Real-Number Vertex Invariants and Schultz-Type Indices Based on Eigenvectors of Adjacency and Distance Matrices

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Eigenvectors corresponding to the lowest eigenvalue of adjacency and distance matrices are used to generate new real-number local vertex invariants (LOVIs), by applying a Schultz-type algorithm. The intramolecular ordering of vertices was tested. From these LOVIs, several new topological indices have been defined and tested on the basis of intermolecular ordering of isomeric alkanes. Correlation with properties such as the normal boiling temperature and octane numbers have also been studied.

1. INTRODUCTION

The essential assumption for quantitative structure−properties relationship (QSPR) studies is that the properties (physical, chemical, or biological) depend on the structure of compounds. The characterization of structures is one of the main problems in chemistry and mathematics. Usually, the experimentally determined properties are already quantified. Thus, if we have an appropriate method for quantifying the structure, we can easily compare the two numbers. One of the simplest methods for doing this is the topological one, based on graph theory.[1−5] The molecules are depicted as hydrogen-depleted graphs with non-hydrogen atoms as vertices and covalent bonds as edges. If there is no cycle in the molecule, one calls this graph a tree (a 4-tree for alkanes). Each vertex has an associated number that can be obtained by different methods. These numbers are called LOcal Vertex Invariants (LOVIs) because they are independent of any arbitrary vertex labeling. By applying various algorithms to these LOVIs, one can obtain numbers that characterize the topological structure of a molecule (topological indices (TIs), global or molecular invariants).

According to a recent classification,[5] three generations of TIs are defined. The first-generation TIs represent integer numbers obtained by simple mathematical operations from integer LOVIs (for instance the sum of all LOVIs, the sum of all squared LOVIs, etc.). Second-generation TIs are real numbers obtained from integer LOVIs (for example: $^1\chi$-Randic index,[6] $^m\chi$-extended connectivity indices defined by Kier and Hall,[7] or the *J*-index[8,9]). Third-generation TIs are real numbers obtained from LOVIs that are also real numbers (examples are TIs based on information on distances,[10,11] solutions of linear equations systems,[12] and eigenvalues or eigenvectors of matrices associated with chemical graphs[13]).

The aim of any method for developing TIs is to obtain TIs with good correlation ability and with low degeneracy.

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The degeneracy is the property of TIs in which different structures have the same value.

In search of new efficient topological indices, Schultz proposed[14] an algorithm to compute new local vertex invariants

$$m_i = [\mathbf{v} \times (\mathbf{A} + \mathbf{D})]_i \qquad (1)$$

and a new TI called MTI (molecular topological index), based on both matrices $\mathbf{A}$ and $\mathbf{D}$:

$$\text{MTI} = \sum_i m_i \qquad (2)$$

$\mathbf{v}$ being the vertex degree vector and $\mathbf{A}$ and $\mathbf{D}$ the adjacency and distance matrices, respectively.[15−18] On the basis of the sum matrix $(\mathbf{A} + \mathbf{D})$, other topological indices were defined: the determinant of the previous matrix, the greatest eigenvalue,[15] etc.

For trees, the index MTI can be computed according to Klein et al.'s[19] formula:

$$\text{MTI} = 4W + 2P_2 - (n - 1)(n - 2) \qquad (3)$$

where W is the Wiener index,[20] P_2 the number of paths of length 2, and n the number of vertices.

The Wiener index and P_2 are molecular invariants with high degeneracy; therefore one can expect the same degeneracy for MTI. This statement is confirmed by the two pairs of octanes with the same MTI value: 2,2,4-trimethylpentane and 3-ethyl-2-methylpentane (which have MTI = 242) and 2,2-dimethylhexane and 3-ethylhexane (with MTI = 260). For nonanes the number of degenerate pairs increases, and one can also observe intramolecular degeneracy of LOVIs as depicted in Figure 1, where a pair of LOVIs in each case (boldface) is equal for nonequivalent vertices.

For decanes there are three isomers with the same MTI index, together with a few degenerate pairs, and for undec-

Table 1. Local Vertex Invariants (**V**i, i = 1, 2, ..., 6) for Heptane Isomers

alkane	**V**i	for given current atom						
		1	2	3	4	5	6	7
C7	**V1**	7.8946	6.0633	4.8397	4.4100	4.8397	6.0633	7.8946
	V2	8.1807	6.9309	5.8884	5.5543	5.8884	6.9309	8.1807
	V3	0.3536	0.6533	0.8536	0.9239	0.8536	0.6533	0.3536
	V4	0.3697	0.7839	0.6660	0.6282	0.6660	0.7839	0.3697
	V5	7.5410	5.4100	3.9861	3.4861	3.9861	5.4100	7.5410
	V6	7.8109	6.1469	5.2224	4.9261	5.2224	6.1469	7.8109
2M−C6	**V1**	5.8193	4.4349	4.1122	4.7236	6.0978	8.0113	5.8193
	V2	6.8407	5.9128	5.1044	5.4377	6.4769	7.7113	6.8407
	V3	0.5577	1.0774	0.9659	0.7887	0.5577	0.2887	0.5577
	V4	0.3099	1.1390	0.6200	0.6605	0.7867	0.3694	0.3099
	V5	5.2616	3.3576	3.1463	3.9349	5.5401	7.7226	5.2616
	V6	6.5309	4.7738	4.4844	4.7772	5.6902	7.3420	6.5309
3M−C6	**V1**	6.3883	4.7403	3.8844	4.1956	5.4075	7.2355	5.1580
	V2	7.1219	5.8218	5.1240	5.0623	6.1316	7.3789	6.1698
	V3	0.4082	0.8041	1.1755	0.9144	0.6255	0.3176	0.5968
	V4	0.3425	0.7311	1.0369	0.6357	0.7700	0.3607	0.2750
	V5	5.9800	3.9362	2.7089	3.2812	4.7820	6.9179	4.5612
	V6	6.7794	5.0908	4.0871	4.4266	5.3616	7.0182	5.8948
3E−C5	**V1**	6.1237	4.4907	3.6742	4.4907	6.1237	4.4907	6.1237
	V2	6.7548	5.4327	4.6792	5.4327	6.7548	5.4327	6.7548
	V3	0.4082	0.8165	1.2247	0.8165	0.4082	0.8165	0.4082
	V4	0.3305	0.7073	0.9916	0.7073	0.3305	0.7073	0.3305
	V5	5.7155	3.6742	2.4495	3.6742	5.7155	3.6742	5.7155
	V6	6.4243	4.7254	3.6876	4.7254	6.4243	4.7254	6.4243
22MM−C5	**V1**	4.7568	3.6727	3.9710	5.2421	7.1118	4.7568	4.7568
	V2	5.7288	5.1520	4.6219	5.6882	6.9170	5.7288	5.7288
	V3	0.6533	1.3725	0.9239	0.5685	0.2706	0.6533	0.6533
	V4	0.2683	1.4943	0.6287	0.7737	0.3604	0.2683	0.2683
	V5	4.1035	2.3001	3.0471	4.6735	6.8412	4.1035	4.1035
	V6	5.4606	3.6577	3.9932	4.9145	6.5566	5.4606	5.4606
33MM−C5	**V1**	5.8692	4.2560	3.5453	4.2560	5.8692	4.6134	4.6134
	V2	6.3081	5.0014	4.7013	5.0014	6.3081	5.3375	5.3375
	V3	0.3941	0.8417	1.4036	0.8417	0.3941	0.6572	0.6572
	V4	0.3285	0.7074	1.4356	0.7074	0.3285	0.2499	0.2499
	V5	5.4751	3.4143	2.1417	3.4143	5.4751	3.9562	3.9562
	V6	5.9795	4.2941	3.2657	4.2941	5.9795	5.0876	5.0876
24MM−C5	**V1**	6.0000	4.5000	4.0000	4.5000	6.0000	6.0000	6.0000
	V2	6.3744	5.4603	4.6441	5.4603	6.3744	6.3744	6.3744
	V3	0.5000	1.0000	1.0000	1.0000	0.5000	0.5000	0.5000
	V4	0.3047	1.1410	0.6094	1.1410	0.3047	0.3047	0.3047
	V5	5.5000	3.5000	3.0000	3.5000	5.5000	5.5000	5.5000
	V6	6.0697	4.3194	4.0347	4.3194	6.0697	6.0697	6.0697
23MM−C5	**V1**	5.4066	4.0302	3.7668	4.7040	6.4175	5.4066	5.0581
	V2	6.0292	5.0851	4.6714	5.3668	6.6534	6.0292	5.7114
	V3	0.5344	1.0971	1.1834	0.7558	0.3682	0.5344	0.5765
	V4	0.2916	1.1086	1.0310	0.7300	0.3401	0.2916	0.2670
	V5	4.8722	2.9330	2.5834	3.9482	6.0494	4.8722	4.4816
	V6	5.7375	3.9765	3.6403	4.6368	6.3134	5.7375	5.4444
223MMM−C4	**V1**	4.7897	3.6515	3.9074	5.3137	4.7897	4.7897	5.3137
	V2	5.2591	4.6966	4.6432	5.5706	5.2591	5.2591	5.5706
	V3	0.6280	1.3660	1.0877	0.5000	0.6280	0.6280	0.5000
	V4	0.2583	1.4954	1.1112	0.2850	0.2583	0.2583	0.2850
	V5	4.1618	2.2854	2.8197	4.8137	4.1618	4.1618	4.8137
	V6	5.0008	3.2012	3.5320	5.2857	5.0008	5.0008	5.2857
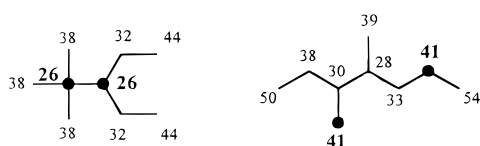
Figure 1. Intramolecular degeneracy of Schultz LOVIs for two nonanes.

