ON TOPOLOGICAL INDICES INDICATING BRANCHING PART 4. THE SUSCEPTIBILITY FOR BRANCHING AS A SOURCE OF RV_A-TYPE REFERENCE VALUES OR OF BI_A-TYPE INDICES

Anton Perdih
Mala vas 12, SI-1000 Ljubljana, Slovenia

Received 11-01-2001

Abstract

Branching indices (BI_M) or reference values (RV_M) obeying the *Methane-based* definition as well as those obeying the *n-Alkane-based* definition of branching (BI_A or RV_A) can be derived from the susceptibility for branching, $S_{i,j}$, of other topological indices or physicochemical properties.

Introduction

In a previous paper,[1] the *Methane-based* definition of branching as well as the *n-Alkane-based* definition of branching was suggested. Later, the relation between the *Methane-based* definition of branching obeying branching indices (BI_M) and the *n-Alkane-based* definition of branching obeying branching indices (BI_A) was presented[2]. On the other hand, the reference values (RV_M) for evaluation of indices intended to be used as BI_M indices, as well as the reference values (RV_A) for evaluation of indices intended to be used as BI_A indices were derived from data of physicochemical properties $\Delta Hf°g$, Tc/Pc, and BP/Tc. Subsequently, BI_M and BI_A indices were derived from 11 most popular topological indices and compared to the reference values mentioned above.[3] Meanwhile, the susceptibility for branching, $S_{i,j}$, used initially to evaluate the suitability of physicochemical properties as references for branching indices[2] as well as the suitability of topological indices as branching indices,[3] has been found to be a possible source of RV_A or BI_A data and this possibility is presented here.

Data

The structures of alkanes are presented in shorthand, e.g. *n*-Oct is *n*-octane, 223M5 is 2,2,3-trimethylpentane, 3Et2M5 is 3-ethyl-2-methylpentane, etc.

The indices

We decided to take into account the group of the most frequently used indices and some novel indices. Altogether 11 indices are used. The data for Wiener[4] index (W), the Hosoya[5] index (Z), the Randić[6] index (χ) were taken from Yang et al[7]. The ID numbers were taken from Randić[8] and the Schultz MTI index from Mihalić et al[9]. The Xu index was taken from Ren[10], whereas the Schultz indices S (Sch-S) and TLFCIR(D) (Sch-TF) were taken from Schultz and Schultz[11]. The indices $\lambda\lambda_1$[12], the largest eigenvalue of the adjacency matrix[13] (λ_1), and the largest eigenvalue of the distance matrix (D) were calculated from corresponding matrices.

The properties

The data for the boiling point (BP), the critical temperature (Tc), the critical pressure (Pc), as well as the standard enthalpy of formation for the ideal gas (ΔHf°g) were taken from CRC Handbook.[14] BP/Tc and Tc/Pc were calculated.

The susceptibility for branching

The susceptibility for branching, $S_{i,j}$, is defined as the normalised difference of the data of properties or indices of alkanes of different degree of branching, Eq. 1.

$$S_{i,j} = X_j / X_i - 1 \qquad (1)$$

where $S_{i,j}$ is the susceptibility for branching and X is a physicochemical property or a topological index. In present paper, *i* refer to data for *n*-octane and *j* refer to data of any octane, i.e. the $S_{n,j}$ data are used.

Results and discussion

The reference values RV_M and RV_A as well as the indices BI_M and BI_A can be derived in different ways.[2,3] It has been dissuaded from the use of the RV_A values and BI_A indices derived by Eq. 2 because their values are too dependent on the magnitude of the source data:[3]

$$Y^*_A = \mathrm{abs}(X_i - X_n) \quad (2)$$

where Y^*_A stands for any potential RV_A or BI_A and *n* stands for the *n*-alkane of the same carbon number, N_C.

There exists a possibility to eliminate the dependency on the magnitude of source data by introducing into Eq. 2 the normalization of data, cf. Eq. 3:

$$Y'_A = \mathrm{abs}(X_i - X_n)/X_n = \mathrm{abs}(X_i/X_n - 1) \equiv \mathrm{abs}(S_{n,j}) \quad (3)$$

According to Eq. 3 a RV'_A value or a BI'_A index is nothing but the absolute value of the susceptibility for branching (in alkanes at the same carbon number), $S_{n,j}$, that has been used previously [2,3] as an indicator of the suitability of a property as a reference as well as of an index as a branching index. In order to ensure that Y'_A derived in Eq. 3 becomes compatible with the relation[2] $Y_M = (N_C - 1) + Y_A$, it is to be modified as follows, Eq. 4 and 5:

$$Y_A = (N_C - 1)*\mathrm{abs}(S_{n,j}) \quad (4)$$
$$Y_M = (N_C - 1)*(1 + \mathrm{abs}(S_{n,j})) \quad (5)$$

