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STRUCTURE AND PROPERTIES OF ORGANIC MOLECULES. 2. GRAPH-THEORETICAL STUDY OF ALKENES AND ALCOHOLS

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Topological indices for describing organic compounds with multiple bonds and heteroatoms are treated. The Schultz indices (including modified ones) and the connectivity indices of various types are calculated for saturated alkenes and alcohols. The discriminating ability of the indices and their applicability for structure–property correlations are examined. Various functions approximating the property–index correlations are tested using regression analysis. The Schultz and connectivity indices possess nearly the same correlation ability, as shown by reference to formation enthalpy, molar volume, evaporation heat, and boiling temperature. They may be effectively used for calculating and predicting the physicochemical properties of the title compounds.

The graph-theoretical approach to structure–property correlation analysis was chiefly tested on alkanes as key compounds [1-8]. For other classes of chemical structures it was developed to a lesser extent. Of all known topological indices (TI) only several indices (mainly the connectivity indices [1, 2, 9-13]) were used for calculating the physicochemical properties of compounds with multiple bonds, heteroatoms, and rings. The possibilities of other TI in respect of these compounds are poorly defined.

It seems worthwhile to examine the molecular topological index (MTI) recently proposed by Schultz [14] and elaborated in a series of publications [15-20]. The index is attractive in having a structural sense (it reflects molecular topology as well as the valence states of atoms). It is easily calculated and may be extended to various classes of organic compounds. Here we discuss the correlations of MTI, its modifications MTI′, and connectivity indices χ (see below) with physicochemical properties of alkenes and alcohols.

The indices are calculated according to the following formulas:

$$\mathrm{MTI} = V(A + D), \tag{1}$$

$$\mathrm{MTI}' = VD, \tag{2}$$

$$^1\chi^v = \sum (\delta_i \delta_j)^{-1/2}, \tag{3}$$

$$^2\chi^v = \sum (\delta_i \delta_j \delta_k)^{-1/2}, \tag{4}$$

$$^3\chi^v = \sum (\delta_i \delta_j \delta_k \delta_m)^{-1/2}, \tag{5}$$

$$\delta_i = Z_i - h_i, \tag{6}$$

where D is a matrix of distances of a molecular graph (MG), A is a connectivity matrix of an MG, V is a valence matrix consisting of elements δ_i, Z_i is the number of valence electrons of the ith atom, and h_i is the number of hydrogen atoms at the ith atom.

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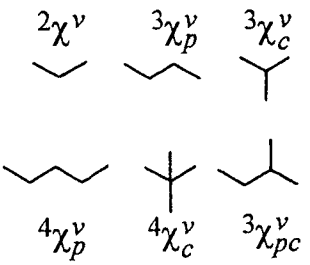

Fig. 1. Connectivity indices for various structural fragments of a molecule.

The connectivity indices were calculated for different structural fragments of the molecule: $^2\chi^v$, $^3\chi_p^v$, $^3\chi_c^v$, $^4\chi_p^v$, $^4\chi_c^v$, $^4\chi_{pc}^v$ (Fig. 1).

Tables 1 and 2 list the indices for alkenes and alcohols. The MTI and MTI′ indices have a moderate discriminating ability. In this series of compounds, MTI fails to discriminate two pairs of alcohols with the number of carbon atoms $n_C = 5$ and a pair and triplet with $n_C = 6$; MTI′ does not discriminate two pairs of alcohols with $n_C = 5$, two pairs and a triplet with $n_C = 6$, and a pair of alkenes with $n_C = 6$. A pair and a triplet of alcohols with $n_C = 6$ are not discriminated by the connectivity indices $^1\chi^v$, and a pair of alcohols with $n_C = 6$ is not discriminated by $^2\chi^v$.