anes the degeneracy is a frequent phenomenon, having four and five isomers with the same MTI index.

Because MTI is an integer number obtained from integer LOVIs, it can be classified as an index of the first generation. In this paper, we propose six new vertex invariants and twelve new third-generation topological indices derived from them, based on eigenvectors of the adjacency and distance matrices.

2. NEW LOCAL VERTEX INVARIANTS

From the adjacency (**A**) and distance matrices (**D**) of C2− C9 alkanes all eigenvectors were calculated.[13] In both cases, only the first eigenvector (corresponding to the lowest eigenvalue and having for all elements the same sign) is used further. **VA** and **VD** denote the first eigenvectors of **A** and **D** matrices, respectively. The new LOVIs are elements of the **V**i vectors (i = 1, 2, ..., 6) defined as follows:

Table 2. Local Vertex Invariants (**Vi**, **i** = 1, 2, ..., 6) for Octane Isomers

alkane	Vi	for given current atom							
		1	2	3	4	5	6	7	8
C8	V1	9.6602	7.5756	6.0284	5.2052	5.2052	6.0284	7.5756	9.6601
	V2	10.0979	8.5998	7.3159	6.7020	6.7020	7.3159	8.5998	10.0979
	V3	0.3030	0.5695	0.7673	0.8725	0.8725	0.7673	0.5695	0.3030
	V4	0.3594	0.7517	0.6395	0.5858	0.5858	0.6395	0.7517	0.3594
	V5	9.3571	7.0061	5.2611	4.3327	4.3327	5.2611	7.0061	9.3571
	V6	9.7385	7.8481	6.6764	6.1162	6.1162	6.6764	7.8481	9.7385
2M−C7	V1	7.0000	5.3902	4.7852	5.0962	6.2022	7.9421	10.1232	7.0000
	V2	8.5463	7.3435	6.2801	6.2718	6.8759	8.1516	9.6345	8.5463
	V3	0.5211	1.0161	0.9390	0.8149	0.6498	0.4522	0.2319	0.5211
	V4	0.3057	1.0829	0.5835	0.5827	0.6389	0.7574	0.3611	0.3057
	V5	6.4789	4.3741	3.8461	4.2813	5.5523	7.4899	9.8913	6.4789
	V6	8.2406	6.2605	5.6966	5.6890	6.2371	7.3942	9.2734	8.2406
3M−C7	V1	7.4641	5.6247	4.5437	4.5929	5.5591	7.2219	9.3533	6.0113
	V2	8.8232	7.2675	6.2865	5.9039	6.5284	7.8136	9.2964	7.6182
	V3	0.3834	0.7625	1.1333	0.9219	0.7004	0.4713	0.2369	0.5698
	V4	0.3324	0.6984	0.9743	0.5674	0.6274	0.7509	0.3574	0.2688
	V5	7.0808	4.8622	3.4104	3.6710	4.8587	6.7506	9.1164	5.4415
	V6	8.4908	6.5691	5.3121	5.3365	5.9010	7.0627	8.9390	7.3494
4M−C7	V1	8.3716	6.3509	4.9075	4.3301	4.9075	6.3509	8.3716	5.7735
	V2	9.0457	7.5411	6.2211	5.9358	6.2211	7.5411	9.0457	7.3123
	V3	0.2887	0.5774	0.8660	1.1547	0.8660	0.5774	0.2887	0.5773
	V4	0.3484	0.7325	0.6043	0.9359	0.6043	0.7325	0.3484	0.2559
	V5	8.0829	5.7735	4.0415	3.1754	4.0415	5.7735	8.0829	5.1962
	V6	8.6973	6.8086	5.6169	4.9999	5.6169	6.8086	8.6973	7.0564
3E−C6	V1	6.9636	5.1513	4.1314	4.6973	6.1467	8.1716	5.1512	6.9636
	V2	8.1638	6.5718	5.5065	5.8301	7.1673	8.6763	6.5718	8.1638
	V3	0.3851	0.7812	1.1996	0.8710	0.5672	0.2796	0.7812	0.3851
	V4	0.3147	0.6628	0.9085	0.5880	0.7229	0.3432	0.6628	0.3147
	V5	6.5785	4.3700	2.9318	3.8263	5.5795	7.8920	4.3700	6.5785
	V6	7.8492	5.9089	4.5980	5.2421	6.4444	8.3331	5.9089	7.8492
22MM−C6	V1	5.3868	4.1577	4.2870	5.4025	7.1747	9.3477	5.3868	5.3868
	V2	7.2131	6.3157	5.4939	6.1053	7.3798	8.8438	7.2131	7.2131
	V3	0.6376	1.3467	0.9313	0.6202	0.3785	0.1792	0.6376	0.6376
	V4	0.2670	1.3994	0.5645	0.6273	0.7583	0.3596	0.2670	0.2670
	V5	4.7492	2.8110	3.3557	4.7823	6.7962	9.1685	4.7492	4.7492
	V6	6.9461	4.9163	4.9294	5.4779	6.6215	8.4842	6.9461	6.9461
33MM−C6	V1	6.5772	4.8137	3.9352	4.4619	5.9454	7.9940	5.1520	5.1520
	V2	7.7514	6.1771	5.5274	5.4290	6.7549	8.2433	6.5157	6.5157
	V3	0.3786	0.8164	1.3822	0.8826	0.5214	0.2417	0.6409	0.6409
	V4	0.3158	0.6679	1.3128	0.5870	0.7304	0.3454	0.2416	0.2416
	V5	6.1987	3.9973	2.5530	3.5793	5.4240	7.7523	4.5111	4.5111
	V6	7.4356	5.5092	4.2146	4.8419	6.0245	7.8979	6.2741	6.2741
23MM−C6	V1	6.2017	4.6475	4.1717	4.8929	6.4559	8.5474	6.2017	5.6115
	V2	7.4797	6.2463	5.5126	5.7843	7.0970	8.5845	7.4797	6.8808
	V3	0.5090	1.0559	1.1722	0.8105	0.5090	0.2454	0.5090	0.5651
	V4	0.2862	1.0430	0.9358	0.6015	0.7380	0.3498	0.2862	0.2517
	V5	5.6926	3.5916	2.9995	4.0824	5.9468	8.3020	5.6926	5.0464
	V6	7.1935	5.2033	4.5767	5.1828	6.3590	8.2347	7.1935	6.6290
24MM−C6	V1	7.0439	5.3076	4.4940	4.6707	5.9270	7.8856	7.0439	6.2534
	V2	7.7478	6.5530	5.4704	5.8477	6.8199	8.3620	7.7478	7.1708
	V3	0.4467	0.9123	0.9695	1.0674	0.6876	0.3367	0.4467	0.5227
	V4	0.2977	1.0767	0.5626	0.9748	0.7013	0.3326	0.2977	0.2649
	V5	6.5972	4.3954	3.5246	3.6033	5.2394	7.5489	6.5972	5.7307
	V6	7.4501	5.4763	4.9078	4.8729	6.1185	8.0294	7.4501	6.9059
25MM−C6	V1	7.6026	5.8138	4.9193	4.9193	5.8138	7.6026	7.6026	7.6026
	V2	8.0882	6.9008	5.8397	5.8397	6.9008	8.0882	8.0882	8.0882
	V3	0.4472	0.8944	0.8944	0.8944	0.8944	0.4472	0.4472	0.4472
	V4	0.3041	1.0899	0.5793	0.5793	1.0899	0.3041	0.3041	0.3041
	V5	7.1554	4.9194	4.0249	4.0249	4.9193	7.1554	7.1554	7.1554
	V6	7.7841	5.8109	5.2604	5.2604	5.8109	7.7841	7.7841	7.7841
34MM−C6	V1	7.3414	5.4340	4.2646	4.2646	5.4340	7.3414	5.7469	5.7469
	V2	8.0197	6.4744	5.4826	5.4826	6.4744	8.0197	6.8211	6.8211
	V3	0.3355	0.7030	1.1374	1.1374	0.7030	0.3355	0.5428	0.5428
	V4	0.3272	0.6914	0.9547	0.9547	0.6914	0.3272	0.2562	0.2562
	V5	7.0059	4.7310	3.1272	3.1272	4.7310	7.0059	5.2041	5.2041
	V6	7.6925	5.7830	4.5279	4.5279	5.7830	7.6925	6.5649	6.5649
234MMM−C5	V1	6.3969	4.7418	4.1214	4.7418	6.3969	6.3969	5.5845	6.3969
	V2	7.0237	5.8061	5.0772	5.8061	7.0237	7.0237	6.4376	7.0237
	V3	0.4647	0.9925	1.1904	0.9925	0.4647	0.4647	0.5573	0.4647
	V4	0.2831	1.0486	0.9345	1.0486	0.2831	0.2831	0.2465	0.2831
	V5	5.9322	3.7493	2.9310	3.7493	5.9322	5.9322	5.0271	5.9322
	V6	6.7406	4.7576	4.1428	4.7576	6.7406	6.7406	6.1912	6.7406