The correlation of RV_A and BI_A data for octanes derived with help of Eq. 4, where the reference values RV_A are derived from data of $\Delta Hf°g$, Tc/Pc, and BP/Tc, whereas the BI_A indices are derived from a set of 11 topological indices tested earlier,[3] is presented in Fig.1 for the topological index Sch-TF and the physicochemical property Tc/Pc, as well as in Table 1 for all the tested topological indices and physicochemical properties. According to Table 1, the best BI_A index compared to the RV_A value derived from $\Delta Hf°g$ is that derived from the topological index Z. In the case of Tc/Pc as the reference property it is that derived from the topological index MTI and in the case of BP/Tc it is that derived from $\lambda\lambda_1$.

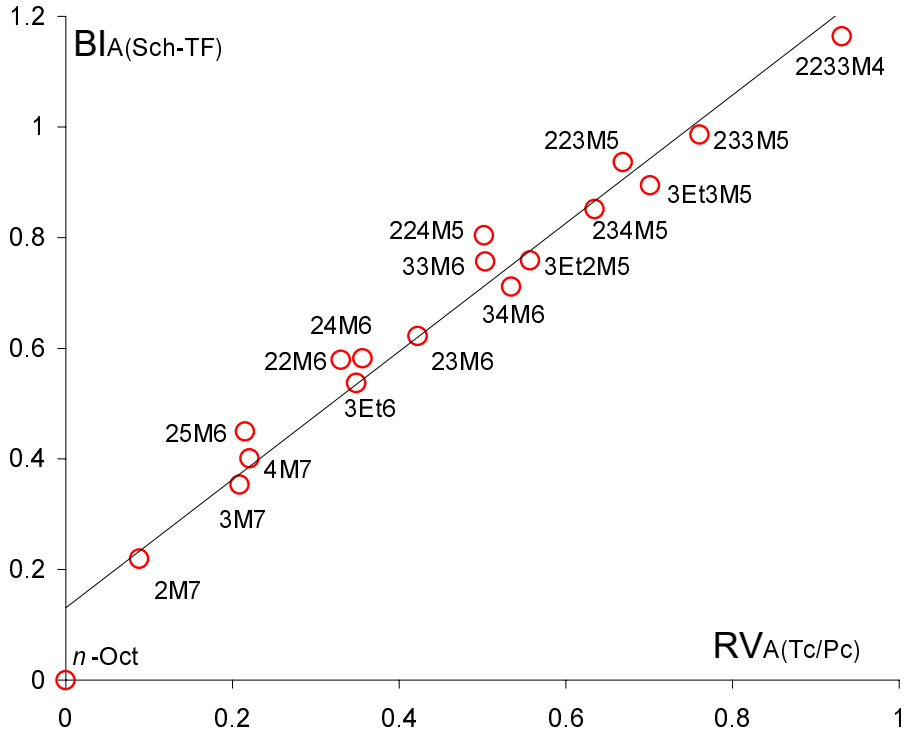

Fig. 1. Correlation between the BI_A index derived from the topological index Sch-TF and the RV_A reference value derived from the physicochemical property Tc/Pc.

Table 1. Correlation coefficient (r) of the linear regression of BI_A and RV_A data of octanes.

RV_A from ΔHf°g		RV_A from Tc/Pc		RV_A from BP/Tc	
BI_A from	r	BI_A from	r	BI_A from	r
Z	0.8958	MTI	0.9841	$\lambda\lambda_1$	0.9851
χ	0.8486	Sch-TF	0.9832	λ_1	0.9744
ID	0.7425	W	0.9829	Xu	0.9722
Sch-S	0.6654	D	0.9809	D	0.9692
$\lambda\lambda_1$	0.5773	Xu	0.9804	Sch-TF	0.9689
λ_1	0.5708	$\lambda\lambda_1$	0.9738	W	0.9685
D	0.5267	λ_1	0.9586	MTI	0.9612
Xu	0.5193	Sch-S	0.9370	Sch-S	0.9582
Sch-TF	0.5061	ID	0.8886	ID	0.9200
W	0.5059	χ	0.7572	χ	0.8187
MTI	0.4666	Z	0.6832	Z	0.7435

Table 2. The *n-Alkane based* definition obeying reference values for branching indices, RV_A, as well as branching indices, BI_A, derived by Eq. 4 from data of physicochemical properties ΔHf°g, Tc/Pc, and BP/Tc, as well as from data of topological indices χ, Sch-TF, and $\lambda\lambda_1$, respectively.