TABLE 1. Topological Indices of Alkenes

No.	Compound	MTI	MTI′	$^1\chi^v$	$^2\chi^v$	$^3\chi_p^v$	$^3\chi_c^v$
1	Ethylene	12	8	0.500	0.000	0.000	0.000
2	Propylene	32	23	0.985	0.408	0.000	0.000
3	1-Butene	63	50	1.523	0.697	0.289	0.000
4	2-Butene	66	52	1.487	0.666	0.333	0.000
5	2-Methylpropene	60	44	1.854	1.208	0.000	0.354
6	1-Pentene	110	93	2.023	1.076	0.493	0.000
7	2-Pentene	115	97	2.025	0.977	0.472	0.000
8	2-Methyl-1-butene	101	81	1.915	1.312	0.604	0.250
9	3-Methyl-1-butene	102	83	1.895	1.479	0.472	0.333
10	2-Methyl-2-butene	108	87	1.866	1.367	0.578	0.289
11	1-Hexene	177	156	2.523	1.432	0.762	0.000
12	2-Hexene	184	162	2.525	1.358	0.692	0.000
13	3-Hexene	186	164	2.563	1.288	0.639	0.000
14	2-Methyl-1-pentene	162	138	2.415	1.915	0.677	0.250
15	3-Methyl-1-pentene	159	136	2.433	1.621	1.047	0.236
16	4-Methyl-1-pentene	165	142	2.378	1.918	0.639	0.408
17	2-Methyl-2-pentene	175	152	2.404	1.690	0.612	0.289
18	3-Methyl-2-pentene	167	142	2.427	1.490	1.051	0.204
19	4-Methyl-2-pentene	172	148	2.397	1.769	0.577	0.333
20	2,3-Dimethyl-1-butene	150	124	2.297	1.713	0.986	0.493
21	3,3-Dimethyl-1-butene	149	122	2.197	2.571	0.612	1.367
22	2,3-Dimethyl-2-butene	164	136	2.250	2.000	1.000	0.500
23	1-Heptene	268	243	3.023	1.786	1.012	0.000
24	1-Octene	381	352	3.523	2.140	1.262	0.000
25	1-Nonene	538	505	4.023	2.494	1.512	0.000
26	1-Decene	725	688	4.523	2.848	1.762	0.438

TABLE 2. Topological Indices of Alcohols

No.	Compound	MTI	MTI′	$^1\chi$	$^1\chi^v$	$^2\chi^v$	$^3\chi_p^v$	$^3\chi_c^v$	$^4\chi_p^v$	$^4\chi_c^v$	$^4\chi_{pc}^v$
1	Methanol	12	6	1.000	0.447	0.000	0.000	0.000	0.000	0.000	0.000
2	Ethanol	32	22	1.414	1.023	0.316	0.000	0.000	0.000	0.000	0.000
3	1-Propanol	66	52	1.914	1.523	0.724	0.224	0.000	0.000	0.000	0.000
4	2-Propanol	60	44	1.732	1.413	1.093	0.000	0.258	0.000	0.000	0.000
5	1-Butanol	118	100	2.414	2.023	1.077	0.511	0.000	0.158	0.000	0.000
6	2-Butanol	104	84	2.270	1.951	1.256	0.590	0.182	0.000	0.000	0.182
7	2-Methyl-1-propanol	108	88	2.270	1.879	1.575	0.182	0.408	0.000	0.000	0.182
8	2-Methyl-2-propanol	96	72	2.000	1.724	1.948	0.000	1.172	0.000	0.224	0.000
9	1-Pentanol	192	170	2.914	2.523	1.432	0.762	0.000	0.362	0.000	0.000
10	2-Pentanol	170	146	2.770	2.451	1.637	0.707	0.182	0.418	0.000	0.129
11	3-Pentanol	162	138	2.808	2.489	1.469	0.942	0.129	0.289	0.000	0.129
12	2-Methyl-1-butanol	170	146	2.808	2.417	1.695	1.008	0.289	0.129	0.000	0.289
13	3-Methyl-1-butanol	178	154	2.770	2.379	1.906	0.707	0.408	0.258	0.000	0.289
14	2-Methyl-2-butanol	150	122	2.561	2.284	2.168	0.866	0.894	0.000	0.158	0.512
15	3-Methyl-2-butanol	156	130	2.643	2.324	1.983	0.964	0.482	0.000	0.000	0.482
16	2,2-Dimethyl-1-propanol	158	130	2.561	2.170	2.720	0.474	1.562	0.000	0.354	0.316
17	1-Hexanol	292	266	3.414	3.023	1.786	1.012	0.000	0.539	0.000	0.000
18	2-Hexanol	262	234	3.270	2.951	1.991	0.976	0.182	0.499	0.000	0.129
19	3-Hexanol	246	218	3.308	2.989	1.850	1.093	0.129	0.537	0.000	0.258
20	2-Methyl-1-pentanol	288	260	3.308	2.917	2.076	0.911	0.289	0.622	0.000	0.333
21	3-Methyl-1-pentanol	260	232	3.308	2.917	2.076	1.319	0.289	0.333	0.000	0.493
22	4-Methyl-1-pentanol	274	246	2.270	2.879	1.683	0.940	0.408	0.499	0.000	0.289
23	2-Methyl-2-pentanol	230	198	3.061	2.784	2.564	0.862	0.512	0.612	0.158	0.362
24	3-Methyl-2-pentanol	232	202	3.181	2.862	1.717	1.467	0.385	0.341	0.000	0.577
25	4-Methyl-2-pentanol	244	214	3.126	2.807	2.477	0.820	0.590	0.577	0.000	0.341
26	2-Methyl-3-pentanol	228	198	3.181	2.862	2.218	1.188	0.438	0.472	0.000	0.446
27	3-Methyl-3-pentanol	218	186	3.121	2.845	2.206	1.544	0.678	0.250	0.112	0.362
28	2-Ethyl-1-butanol	246	218	3.346	2.955	1.865	1.414	0.204	0.547	0.000	0.499
29	2,2-Dimethyl-1-butanol	230	198	2.121	2.730	2.678	1.386	1.208	0.112	0.250	0.724
30	2,3-Dimethyl-1-butanol	240	210	3.181	2.790	2.402	1.425	0.569	0.105	0.000	0.577
31	3,3-Dimethyl-1-butanol	246	214	3.061	2.670	3.036	0.862	1.562	0.336	0.354	0.500
32	2,3-Dimethyl-2-butanol	212	178	2.943	2.667	2.810	0.996	1.060	0.000	0.129	0.707
33	3,3-Dimethyl-2-butanol	214	180	2.943	2.624	3.043	1.254	1.496	0.000	0.289	0.707
34	1-Heptanol	422	392	3.914	3.523	2.138	1.262	0.000	0.716	0.000	0.000
35	1-Octanol	586	552	4.414	4.023	2.492	1.512	0.000	0.891	0.000	0.000
36	1-Nonanol	788	750	4.914	4.523	2.845	1.762	0.000	1.067	0.000	0.000
37	1-Decanol	1032	990	5.414	5.023	3.199	2.012	0.000	1.243	0.000	0.000