Table 2 (Continued)

alkane	Vi	for given current atom							
		1	2	3	4	5	6	7	8
223MMM−C5	V1	5.4047	4.0935	4.1472	5.4031	7.3721	5.4047	5.4047	5.6542
	V2	6.4054	5.5062	5.0641	6.0434	7.5713	6.4054	6.4054	6.3904
	V3	0.6019	1.3278	1.1233	0.6409	0.2905	0.6019	0.6019	0.5092
	V4	0.2527	1.3831	0.9567	0.6957	0.3278	0.2527	0.2527	0.2518
	V5	4.8027	2.7657	3.0239	4.7622	7.0815	4.8027	4.8027	5.1450
	V6	6.1526	4.1231	4.1074	5.3477	7.2435	6.1526	6.1526	6.1387
224MMM−C5	V1	5.7276	4.3666	4.3179	5.3199	7.1586	5.7276	5.7276	7.1586
	V2	6.7546	5.8738	5.0484	6.1272	7.3021	6.7546	6.7546	7.3021
	V3	0.6015	1.2926	0.9732	0.7989	0.3717	0.6015	0.6015	0.3717
	V4	0.2622	1.4070	0.5582	1.0862	0.2959	0.2622	0.2622	0.2959
	V5	5.1261	3.0740	3.3446	4.5210	6.7869	5.1261	5.1261	6.7869
	V6	6.4923	4.4668	4.4903	5.0410	7.0062	6.4923	6.4923	7.0062
233MMM−C5	V1	5.9648	4.3806	3.9208	4.8848	6.7223	5.9648	5.1846	5.1846
	V2	6.6780	5.4496	5.0949	5.7320	7.2919	6.6780	6.0701	6.0701
	V3	0.4700	1.0441	1.3795	0.7788	0.3505	0.4700	0.6210	0.6210
	V4	0.2749	1.0321	1.3163	0.6694	0.3151	0.2749	0.2352	0.2352
	V5	5.4949	3.3366	2.5413	4.1060	6.3718	5.4949	4.5636	4.5636
	V6	6.4030	4.4174	3.7786	5.0627	6.9769	6.4030	5.8349	5.8349
3E−2M−C5	V1	6.0926	4.5249	4.0393	5.1255	6.9938	6.0926	5.1255	6.9938
	V2	7.1024	5.8531	5.0786	6.1379	7.7166	7.1024	6.1379	7.7166
	V3	0.5000	1.0505	1.2071	0.7428	0.3536	0.5000	0.7428	0.3536
	V4	0.2773	1.0232	0.9057	0.6645	0.3142	0.2773	0.6645	0.3142
	V5	5.5926	3.4744	2.8321	4.3826	6.6403	5.5926	4.3826	6.6403
	V6	6.8251	4.8299	4.1729	5.4734	7.4024	6.8251	5.4734	7.4024
3E−3M−C5	V1	6.4956	4.7165	3.8335	4.7165	6.4956	5.0411	4.7165	6.4956
	V2	7.3699	5.7852	5.0955	5.7852	7.3699	6.1180	5.7852	7.3699
	V3	0.3713	0.8128	1.4078	0.8128	0.3713	0.6432	0.8128	0.3713
	V4	0.3079	0.6527	1.2769	0.6527	0.3079	0.2291	0.6527	0.3079
	V5	6.1243	3.9037	2.4257	3.9037	6.1243	4.3980	3.9037	6.1243
	V6	7.0620	5.1325	3.8186	5.1325	7.0620	5.8890	5.1325	7.0620
2233M4−C4	V1	5.4506	4.0750	4.0750	5.4506	5.4506	5.4506	5.4506	5.4506
	V2	5.9609	5.0844	5.0844	5.9609	5.9609	5.9609	5.9609	5.9609
	V3	0.5651	1.3013	1.3013	0.5651	0.5651	0.5651	0.5651	0.5651
	V4	0.2470	1.3946	1.3946	0.2470	0.2470	0.2470	0.2470	0.2470
	V5	4.8855	2.7737	2.7737	4.8855	4.8855	4.8855	4.8855	4.8855
	V6	5.7139	3.6898	3.6898	5.7139	5.7139	5.7139	5.7139	5.7139