Octane	$RV_{A(\Delta Hf°g)}$	$RV_{A(Tc/Pc)}$	$RV_{A(BP/Tc)}$	$BI_{A(\chi)}$	$BI_{A(Sch\text{-}TF)}$	$BI_{A(\lambda\lambda 1)}$
n-Oct	0	0	0	0	0	0
2M7	0.2361	0.0882	0.0279	0.2577	0.2193	0.0751
3M7	0.1405	0.2084	0.0551	0.1897	0.3532	0.1092
4M7	0.1222	0.2206	0.0529	0.0610	0.4005	0.1192
3Et6	0.0787	0.3487	0.0844	0.1218	0.5370	0.1538
22M6	0.5466	0.3301	0.1002	0.6322	0.5791	0.2131
23M6	0.1841	0.4226	0.1117	0.4176	0.6224	0.2074
24M6	0.3681	0.3562	0.0990	0.4476	0.5817	0.1905
25M6	0.4763	0.2150	0.0615	0.5156	0.4491	0.1527
33M6	0.3920	0.5032	0.1583	0.5238	0.7563	0.2684
34M6	0.1532	0.5343	0.1394	0.3496	0.7117	0.2354
3Et2M5	0.0927	0.5571	0.1547	0.3496	0.7590	0.2459
3Et3M5	0.2192	0.7011	0.2222	0.4153	0.8942	0.3142
223M5	0.3920	0.6684	0.2140	0.7740	0.9362	0.3507
224M5	0.5269	0.5019	0.1648	0.8901	0.8036	0.2988
233M5	0.2684	0.7606	0.2474	0.7336	0.9861	0.3682
234M5	0.3021	0.6347	0.1849	0.6452	0.8509	0.2999
2233M4	0.5859	0.9313	0.3261	1.1878	1.1634	0.4741

Table 2 presents for octanes the RV_A values derived from data of ΔHf°g, Tc/Pc, and BP/Tc, as well as the BI_A indices derived from data of topological indices χ, Sch-TF, and $\lambda\lambda_1$ as examples. The indices χ and Sch-TF were the second best ones in Table 1. They are used in Table 2 instead of indices Z and MTI because the latter ones cannot be considered good indices for other reasons[3].

Comparing in Table 2 the BI_A to RV_A we can see that the presented "best" BI_A indices are more susceptible to branching than the reference values to them they correlate the best. An exception is $BI_{A(\chi)}$ compared to $RV_{A(\Delta Hf°g)}$ at 4-methyl heptane.

References

1. A. Perdih, M. Perdih, *Acta Chim. Slov*. **2000**, *47*, 231-259.
2. A. Perdih, *Acta Chim. Slov*. **2000**, *47*, 293-316.
3. A. Perdih, *Acta Chim. Slov*. **2000**, *47*, 435-452.
4. H. Wiener, *J. Am. Chem. Soc*. **1947**, *69*, 17-20.
5. H. Hosoya, *Bull. Chem. Soc. Japan* **1971**, *44*, 2332-2339.
6. M. Randić, *J. Am. Chem. Soc*. **1975**, *97*, 6609-6615.
7. L. Lovasz, J. Pelikan, *Period. Math. Hung*. **1973**, *3*, 175-182.
8. Y.-Q. Yang, L. Xu, C.-Y. Hu, *J. Chem. Inf. Comput. Sci*. **1994**, *34*, 1140-1145.
9. M. Randić, *J. Chem. Inf. Comput. Sci*. **1984**, *24*, 164-175.
10. Z. Mihalić, S. Nikolić, N. Trinajstić, *J. Chem. Inf. Comput. Sci*. **1992**, *32*, 28-37.
11. B. Ren, *J. Chem. Inf. Comput. Sci*. **1999**, *39*, 139-143.
12. H.P. Schultz, T.P. Schultz, *J. Chem. Inf. Comput. Sci*. **2000**, *40*, 107-112.
13. M. Randić, *Acta Chim. Slov*. **1997**, *44*, 57-77.
14. D.R. Lide, CRC Handbook of Chemistry and Physics, 76th Ed., CRC Press, Boca Raton 1995-96.

Povzetek

Indekse razvejanosti (BI_M) oziroma referenčne vrednosti zanje (RV_M), ki sledijo metanski definiciji razvejanosti, kakor tudi indekse razvejanosti (BI_A) oziroma referenčne vrednosti zanje (RV_A) po *n*-alkanski definiciji razvejanosti lahko izvedemo iz topoloških indeksov oz. fizikokemijskih lastnosti s pomočjo občutljivosti za razvejanje, $S_{i,j}$.