The correlation ability of TI was investigated by reference to the formation enthalpy $\Delta_f H^0$ (g, 298 K), molar volume V_M, evaporation heat at normal boiling temperature λ_{nbt}, and normal boiling temperature t_b of alkenes and alcohols. For constructing correlation dependences we used the experimental data of [21, 22]. For approximating functions we tested the following dependences:

$$F(x) = ax + b, \quad (7)$$
$$F(x) = ax^2 + bx + c, \quad (8)$$
$$F(x) = a \exp(bx), \quad (9)$$
$$F(x) = a \ln(x) + b, \quad (10)$$
$$F(x) = ax^b, \quad (11)$$
$$F(x) = ax_1 + bx_2 + cx_3 + \ldots + nx_n + d. \quad (12)$$

Tables 3 and 4 give the correlation coefficients r and standard deviations s, indicating the form of the optimal function (with maximal r) for the given property–index correlations. Regression equations corresponding to the best correlation are given below.

I. Alkenes:

$$-\Delta_f H^0 \text{ (g, 298 K)} = -12.41{}^1\chi^v - 30.81{}^2\chi^v - 16.37{}^3\chi_p^v + 5.56{}^3\chi_c^v + 41.58 \ (r = 0.9785),$$

$$V_M = 21.20{}^1\chi^v + 14.64{}^2\chi^v + 6.12{}^3\chi_p^v - 4.19{}^3\chi_c^v + 44.05 \ (r = 0.9940),$$

$$\lambda_{nbt} = 7.615(\text{MTI})^{0.256} \ (r = 0.9947),$$

$$t_b = 67.143 \ln(\text{MTI}) - 280.95 \ (r = 0.9936).$$

II. Alcohols:

$$-\Delta_f H^0 \text{ (g, 298 K)} = -59.51{}^1\chi + 75.80{}^1\chi^v + 43.12{}^2\chi^v + 227.04 \ (r = 0.9996),$$

$$V_M = -5.32{}^1\chi + 32.32{}^1\chi^v + 8.15{}^2\chi^v + 30.61 \ (r = 0.9996),$$

$$\lambda_{nbt} = -0.0003(\text{MTI}')^2 + 0.181\text{MTI}' + 33.133 \ (r = 0.8959),$$

$$t_b = -0.0002(\text{MTI}')^2 + 0.346\text{MTI}' + 72.445 \ (r = 0.9749).$$

TABLE 3. Correlations between the Physicochemical Properties and the Topological Indices of Alkenes

