Delta H_f^\circ > T_c/P_c > T_c^2/P_c > BP/T_c > \omega > C$. Regarding the $\Delta \Delta n_{orm_i \min}$ they would be ranked $T_c/P_c > BP/T_c > T_c^2/P_c > \Delta H_f^\circ$, ω , C. The three best properties are in this respect ΔH_f° , T_c/P_c , and BP/T_c .
- Regarding the criterion No. 7, the linearity of the increase of the values for *n*-alkanes, the three best properties are ranked $\Delta H_f^\circ > T_c/P_c > BP/T_c$.

- Regarding the increase on branching (obeying the Methane-based definition of branching) ΔH_f° would be the most appropriate and C the least appropriate.
- Regarding the evenness of the distribution of data for alkanes at the fixed value of N_C and the fixed value of N_{br} , the six best properties would be ranked ΔH_f° , Tc/Pc > BP/Tc >> Tc²/Pc, $\omega > C$.
- Regarding the contribution of the number of branches to its value, ΔH_f° is not a good reference, whereas regarding the contribution of the (mutual) position of branches, and of the symmetry of molecules it is one of the best reference properties.

As a result of this comparison it can be concluded that no one of the tested properties is a single best reference to judge the branching indices. Among the best ones seem to be ΔH_f° and Tc/Pc, followed by BP/Tc. All of them are to be considered simultaneously. The properties ω , Tc²/Pc, and C do not seem sufficiently good to serve as reference properties, whereas all the other tested properties are not to be used for this purpose unless their peculiarities are taken into account.

Based on data of the best three properties, i.e. ΔH_f° , Tc/Pc, and BP/Tc, there were derived reference values for branching indices obeying the Methane-based rule of branching as well as those for branching indices obeying the n-Alkane-based rule of branching.

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Povzetek

Občutljivost za razvejanost, $S_{i,j}$, normalizirane razlike podatkov za oktane, $\Delta_{norm i}$, in še vrsta dodatnih kriterijev je bila preizkušena za vrednotenje 24 fizikokemijskih lastnosti alkanov kot referenčnih lastnosti pri ugotavljanju razvejanosti. Najprimernejše referenčne lastnosti za vrednotenje razvejanosti so videti ΔH_f° , Tc/Pc (uporabljena namesto b_0) in T_{vrej}/T_c . Naslednje lastnosti: T_c^2/P_c (uporabljena namesto a_0), ω in C, se kažejo kot manj primerne. Druge preizkušene fizikokemijske lastnosti alkanov niso primerna merila razvejanosti. Iz podatkov za ΔH_f° , Tc/Pc in BP/Tc so pripravljene referenčne vrednosti za indekse razvejanja, ki ustrezajo metanskemu pravilu, kot tudi za tiste, ki ustrezajo *n*-alkanskemu pravilu razvejanosti.