CROATICA CHEMICA ACTA CCACAA **75** (4) 847–868 (2002)

ISSN-0011-1643
CCA-2836

Original Scientific Paper

Harary Index – Twelve Years Later*

*Bono Lučić, Ante Miličević, Sonja Nikolić,** and Nenad Trinajstić*

The Rugjer Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia

Received May 2, 2002; revised July 4, 2002; accepted July 8, 2002

»In 2001 I'm due to become 80,
But my lecture then will be light, not weighty.«
Frank Harary[1]

A modification of the Harary index, denoted by H and introduced twelve years ago, is proposed. Unlike the original index, this index, called the modified Harary index and denoted by ${}^{m}H$, consists of two parts: the first relates to greater contributions of outer bonds and the second to smaller contributions of inner bonds of an alkane, which is in accordance with the chemists' intuition. The Wiener index W, Harary index and modified Harary index are compared in the structure-property modeling of eight representative properties of lower alkanes. The models considered were linear, Wiener-like and linear and nonlinear multivariate. Multivariate models were obtained using our variable selection procedure CROMRsel (B. Lučić and N. Trinajstić, *J. Chem. Inf. Comput. Sci.* **39** (1999) 121–132). Multivariate models represent considerable improvements over the other two kinds of models. For example, the standard error of estimate improves on going from the best linear structure-boiling point model involving ${}^{m}H$ (S = 7.6 °C) to the best Wiener-like model based on the reduced Wiener number W/N^2 and the number of paths of the length of three p_3 (S = 6.2 °C) to the best four-parameter multivariate model containing ln values of W, H and ${}^{m}H$, and p_3 (S = 1.5 °C). All good models obtained in this work involve ${}^{m}H$, suggesting that this index has a great potential to be used in QSPR. Its advantage over W and H is due to the fact that the main contribution to ${}^{m}H$ comes from the outer, more exposed, bonds, which is not the case of the other two indices.

Key words: Harary index, lower alkanes, modified Harary index, structure-property modeling, Wiener index.

---

* Dedicated to Professor Frank Harary on the happy occasion of his 80th birthday.

** Author to whom correspondence should be addressed. (E-mail: sonja@rudjer.irb.hr)

INTRODUCTION

Twelve years ago a group of Zagreb mathematical and computational chemists (Zlatko Mihalić, Sonja Nikolić, Dejan Plavšić and Nenad Trinajstić) devised a graph-theoretical invariant (topological index) for the characterization of chemical graphs, which was named the *Harary index* in honor of Professor Frank Harary, the grandmaster of both graph theory and chemical graph theory, on the occasion of his 70th birthday. They reported their work at the symposium held in his honor at the University of Saskatchewan (Saskatoon, Canada; September 12–14, 1991). Two years later, a paper based on this report appeared.[2] The Harary index, denoted by H, is derived from the reciprocal distance matrix and has a number of interesting properties.[3–5] At that time the Zagreb group did not know that the same graph-theoretical invariant, though under a different name – the reciprocal distance sum (RDSUM) index – was also independently designed by the Bucharest group (Ovidiu Ivanciuc, Teodor-Silviu Balaban and Alexandru T. Balaban). Their report was also published in the same issue of the *Journal of Mathematical Chemistry* as the paper by Plavšić *et al*.[2] Balaban and his coworkers accepted the suggested name – Harary index.[6] This index is based on the chemists' intuitive expectation that distant sites in a structure should influence each other less than the near sites.

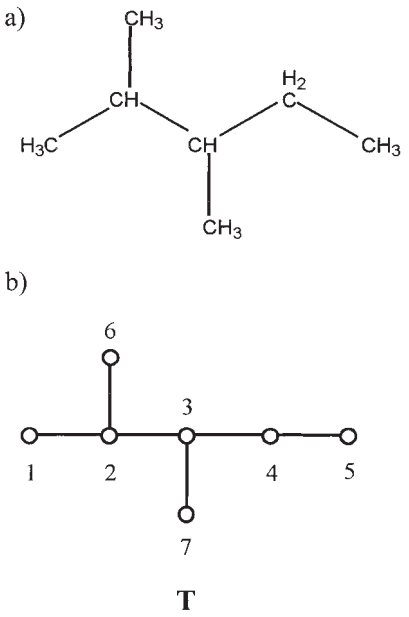

Figure 1. (a) 2,3-Dimethylpentane; (b) A labeled tree (T) representing the hydrogen-depleted skeleton of 2,3-dimethylpentane.