$$V1 = VA \times (A + D)$$

$$V2 = VD \times (A + D)$$

$$V3 = VA \times A$$

$$V4 = VD \times A$$

$$V5 = VA \times D$$

$$V6 = VD \times D \qquad (4)$$

Tables 1 and 2 present these new LOVIs for heptane and octane isomers with the IUPAC convention for the vertex numbering. The substituents are labeled M for methyl and E for ethyl, the numbers before these labels being the position on the C_x chain, where x is the number of carbon atoms in the longest (main) chain.

It will be observed from Tables 1 and 2 that the six LOVIs can be classified into two sets: the first one containing **V1, V2**, **V5**, and **V6** and the second one with **V3** and **V4**.

The variation of values in the first set is similar to that of the **VD** vector: *higher values* correspond to vertices of lower degree, further from the center of the graph. In the second set, the variation of values for **V3** is similar to that of the **VA** vector: *higher values* correspond to vertices of higher degree, closer to the center. The variation of **V4** is the least regular, as seen with the two *n*-alkanes. Therefore we can say that in the first set the "ruling matrix" is **D**, while in the second one the ruling matrix is **A**.

For four structures intramolecular degeneracy (which means the same values of LOVIs for chemically or topologically nonequivalent vertices) of **V3** values was found, as illustrated in Figure 2.

One may conclude that the use of LOVIs on the basis of topological distances offers more information and leads to a better discrimination between vertices. The only intramolecular degeneracy appears in the case of **V3** values, a LOVI based on a vector and matrix having no connection with the **D** matrix or its first eigenvector **VD**.
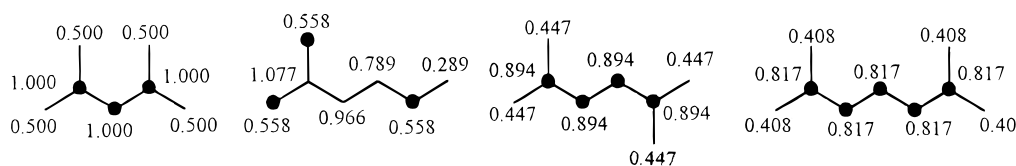

Figure 2. Graphs with intramolecular degeneracy for **V3** values (two isomers of heptane, one of octane, and one of nonane).

Table 3. Normal Boiling Points for the 74 Alkanes C2–C9, Posted Octane Numbers for 45 Alkanes C2–C10, and Topological Indices XMTi

alkane	bp	PON	XMT1	XMT2	XMT3	XMT4	XMT5	XMT6
C2	−88.5	106.95	2.8284	2.8284	1.4142	1.4142	1.4142	1.4142
C3	−44.5	103.80	6.8284	6.8625	2.4142	2.1753	4.4142	4.6872
C4	−0.5	91.55	12.4225	12.9923	3.1495	2.8011	9.2730	10.1912
2M−C3	−10.5	99.55	11.5911	11.8336	3.3461	2.6709	8.2450	9.1626
C5	36.5	62.50	19.9697	21.6077	3.7320	3.3437	16.2376	18.2640
2M−C4	27.9	91.35	18.2962	19.6482	3.9375	3.2231	14.3586	16.4251
22MM−C3	9.5	82.85	16.9706	17.6317	4.2426	3.0733	12.7279	14.5584
C6	68.7	25.40	29.7517	33.0330	4.2199	3.8278	25.5317	29.2052
3M−C5	63.2	73.90	26.3849	29.5692	4.4448	3.6960	21.9402	25.8732
2M−C5	60.2	73.45	27.3477	30.4033	4.3992	3.7330	22.9484	26.6703
23MM−C4	58.1	99.25	25.4034	27.7390	4.6188	3.6181	20.7846	24.1209
22MM−C4	49.7	92.60	24.4485	26.8914	4.7408	3.5755	19.7077	23.3159
C7	98.4	0.00	42.0051	47.5542	4.6447	4.2676	37.3605	43.2865
3E−C5	93.5	67.15	35.5176	41.2418	4.8990	4.1050	30.6186	37.1369
3M−C6	91.8	53.50	37.0095	42.8103	4.8421	4.1519	32.1674	38.6585
2M−C6	90.0	44.40	39.0184	44.3245	4.7937	4.1954	34.2248	40.1292
23MM−C5	89.8	89.80	34.7898	39.5465	5.0497	4.0600	29.7400	35.4864
33MM−C5	86.0	83.70	33.0226	37.9953	5.1896	4.0072	27.8329	33.9881
223MMM−C4	80.9	106.70	32.5554	36.2582	5.3376	3.9513	27.2178	32.3069
24−MMC5	80.5	83.45	37.0000	41.0624	5.0000	4.1101	32.0000	36.9523
22MM−C5	79.2	94.20	34.2677	39.5657	5.0954	4.0619	29.1723	35.5038
C8	125.8	0.00	56.9386	65.4313	5.0245	4.6729	51.9142	60.7584
3E−C6	118.9	42.95	47.3768	56.6514	5.2501	4.5176	42.1266	52.1338
3M−C7	118.8	30.90	50.3711	59.5377	5.1796	4.5770	45.1915	54.9607
34MM−C6	118.7	79.00	45.5738	53.5956	5.4375	4.4589	40.1363	49.1367
3E−3M−C5	118.2	84.75	42.5110	50.6788	5.6034	4.3877	36.9075	46.2911
4M−C7	117.7	32.85	49.3635	58.8640	5.1962	4.5621	44.1673	54.3019
2M−C7	117.6	22.75	53.5390	61.6500	5.1462	4.6179	48.3929	57.0321
3E−2M−C5	115.6	87.70	44.9879	52.8456	5.4503	4.4410	39.5375	48.4046
23MM−C6	115.3	75.10	46.7303	55.0647	5.3762	4.4922	41.3541	50.5725
233MMM−C5	114.6	102.75	42.2074	49.0645	5.7347	4.3530	36.4726	44.7115
234MMM−C5	113.4	99.30	44.7771	51.2218	5.5915	4.4103	39.1855	46.8115
33MM−C6	112.0	79.45	44.0315	52.9145	5.5047	4.4426	38.5268	48.4719
223MMM−C5	110.5	104.75	42.8839	49.7915	5.6975	4.3732	37.1864	45.4182
24MM−C6	109.4	67.55	48.6262	55.7193	5.3897	4.5083	43.2365	51.2111
25MM−C6	108.4	55.60	51.8768	57.8338	5.3666	4.5545	46.5102	53.2792
22MM−C6	107.0	74.95	46.5300	55.7778	5.3687	4.5101	41.1613	51.2677
2233MMMM−C4	106.0		40.8535	45.9343	5.9932	4.2713	34.8603	41.6630
224MMM−C5	99.3	100.00	45.5043	51.9175	5.6127	4.4300	39.8916	47.4874
C9	150.6		74.7416	86.9040	5.3708	5.0502	69.3709	81.8538
33EE−C5	146.2	87.80	52.8007	64.7543	5.9907	4.7320	46.8100	60.0222
3E−C7	143.0		62.0278	75.9008	5.5418	4.9135	56.4860	70.9873
3M−C8	143.0		66.6396	79.9504	5.4772	4.9722	61.1623	74.9783
4M−C8	142.5		64.5532	78.6917	5.4985	4.9520	59.0547	73.7397
2M−C8	142.5		71.1178	82.6087	5.4694	5.0080	65.6484	77.6007
3E−23MM−C5	141.6		52.6189	63.2471	6.1093	4.7084	46.5096	58.5386
2334MMMM−C5	141.5		52.5508	61.7018	6.2272	4.6839	46.3236	57.0179
4E−C7	141.2		60.6803	74.5782	5.5704	4.8915	55.1100	69.6867
3E−3M−C6	140.6		54.5303	67.5920	5.8890	4.7839	48.6413	62.8081
334MMM−C6	140.5		53.6818	64.6524	6.0641	4.7368	47.6177	59.9156
23MM−C7	140.5		61.3140	74.3994	5.6389	4.8991	55.6751	69.5002
4E−3M−C6	140.4		56.9898	68.8866	5.8051	4.8082	51.1848	64.0784
2233MMMM−C5	140.3	105.90	51.4732	60.3220	6.3417	4.6541	45.1315	55.6679
34MM−C7	140.1		58.9654	71.6968	5.7300	4.8550	53.2354	66.8418
234MMM−C6	139.0		57.0300	67.3517	5.9338	4.7890	51.0962	62.5627
3E−2M−C6	138.0		57.9004	70.2922	5.7478	4.8314	52.1525	65.4608
233MMM−C6	137.7		54.2976	66.0859	6.0046	4.7634	48.2930	61.3225
33MM−C7	137.3		57.4684	71.7143	5.7399	4.8564	51.7285	66.8579
3E−24MM−C5	136.7	100.95	55.7785	65.9590	5.9533	4.7625	49.8252	61.1965
25MM−C7	136.0		65.9646	75.6114	5.7231	4.9207	60.2415	70.6907
35MM−C7	136.0		62.1021	72.9457	5.7475	4.8780	56.3546	68.0676
44MM−C7	135.2		56.3624	70.4146	5.7973	4.8318	50.5651	65.5828
26MM−C7	135.2		70.2187	78.2756	5.7155	4.9606	64.5032	73.3150
4E−2M−C6	133.8		60.6497	71.5648	5.7545	4.8552	54.8952	66.7096
3E−22MM−C5	133.8	105.80	53.9560	64.6071	6.0461	4.7366	47.9099	59.8705
24MM−C7	133.5		62.9003	74.3680	5.6940	4.8986	57.2063	69.4693
2234MMMM−C5	133.0		54.3075	63.0324	6.1806	4.7139	48.1269	58.3185
22MM−C7	132.7	55.40	61.2884	75.7101	5.5839	4.9218	55.7045	70.7882
223MMM−C6	131.7		55.5819	67.4293	5.9475	4.7900	49.6345	62.6392
235MMM−C6	131.3		60.4392	70.0308	5.8733	4.8383	54.5659	65.1925
224MMM−C6	126.5		58.6822	68.6578	5.9445	4.8155	52.7377	63.8423
244MMM−C6	126.5		56.6601	67.3352	5.9720	4.7900	50.6881	62.5452
225MMM−C6	124.0		61.2988	71.3287	5.8525	4.8634	55.4463	66.4653