Index	$\Delta_f H^0$ (g, 298 K), kJ/mole			λ_{nbt}, kJ/mole		
	Function	r	s	Function	r	s
MTI	(10)	0.9698	8.94	(11)	0.9947	0.743
MTI'	(10)	0.9649	9.63	(11)	0.9945	0.757
${}^1\chi^v$	(8)	0.9578	10.53	(8)	0.9801	1.439
${}^1\chi^v, {}^2\chi^v$	(12)	0.9751	8.31	(12)	0.9856	1.276
${}^1\chi^v, {}^2\chi^v, {}^3\chi_p^v$	(12)	0.9784	7.92	(12)	0.9870	1.259
${}^1\chi^v, {}^2\chi^v, {}^3\chi_p^v, {}^3\chi_c^v$	(12)	0.9785	8.07	(12)	0.9876	1.298
	t_b, °C			V_M, ml/mole		
MTI	(10)	0.9936	6.39	(11)	0.9900	4.11
MTI'	(1)	0.9926	6.86	(11)	0.9894	4.23
${}^1\chi^v$	(8)	0.9854	9.64	(8)	0.9871	4.66
${}^1\chi^v, {}^2\chi^v$	(12)	0.9728	13.39	(12)	0.9931	3.47
${}^1\chi^v, {}^2\chi^v, {}^3\chi_p^v$	(12)	0.9759	12.90	(12)	0.9939	3.35
${}^1\chi^v, {}^2\chi^v, {}^3\chi_p^v, {}^3\chi_c^v$	(12)	0.9793	12.25	(12)	0.9940	3.39

TABLE 4. Correlations between the Physicochemical Properties and the Topological Indices of Alcohols

Index	$\Delta_f H^0$ (g, 298 K), kJ/mole			λ_{nbt}, kJ/mole		
	Function	r	s	Function	r	s
MTI	(11)	0.9441	17.09	(8)	0.8745	4.73
MTI′	(11)	0.9393	17.79	(8)	0.8959	4.33
$^1\chi^v$	(11)	0.9381	17.96	(8)	0.8294	5.44
$^1\chi$, $^1\chi^v$	(12)	0.9753	12.36	(12)	0.8420	5.67
$1/^1\chi$, $^1\chi^v$	(12)	0.9328	20.18	(12)	0.8280	5.90
$^1\chi$, $^1\chi^v$, $^2\chi^v$	(12)	0.9996	1.62	(12)	0.8540	5.99
	t_b, °C			V_M, ml/mole		
MTI	(8)	0.9664	8.98	(11)	0.9894	4.29
MTI′	(8)	0.9749	7.79	(11)	0.9892	4.32
$^1\chi^v$	(8)	0.9637	9.33	(2)	0.9918	3.77
$^1\chi$, $^1\chi^v$	(12)	0.9570	10.19	(12)	0.9931	3.95
$1/^1\chi$, $^1\chi^v$	(12)	0.9640	9.40	(12)	0.9916	3.88
$^1\chi$, $^1\chi^v$, $^2\chi^v$	(12)	0.9661	9.29	(12)	0.9991	1.27

TABLE 5. Correlations between the Molecular Connectivity Indices and the Boiling Temperatures of Alcohols

Index	t_b, °C	
	r	s
$^1\chi^v$	0.9571	10.13
$^1\chi$, $^1\chi^v$	0.9571	10.19
$^1\chi$, $^1\chi^v$, $^2\chi^v$	0.9661	9.29
$^1\chi$, $^1\chi^v$, $^2\chi^v$, $^3\chi_p^v$	0.9666	9.37
$^1\chi$, $^1\chi^v$, $^2\chi^v$, $^3\chi_p^v$, $^3\chi_c^v$	0.9671	9.42
$^1\chi$, $^1\chi^v$, $^2\chi^v$, $^3\chi_p^v$, $^3\chi_c^v$, $^4\chi_p^v$	0.9677	9.52
$^1\chi$, $^1\chi^v$, $^2\chi^v$, $^3\chi_p^v$, $^3\chi_c^v$, $^4\chi_p^v$, $^4\chi_c^v$	0.9677	9.67
$^1\chi$, $^1\chi^v$, $^2\chi^v$, $^3\chi_p^v$, $^3\chi_c^v$, $^4\chi_p^v$, $^4\chi_c^v$, $^4\chi_{pc}^v$	0.9677	9.85
$(1/^1\chi)$, $^1\chi^v$	0.964	9.40
$(1/^1\chi)$, $^1\chi^v$, $^2\chi^v$	0.968	9.03

Figure 2 shows an exponential function approximating the dependence of the molar volume of alcohols on the MTI index.