The Harary index and the related indices such as its extension to heterosystems[7] and the hyper-Harary index[3] have shown a modest success in structure-property correlations,[4,5,8–10] but the use of these indices in combination with other descriptors[11] appears to be very efficacious in improving the QSPR (quantitative structure-property relationship) models.

A part of the Sixteenth Dubrovnik International Course and Conference MATH/CHEM/COMP 2001 (Dubrovnik, Croatia; June 24–30, 2001) was dedicated to Professor Frank Harary in honor of his 80th birthday. We gave the progress report on the Harary index at the meeting. The summary of the report is given in the present paper.

In order to simplify the presentation, we will use the (chemical) graph theoretical terminology in referring to molecules and their structural characteristics.[12,13] Thus, a vertex will represent an atom and an edge a given bond in a molecule. In Figure 1, we give as an example a hydrogen-depleted tree representing 2,3-dimethylpentane.

DEFINITION OF THE HARARY INDEX

The Harary index, $H = H(\mathrm{G})$, of a molecular graph G with N vertices is based on the concept of reciprocal distance and is defined, in parallel to the Wiener index,[14–16] as the half-sum of the off-diagonal elements of the reciprocal molecular distance matrix $\boldsymbol{D}^{\boldsymbol{r}} = \boldsymbol{D}^{\boldsymbol{r}}(\mathrm{G})$:

$$H = (1/2) \sum_{i=1}^{N} \sum_{j=1}^{N} [\boldsymbol{D}^{\boldsymbol{r}}]_{ij} \tag{1}$$

The reciprocal distance matrix $\boldsymbol{D}^{\boldsymbol{r}}$ can be simply obtained by replacing all off-diagonal elements of the distance matrix $[\boldsymbol{D}]_{ij}$ by their reciprocals:

$$[\boldsymbol{D}^{\boldsymbol{r}}]_{ij} = 1/[\boldsymbol{D}]_{ij} \tag{2}$$

It should be noted that diagonal elements $(\boldsymbol{D}^{\boldsymbol{r}})_{ii}$ are all equal to zero by definition. This matrix was first mentioned by Balaban *et al.*[17]

The distance matrix $\boldsymbol{D}$ with the corresponding Wiener index W and the reciprocal distance matrix $\boldsymbol{D}^{\boldsymbol{r}}$ with the corresponding Harary index H for the 2,3-dimethylpentane tree are given below.

$$\boldsymbol{D} = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 & 2 & 3 \\ 1 & 0 & 1 & 2 & 3 & 1 & 2 \\ 2 & 1 & 0 & 1 & 2 & 2 & 1 \\ 3 & 2 & 1 & 0 & 1 & 3 & 2 \\ 4 & 3 & 2 & 1 & 0 & 4 & 3 \\ 2 & 1 & 2 & 3 & 4 & 0 & 3 \\ 3 & 2 & 1 & 2 & 3 & 3 & 0 \end{bmatrix} \qquad W = 46$$

$$\boldsymbol{D^r} = \begin{bmatrix} 0 & 1 & 1/2 & 1/3 & 1/4 & 1/2 & 1/3 \\ 1 & 0 & 1 & 1/2 & 1/3 & 1 & 1/2 \\ 1/2 & 1 & 0 & 1 & 1/2 & 1/2 & 1 \\ 1/3 & 1/2 & 1 & 0 & 1 & 1/3 & 1/2 \\ 1/4 & 1/3 & 1/2 & 1 & 0 & 1/4 & 1/3 \\ 1/2 & 1 & 1/2 & 1/3 & 1/4 & 0 & 1/3 \\ 1/3 & 1/2 & 1 & 1/2 & 1/3 & 1/3 & 0 \end{bmatrix} \qquad H = 12.0$$

MODIFIED HARARY INDEX

A problem of the Harary index, as well as of many other topological indices, such as the Wiener index[14] and the reversed Wiener index,[18] is that it gives greater weights to the inner (interior) edges and smaller weights to the outer (terminal) edges of an alkane tree.[19] We can illustrate this as follows. The elements of the distance matrix can be represented in terms of the shortest paths of different length; each path being broken into contributions of individual edges that make up the path. Note that a path is a sequence of adjacent edges, which do not pass through the same vertex more than once.[12] Similarly, the elements of the reciprocal distance matrix can be represented in terms of reciprocal shortest paths of different length. This is shown in Figure 2.