REAL-NUMBER LOVIs AND SCHULTZ-TYPE INDICES

J. Chem. Inf. Comput. Sci., Vol. 38, No. 6, 1998 **1043**

Table 3 (Continued)

alkane	bp	PON	XMT1	XMT2	XMT3	XMT4	XMT5	XMT6
2244MMMM−C5	122.7		57.0132	64.3208	6.2361	4.7437	50.7771	59.5771
335MMM−C7		87.55	64.4100	79.3226	6.5634	5.0483	57.8466	74.2743
2233MMMM−C6		102.60	71.1767	86.4653	6.2706	5.1508	64.9061	81.3145

3. NEW TOPOLOGICAL INDICES AND INTERMOLECULAR ORDERING OF ALKANES

From **Vi** values we calculated two types of third-generation topological indices: the first is represented by the sum of LOVIs denoted by XMTi, where i is the same number as in the vector **Vi** (i = 1, 2, ..., 6):

$$XMTi = \sum_j \mathbf{Vi}(j) \qquad (5)$$

The second one is based on a Randic-type formula[6] applied to the six vectors **Vi** (i = 1, 2, ..., 6), where r and s are edge end points:

$$XMTiR = \sum_{edges} [\mathbf{Vi}(r) \cdot \mathbf{Vi}(s)]^{-1/2} \qquad (6)$$

The results of relations 5 and 6 are listed in Tables 3 and 4 together with the boiling points of alkanes at normal pressure and the posted octane numbers[21] for 45 alkanes (which includes two C10 isomers not involved in the boiling temperature analysis). The alkanes are ordered according to their decreasing normal boiling points.

For topological indices, one of the criteria of analysis is the intermolecular ordering of alkane isomers. This ordering was discussed in connection with the J index[8,9] and with Bertz's graph derivatives.[22]

For heptanes, the intermolecular ordering is the same as that based on the J index for XMT2 and XMT6R indices, which is normal, considering that the origin of these two indices is the distance matrix. For XMT1 and XMT5, if we consider the *descending* ordering, we will find a similarity with the former two indices (XMT2 and XMT6R). One can conclude that the order is defined by the distance elements, while the ascending or descending way is defined by the adjacency elements.

The best intermolecular ordering of octanes is given by analyzing the ordering of dimethylhexanes. Table 5 displays the ordering of dimethylhexanes induced by the twelve TIs comparatively to the J index and to Bertz's criteria.

As one can observe, the order is similar to that of Bertz's graph derivatives only for the index XMT5R; XMT1R ordering differs from it by the permutation 2,2-dimethylhexane/3,4-dimethylhexane and from the order based on the J index by the permutation 2,3-dimethylhexane/2,2-dimethylhexane. For other indices, such as XMT1 and XMT5, we have to consider the inverse order of isomers, when we obtain the same permutations as before. For the indices XMT4R and XMT6R the order is similar to that induced by the J index except for the permutation 2,4-dimethylhexane/2,2-dimethylhexane. For XMT3 and XMT4 we must again consider the inverse order, and we obtain the same permutation. An unusual ordering is generated by XMT3R, which finds as the most branched alkanes those which have vicinal tertiary carbon atoms and as less branched those which have *tert*-butyl-like carbon atoms at one or both ends of the main chain.

Concerning the range of variation, the indices XMT1, XMT2, XMT5, XMT6 (based on distance elements) and XMT3R, XMT4R (based on adjacency) present suitable values, useful in degeneracy analysis and correlation studies.

The most degenerate index from the two groups (XMTi and XMTiR) is XMT4, which has one pair with the same value for C9. XMT5R and XMT6R have a degenerate pair for C10, while XMT4R and XMT3 have one and two pairs, respectively, for C11. The least degenerate indices are XMT5 with only one pair for C14 and twelve pairs for C15 and XMT6 with four pairs for C14 and 10 pairs for C15.

The intercorrelation of these twelve indices among themselves and also with n was tested for a set of 74 alkanes with n = 2−9 carbon atoms. The result is presented in Table 6.