It follows from Table 5 that as the number of parameters in the regression increases, the quality of correlation for the connectivity indices is improved.

The MTI and MTI′ indices give correlations that are comparable in quality to the connectivity indices. In some cases (Tables 3 and 4), the correlation equations with MTI and MTI′ possess even better statistical characteristics and are applicable to calculations and predictions of physicochemical properties for alkenes and alcohols.

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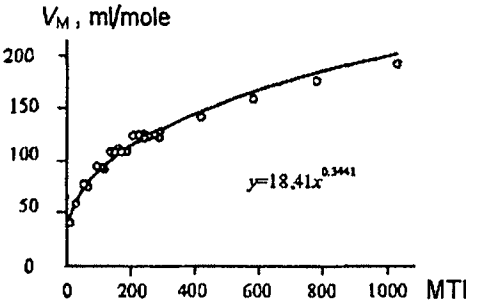

Fig. 2. Approximation of the dependence of the molar volume of alcohols on the MTI index by an exponential function.

REFERENCES

1. D. Jain, S. Sukhbir, and V. Gombar, *Proc. Ind. Acad. Sci. (Chem. Sci.)*, **93**, 927-945 (1984).
2. P. G. Seybold, M. May, and U. A. Bagal, *J. Chem. Educ.*, **64**, 575-581 (1987).
3. P. J. Hansen and P. C. Jurs, *ibid.*, **65**, 574-580 (1988).
4. Z. Mihalic and N. Trinajstic, *ibid.*, **69**, 701-702 (1992).
5. Z. Mihalic, S. Nikolic, and N. Trinajstic, *J. Chem. Inf. Comput. Sci.*, **32**, 28-37 (1992).
6. Yu. G. Papulov, T. I. Chernova, V. M. Smolyakov, and M. N. Polyakov, *Zh. Fiz. Khim.*, **67**, 203-209 (1993).
7. M. G. Vinogradova, Yu. G. Papulov, V. M. Smolyakov, and M. N. Saltykova, *ibid.*, **70**, 680-775 (1996).
8. Yu. G. Papulov and V. M. Smolyakov, *Mathematical Methods in Contemporary Chemistry*, Gordon and Breach, New York (1996), pp. 143-180.
9. W. J. Murray, L. H. Hall, and L. B. Kier, *J. Pharm. Sci.*, **64**, 1978-1981 (1975).
10. L. B. Kier and L. H. Hall, *ibid.*, **65**, 1806-1809 (1976).
11. L. B. Kier and L. H. Hall, *ibid.*, **70**, 583-589 (1981).
12. L. B. Kier and L. H. Hall, *Molecular Connectivity in Chemistry and Drug Research*, Academic Press, New York (1976).
13. L. B. Kier and L. H. Hall, *Molecular Connectivity in Structure–Property Analysis*, Wiley, New York (1986).
14. H. P. Schultz, *J. Chem. Inf. Comput. Sci.*, **29**, 227-228 (1989).
15. H. P. Schultz, E. B. Schultz, and T. P. Schultz, *ibid.*, **30**, 27-29 (1990).
16. H. P. Schultz and T. P. Schultz, *ibid.*, **31**, 144-147 (1991).
17. H. P. Schultz, E. B. Schultz, and T. P. Schultz, *ibid.*, **32**, 69-72 (1992).
18. H. P. Schultz and T. P. Schultz, *ibid.*, 364-368.
19. H. P. Schultz and T. P. Schultz, *ibid.*, **33**, 240-244 (1993).
20. H. P. Schultz, E. B. Schultz, and T. P. Schultz, *ibid.*, 863-867.
21. *Chemist's Guide* [in Russian], Vols. 1, 2, Khimiya, Leningrad (1971).
22. V. M. Tatevskii (ed.), *Physicochemical Properties of Individual Hydrocarbons* [in Russian], Gostoptekhizdat, Moscow (1960).