This observation opposes intuitive reasoning that the outer bonds, more exposed bonds, should have greater weights than inner bonds because the outer bonds are associated with the larger part of the molecular surface and are consequently expected to make a greater contribution to physical and chemical properties. The Wiener index has been successfully modified – the modification gives greater weights to outer than to inner edges in acyclic graphs.[19–21] Here we present a possible way of modifying the Harary index. We associate the *Harary matrix* $\boldsymbol{H}$ with the superimposed structure (such as

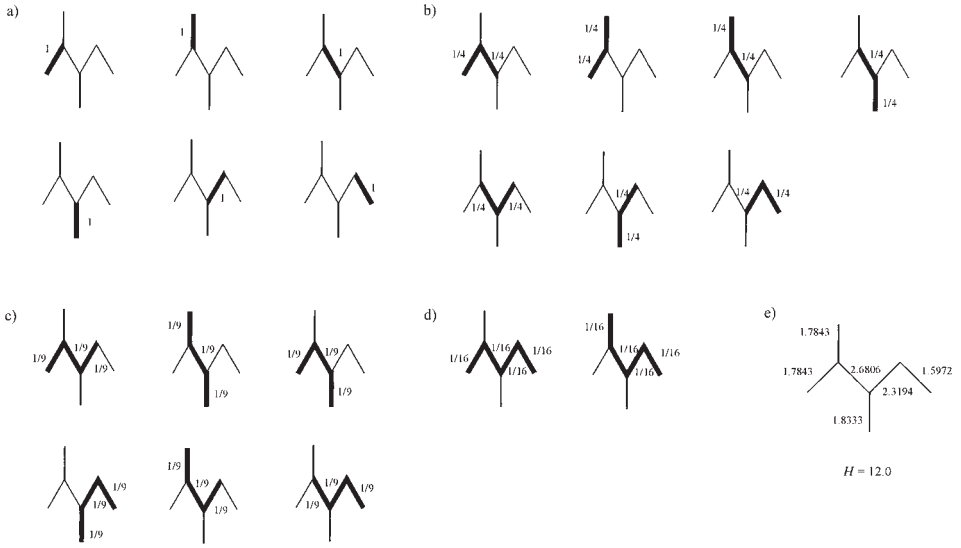

Figure 2. Weights of individual edges making up paths of different length that are used in the computation of the Harary index for the 2,3-dimethylpentane tree. (a) Weighted paths of length 1; (b) Weighted paths of length 2; (c) Weighted paths of length 3; (d) Weighted paths of lenght 4; (e) The superimposed structure.

the one given in Figure 2). This matrix corresponds to the *weighted* adjacency matrix of a graph because the non-vanishing matrix elements are equal to edge contributions to the Harary index, hence the name Harary matrix. The Harary matrix corresponding to the superimposed structure in Figure 2 is:

$$\boldsymbol{H} = \begin{bmatrix} 0 & 1.7847 & 0 & 0 & 0 & 0 & 0 \\ 1.7847 & 0 & 2.6806 & 0 & 0 & 1.7847 & 0 \\ 0 & 2.6806 & 0 & 2.3194 & 0 & 0 & 1.8333 \\ 0 & 0 & 2.3194 & 0 & 1.5972 & 0 & 0 \\ 0 & 0 & 0 & 1.5972 & 0 & 0 & 0 \\ 0 & 1.7847 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1.8333 & 0 & 0 & 0 & 0 \end{bmatrix}$$