The first set of indices (XMT1 through XMT6, the "sum" indices) exhibit a strong intercorrelation, with r > 0.80. The two pairs with the strongest intercorrelations are XMT1 with XMT5 and XMT2 with XMT6, indicating that the contribution of the adjacency matrix **A** in the sum **A** + **D** is negligible.

For the second set (XMT1R through XMT6R, based on a Randic-type formula), the intercorrelated pairs are XMT1R−XMT2R (r = 0.938), XMT2R−XMT5R (r = 0.844), XMT3R−XMT4R (r = 0.936), and XMT5R−XMT6R (r = 0.871).

The intercorrelation between these two sets of indices reveals significant values (r > 0.80) for all the possible pairwise combinations from the four indices XMT3, XMT4, XMT3R, and XMT4R, except for the pair XMT3−XMT3R. The indices XMT3R and XMT4R intercorrelate strongly with all indices of the first set. This is due to the fact that the "ruling matrix" for indices with numbers 3 and 4 is the adjacency matrix **A** with low information content.

Strong intercorrelations with the number of carbon atoms n result for the first set (XMT1−XMT6) and two indices from the second set, namely, XMT3R and XMT4R. For the last two indices the ruling matrix is again the adjacency matrix **A**. The strongest intercorrelations with n are provided by XMT4 and XMT4R; these two TIs are based on the **V4** LOVI resulting by combining the low information content matrix **A** with the first eigenvector **VD** of the distance matrix **D**. This combination leads to an irregular intramolecular variation, and irrespective of the two methods employed for converting the **V4** LOVI into TIs, one obtains two TIs with a much narrower range of variation for isomers than for the ten remaining TIs. Indices XMT5R and XMT6R do not intercorrelate with n; therefore they reflect only the degree of branching (topological shape) and should be employed in biparametric correlations when the property is also influenced by the size of the molecule.

Table 4. Normal Boiling Points for the 74 Alkanes C2−C9, Posted Octane Numbers for 45 Alkanes C2−C10, and Topological Indices XMTiR

alkane	bp	PON	XMT1R	XMT2R	XMT3R	XMT4R	XMT5R	XMT6R
C2	−88.5	106.95	0.7071	0.7071	1.4142	1.4142	1.4142	1.4142
C3	−44.5	103.80	0.9102	0.8556	2.3784	2.6322	1.5307	1.3625
C4	−0.5	91.55	1.0216	0.9366	3.6414	4.1438	1.4758	1.2641
2−M−C3	−10.5	99.55	1.0981	0.9842	3.2237	3.9843	1.7721	1.4854
C5	36.5	62.50	1.0744	0.9581	5.1885	5.7855	1.4072	1.1751
2M−C4	27.9	91.35	1.1800	1.0402	4.6704	5.7300	1.6738	1.3618
22MM−C3	9.5	82.85	1.2649	1.1005	4.0000	5.3707	2.0000	1.6261
C6	68.7	25.40	1.0926	0.9499	7.0085	7.5971	1.3407	1.0997
3M−C5	63.2	73.90	1.2455	1.0659	6.3469	7.6703	1.6447	1.2921
2M−C5	60.2	73.45	1.1977	1.0292	6.5144	7.4529	1.5461	1.2370
23MM−C4	58.1	99.25	1.2887	1.1233	5.7650	7.4624	1.7423	1.4149
22MM−C4	49.7	92.60	1.3413	1.1428	5.6102	7.3111	1.9139	1.4899
C7	98.4	0.00	1.0912	0.9284	9.0921	9.5746	1.2803	1.0359
3E−C5	93.5	67.15	1.3106	1.0902	8.1962	9.7871	1.6547	1.2632
3M−C6	91.8	53.50	1.2557	1.0408	8.4985	9.5782	1.5586	1.1966
2M−C6	90.0	44.40	1.1841	0.9963	8.7064	9.3614	1.4348	1.1369
23MM−C5	89.8	89.80	1.3338	1.1270	7.6535	9.5183	1.7040	1.3344
33MM−C5	86.0	83.70	1.4096	1.1678	7.3949	9.4726	1.8893	1.4194
223MMM−C4	80.9	106.70	1.4210	1.2110	6.7715	9.1573	1.9095	1.5101
24−MMC5	80.5	83.45	1.2412	1.0752	7.6569	9.1827	1.5289	1.2603
22MM−C5	79.2	94.20	1.3626	1.1116	7.9855	9.0976	1.7961	1.3348
C8	125.8	0.00	1.0789	0.9016	11.4309	11.7069	1.2261	0.9816
3E−C6	118.9	42.95	1.3217	1.0635	10.6241	11.8664	1.5975	1.1896
3M−C7	118.8	30.90	1.2398	0.9999	11.1256	11.6501	1.4696	1.1100
34MM−C6	118.7	79.00	1.3706	1.1227	9.7794	11.7585	1.6829	1.2784
3E−3M−C5	118.2	84.75	1.4750	1.1911	9.3160	11.8276	1.8946	1.3868
4M−C7	117.7	32.85	1.2664	1.0151	10.9521	11.6682	1.5113	1.1291
2M−C7	117.6	22.75	1.1569	0.9577	11.2222	11.4378	1.3423	1.0575
3E−2M−C5	115.6	87.70	1.3884	1.1424	9.6624	11.7482	1.7109	1.3038
23MM−C6	115.3	75.10	1.3402	1.0867	10.2677	11.5353	1.6351	1.2311
233MMM−C5	114.6	102.75	1.4791	1.2207	8.7281	11.4503	1.9029	1.4436
234MMM−C5	113.4	99.30	1.3871	1.1696	8.9576	11.4464	1.7120	1.3543
33MM−C6	112.0	79.45	1.4295	1.1306	10.0614	11.4535	1.8152	1.3042
223MMM−C5	110.5	104.75	1.4567	1.1989	8.9927	11.3011	1.8582	1.4118
24MM−C6	109.4	67.55	1.2715	1.0697	9.7634	11.4158	1.5153	1.2087
25MM−C6	108.4	55.60	1.1789	1.0217	9.6787	11.1919	1.3721	1.1466
22MM−C6	107.0	74.95	1.3613	1.0597	11.3500	11.0784	1.6984	1.2084
2233MMMM−C4	106.0		1.5185	1.2866	7.7653	10.9397	1.9905	1.5778
224MMM−C5	99.3	100.00	1.3629	1.1387	9.0980	10.8790	1.6858	1.3271
C9	150.6		1.0608	0.8734	14.0174	13.9833	1.1776	0.9346
33EE−C5	146.2	87.80	1.5386	1.2155	11.3489	14.3493	1.9161	1.3755
3M−C8	143.0		1.2131	0.9566	14.2605	13.8719	1.3906	1.0371
3E−C7	143.0		1.3091	1.0194	13.7184	14.0969	1.5288	1.1118
2M−C8	142.5		1.1243	0.9195	14.0458	13.6678	1.2652	0.9931
4M−C8	142.5		1.2540	0.9767	13.9340	13.9040	1.4494	1.0611
3E−23MM−C5	141.6		1.5390	1.2371	10.7870	13.9306	1.9187	1.4147
2334MMMM−C5	141.5		1.5345	1.2597	10.1432	13.5161	1.9124	1.4563
4E−C7	141.2		1.3363	1.0428	13.3157	14.1121	1.5679	1.1397
3E−3M−C6	140.6		1.4959	1.1551	12.2406	13.9850	1.8474	1.2977
23MM−C7	140.5		1.3305	1.0344	13.7944	13.7098	1.5682	1.1371
334MMM−C6	140.5		1.5100	1.2045	11.1677	13.7792	1.8687	1.3715
4E−3M−C6	140.4		1.4193	1.1352	11.9902	14.1543	1.6971	1.2614
2233MMMM−C5	140.3	105.90	1.5672	1.2839	9.9443	13.3320	1.9797	1.5031
34MM−C7	140.1		1.3764	1.0822	12.7245	13.9481	1.6346	1.1960
234MMM−C6	139.0		1.4124	1.1540	11.3151	13.8003	1.6894	1.2943
3E−2M−C6	138.0		1.4012	1.1087	12.5119	13.9354	1.6706	1.2281
233MMM−C6	137.7		1.5003	1.1743	11.8202	13.5477	1.8580	1.3322
33MM−C7	137.3		1.4320	1.0747	14.0023	13.5992	1.7480	1.1958
3E−24MM−C5	136.7	100.95	1.4450	1.1840	11.1208	13.7912	1.7388	1.3321
25MM−C7	136.0		1.2019	1.0125	11.9956	13.5813	1.3705	1.1101
35MM−C7	136.0		1.2884	1.0577	12.1164	13.8017	1.4949	1.1656
44MM−C7	135.2		1.4501	1.1004	12.9604	13.6264	1.7737	1.2285
26MM−C7	135.2		1.1177	0.9711	11.8272	13.3685	1.2542	1.0598
4E−2M−C6	133.8		1.3217	1.0832	11.9736	13.8132	1.5434	1.1962
3E−22MM−C5	133.8	105.80	1.5004	1.2052	11.2437	13.6174	1.8465	1.3713
24MM−C7	133.5		1.2767	1.0348	12.5607	13.6152	1.4802	1.1375
2234MMMM−C5	133.0		1.4801	1.2268	10.2935	13.2936	1.8123	1.4106
22MM−C7	132.7	55.40	1.3537	1.0057	16.0756	13.2289	1.6258	1.1095
223MMM−C6	131.7		1.4699	1.1455	12.5108	13.4006	1.8046	1.2938
235MMM−C6	131.3		1.3233	1.1003	11.3669	13.4463	1.5507	1.2260
224MMM−C6	126.5		1.3694	1.1185	11.6498	13.1924	1.6310	1.2585
244MMM−C6	126.5		1.4230	1.1460	11.3428	13.3500	1.7215	1.2947

Table 4 (Continued)

alkane	bp	PON	XMT1R	XMT2R	XMT3R	XMT4R	XMT5R	XMT6R
225MMM−C6	124.0		1.3099	1.0681	12.0418	12.9618	1.5449	1.1941
2244MMMM−C5	122.7		1.3953	1.1869	9.9164	12.6188	1.6732	1.3683
335MMM−C7		87.55	1.5923	1.2288	13.7355	15.5180	1.9530	1.3856
2233MMMM−C6		102.60	1.4251	1.1212	14.2508	15.8124	1.6720	1.2352

Table 5. Ordering of Dimethylhexanes[a]

Bertz	2,5	2,4	2,3	3,4	2,2	3,3
J	2,5	2,4	2,2	2,3	3,4	3,3
XMT1	3,3	3,4	2,2	2,3	2,4	2,5
XMT2	2,5	2,2	2,3	2,4	3,4	3,3
XMT3	3,3	3,4	2,3	2,4	2,2	2,5
XMT4	3,3	3,4	2,3	2,4	2,2	2,5
XMT5	3,3	3,4	2,2	2,3	2,4	2,5
XMT6	3,3	3,4	2,3	2,4	2,2	2,5
XMT1R	2,5	2,4	2,3	2,2	3,4	3,3
XMT2R	2,5	2,4	3,4	3,3	2,3	2,2
XMT3R	2,2	2,5	2,4	3,3	2,3	3,4
XMT4R	2,5	2,2	2,4	2,3	3,4	3,3
XMT5R	2,5	2,4	2,3	3,4	2,2	3,3
XMT6R	2,5	2,2	2,4	2,3	3,4	3,3

[a] Digits indicate the locants of the two methyl groups.

4. CORRELATIONS WITH BOILING TEMPERATURES OF ALKANES

When a new topological index is defined, especially if no heteroatom is included, the most usual test is the correlation with the normal boiling temperature of alkanes due to the weak forces between nonpolar molecules in liquid state. However, as seen from Tables 3 and 4, the normal boiling points do not correlate exactly with the degree of branching.

Monoparametric correlations for the 74 alkanes with $n = 2-9$ carbon atoms were tested. The equations bp = a(TI) + b are listed in Table 7, where bp is the boiling point (°C) at normal pressure, TI is the topological index, r is the correlation coefficient, s is the standard deviation, EV is the explained variance, and F is the Fisher test for 72 degrees of freedom. Due to the intercorrelation between n and some of the topological indices, the dependence of the boiling temperature on the number of carbon atoms is also listed in Table 7.

It can be seen that the best correlation coefficient is obtained for XMT4, corresponding to a standard deviation of less than 7 °C; 98% of the variance is accounted for by the equation. The complete equation is listed below (t being the Student test for 72 degrees of freedom):

$$bp = (66.884 \pm 1.126)XMT4 - (186.466 \pm 4.989) \quad (7)$$
$$t = 59.377 \qquad t = 37.376$$

Another reasonable correlation is given by XMT4R, with standard deviation less than 10 °C and explained variance of 96%. In this case, a better correlation is obtained considering a monoparametric parabolic dependence:

$$bp = -115.80253 + 28.72183\ XMT4R - 0.74821(XMT4R)^2 \quad (8)$$

The correlation coefficient is $r = 0.9953$, the standard deviation $s = 4.55$ °C, the explained variance is 99.03%, and the F-test is 3733. The fact that the parabolic regression gives better results is in agreement with the nonlinear dependence of boiling points of alkanes with the increasing number of carbon atoms.

Considering only the set of 35 isomeric nonanes, the best linear monoparametric correlation is also obtained for the XMT4R index:

$$bp = (14.024 \pm 1.71)XMT4R - (54.494 \pm 23.38) \quad (9)$$
$$r = 0.8188 \qquad s = 3.56\ °C$$

The utilization of all other indices for nonanes results in correlations with $r < 0.35$. Polynomial or other nonlinear monoparametric correlations do not improve the correlation coefficient.

Biparametric linear correlations were also tested, with n being the number of carbon atoms and TI as independent variables. The correlation with the XMT4 index is improved slightly, as can be seen from Table 8, where this is still the best result. The same slight improvement holds for XMT3R and all other indices from the first set (XMT1−XMT6). However, the biparametric correlations with XMT1R, XMT2R, XMT5R, and XMT6R undergo dramatic improvement.

Multilinear correlations were tested involving only topological indices. The selection of the independent variables was made by avoiding, when possible, the strong intercorrelations between them. The best two equations for three

Table 6. Intercorrelation Matrix for Alkanes C2−C9

	n	XMT1	XMT2	XMT3	XMT4	XMT5	XMT6	XMT1R	XMT2R	XMT3R	XMT4R	XMT5R	XMT6R
n	1.000	0.948	0.952	0.954	0.984	0.938	0.949	0.659	0.456	0.922	0.992	0.074	−0.304
XMT1	0.948	1.000	0.996	0.823	0.953	0.999	0.996	0.396	0.169	0.960	0.956	−0.203	−0.526
XMT2	0.952	0.996	1.000	0.821	0.951	0.996	1.000	0.421	0.176	0.976	0.964	−0.170	−0.516
XMT3	0.954	0.823	0.821	1.000	0.923	0.804	0.816	0.819	0.685	0.777	0.923	0.307	−0.054
XMT4	0.984	0.953	0.951	0.923	1.000	0.944	0.948	0.581	0.368	0.934	0.972	−0.042	−0.428
XMT5	0.938	0.999	0.996	0.804	0.944	1.000	0.996	0.367	0.137	0.961	0.947	−0.230	−0.547
XMT6	0.949	0.996	1.000	0.816	0.948	0.996	1.000	0.414	0.169	0.976	0.962	−0.175	−0.518
XMT1R	0.659	0.396	0.421	0.819	0.581	0.367	0.414	1.000	0.938	0.416	0.628	0.774	0.433
XMT2R	0.456	0.169	0.176	0.685	0.368	0.137	0.169	0.938	1.000	0.129	0.411	0.844	0.646
XMT3R	0.922	0.960	0.976	0.777	0.934	0.961	0.976	0.416	0.129	1.000	0.936	−0.166	−0.562
XMT4R	0.992	0.956	0.964	0.923	0.972	0.947	0.962	0.628	0.411	0.936	1.000	0.050	−0.330
XMT5R	0.074	−0.203	−0.170	0.307	−0.042	−0.230	−0.175	0.774	0.844	−0.166	0.050	1.000	0.871
XMT6R	−0.304	−0.526	−0.516	−0.054	−0.428	−0.547	−0.518	0.433	0.646	−0.562	−0.330	0.871	1.000

Table 7. Significant Regression Coefficients and Statistical Parameters for Monoparametric Correlations (bp = a(TI) + b) for Boiling Points of the 74 Alkanes with n = 2−9 Carbon Atoms

index	a	b	r	s °C	EV	F
n	28.87	−120.04	0.9850	8.04	0.970	2350
XMT1	2.72	−21.08	0.9304	17.08	0.864	463.7
XMT2	2.21	−15.54	0.9334	16.72	0.870	487.3
XMT3	49.84	−157.50	0.9370	16.29	0.876	517.6
XMT4	66.88	−186.46	0.9899	6.59	0.980	3523.4
XMT5	2.81	−10.67	0.9200	18.26	0.844	396.9
XMT6	2.28	−9.24	0.9297	17.17	0.862	458.4
XMT1R	186.38	−138.56	0.6400	35.81	0.401	49.9
XMT3R	13.91	−31.80	0.9145	18.86	0.834	367.6
XMT4R	14.86	−61.57	0.9796	9.37	0.960	1708.0

Table 8. Biparametric Correlations bp = a_0 + $a_1 n$ + a_2(TI) for Boiling Points of the 74 Alkanes C2−C9

index	a_0	a_1	a_2	R	s °C	EV	F
XMTI1	−123.02	29.89	−0.12	0.9851	8.07	0.970	1164.5
XMTI2	−123.68	30.03	−0.10	0.9851	8.07	0.970	1165.5
XMTI3	−118.10	29.74	−1.66	0.9851	8.08	0.970	1162.5
XMTI4	−165.60	9.96	44.27	0.9917	6.02	0.983	2123.2
XMTI5	−122.76	29.72	−0.09	0.9851	8.08	0.970	1163.6
XMTI6	−124.51	30.20	−0.11	0.9851	8.06	0.970	1168.3
XMTI1R	−116.39	29.17	−4.59	0.9851	8.07	0.970	1164.7
XMTI2R	−113.15	29.13	−8.22	0.9852	8.05	0.970	1170.7
XMTI3R	−117.33	27.67	0.68	0.9852	8.05	0.970	1171.1
XMTI4R	−111.65	24.56	2.25	0.9852	8.04	0.970	1173.1
XMTI5R	−105.17	28.96	−9.49	0.9859	7.85	0.971	1231.9
XMTI6R	−87.23	28.25	−22.13	0.9872	7.47	0.974	1365.0

variables are listed below (*F* being the Fisher test for 70 degrees of freedom):

$$bp = (-16.071 \pm 8.81) + (39.010 \pm 2.52)\text{XMT3} + (64.394 \pm 15.28)\text{XMT1R} - (133.572 \pm 9.62)\text{XMT6R} \quad (10)$$

$$R = 0.9902 \quad s = 6.59\,°C \quad EV = 0.980 \quad F = 1177$$

$$bp = (-10.369 \pm 9.47) + (45.231 \pm 1.30)\text{XMT3} + (45.075 \pm 11.34)\text{XMT5R} - (155.731 \pm 15.06)\text{XMT6R} \quad (11)$$

$$R = 0.9900 \quad s = 6.67\,°C \quad EV = 0.979 \quad F = 1150$$

The use of these variables leads to good statistical parameters, better than any simple linear equation involving each of them.

6. CORRELATIONS WITH OCTANE NUMBERS OF ALKANES

The antiknock properties of alkanes depend on their branching,[21] so it is useful to find correlations between octane numbers of these molecules and their chemical structure. The octane number used in this paper is the posted octane number (PON), an arithmetic average between two others scales: RON (research octane number) and MON (motor octane number), which represent experimentally measured quantities under different operating conditions.[21] Correlations for the twelve Schultz-type indices calculated for 45 alkanes isomers with n = 2−10 carbon atoms were tested. No simple linear correlation with good statistical parameters was found. Multilinear correlations were also tested, but for correlation coefficients greater than 0.9 one needs four to six independent variables, some of them being strongly intercorrelated.

Considering a nonlinear dependence between PON and TIs, the best equation involves the natural logarithm and inverse square of the XMT6R index, which do not depend on the size of the molecules:

$$PON = (-9.620 \pm 5.48) + (610.50 \pm 37.4)\frac{\log(\text{XMT6R})}{(\text{XMT6R})^2} \quad (12)$$

$$R = 0.9279 \quad s = 10.80\,°C \quad EV = 0.861 \quad F = 266.5$$

A slightly better correlation holds if in the previous equation is included the inverse of the natural logarithm of the XMT5R index, another index which does not depend on the size of the molecules:

$$PON = (-45.09 \pm 19.1) + (731.874 \pm 74.41)\frac{\log(\text{XMT6R})}{(\text{XMT6R})^2} + \frac{8.188 \pm 4.49}{\log(\text{XMT5R})} \quad (13)$$

$$R = 0.9430 \quad s = 9.77\,°C \quad EV = 0.867 \quad F = 164.7$$

These results confirm the dependency of the posted octane number only on the branching degree of alkanes.

7. CONCLUSIONS

In this paper we have proposed six new local vertex invariants based on the first eigenvector of adjacency and distance matrices. On the basis of these six LOVIs, twelve third-generation topological indices were derived by applying the algorithm for the MTI index.[14] We have analyzed the intramolecular ordering of vertices induced by these LOVIs and also their degeneracy. We found that only one LOVI (**V3**) has high degeneracy in the case of three symmetrical 4-trees with 7−9 vertices. The TIs were analyzed having as the main criteria the intermolecular ordering of isomeric alkanes. The ability of these TIs to correlate with the normal boiling points of alkanes and with the posted octane numbers was tested through monoparametric (linear and nonlinear) and multiparametric correlations (linear and nonlinear, with the number of carbon atoms or only with topological indices as independent variables).

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REAL-NUMBER LOVIS AND SCHULTZ-TYPE INDICES

J. Chem. Inf. Comput. Sci., Vol. 38, No. 6, 1998 **1047**

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