The Harary matrix is a sparse matrix and the summation of the elements in the upper (or lower) half of the matrix gives the Harary index. We can modify the Harary matrix by replacing each non-zero element of the

matrix by its reciprocal. Thus, we obtained the *modified* Harary matrix $^{m}\boldsymbol{H}$. The sum of the elements in the upper (or lower) half of the modified Harary matrix gives the *modified* Harary index ^{m}H. The modified Harary matrix and the corresponding modified Harary index of the 2,3-dimethylpentane tree by utilizing the Harary matrix ($\boldsymbol{H}$) are:

$$^{m}\boldsymbol{H} = \begin{bmatrix} 0 & 0.5603 & 0 & 0 & 0 & 0 & 0 \\ 0.5603 & 0 & 0.3731 & 0 & 0 & 0.5603 & 0 \\ 0 & 0.3701 & 0 & 0.4311 & 0 & 0 & 0.5455 \\ 0 & 0 & 0.4311 & 0 & 0.6261 & 0 & 0 \\ 0 & 0 & 0 & 0.6261 & 0 & 0 & 0 \\ 0 & 0.5603 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.5455 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad ^{m}H = 3.0964$$

The superimposed structure corresponding to the modified Harary matrix is given in Figure 3.

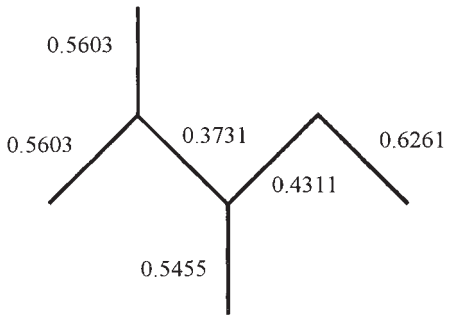

Figure 3. The superimposed structure, corresponding to the 2,3-dimethylpentane tree, related to the modified Harary matrix $^{m}\boldsymbol{H}$.

It is easily seen that the modified Harary index partitions into contributions that are greater for outer edges and smaller for inner edges of an alkane tree. Thus, the modified Harary index can be written as the following sum:

$$^{m}H = {}^{m}H(\text{outer edges}) + {}^{m}H(\text{inner edges}) \qquad (3)$$

In the example considered, ${}^{m}H$(outer edges) = 2.2922 and ${}^{m}H$(inner edges) = 0.8042.

Now we need to find out how this modification compares with the original Harary index in the QSPR modeling. Additionally, we will also consider the use of ${}^{m}H$(outer edges) in the modeling.

COMPARISON BETWEEN THE WIENER INDEX, HARARY INDEX AND MODIFIED HARARY INDEX

In Table I we give the Wiener indices W, Harary indices H, modified Harary indices ${}^{m}H$, the modified Harary indices for outer carbon-carbon bonds ${}^{m}H$(outer bonds), the number of paths of length three p_3 and the number of atoms N for 74 lower alkanes.

We will consider their eight representative physical properties: Boiling points at 20 °C (bp), molar volumes at 20 °C (mv), molar refractions at 20 °C (mr), heats of vaporization at 25 °C (hv), critical temperatures (ct), critical pressures (cp), surface tensions at 20 °C (st) and melting points (mp). Values of these properties are taken from Needham *et al*.[22] They are given in Table II.

TABLE I

Wiener indices W, Harary indices H, modified Harary indices ${}^{m}H$, modified Harary indices for outer bonds ${}^{m}H$(outer bonds) = ${}^{m}H$(ob), the number of paths of length three p_3 and the number of atoms N of 74 lower alkanes

Alkane	W	H	${}^{m}H$	${}^{m}H$(ob)	p_3	N
Ethane	1	1.0000	1.0000	1.0000	0	2
Propane	4	2.5000	1.6000	1.6000	0	3
Butane	10	4.3333	2.0901	1.4694	1	4
2-Methylpropane	9	4.5000	2.0000	2.0000	0	4
Pentane	20	6.4167	2.5254	1.4048	2	5
2-Methylbutane	18	6.6667	2.4276	1.9206	2	5
2,2-Dimethylpropane	16	7.0000	2.2857	2.2857	0	5
Hexane	35	8.7000	2.9267	1.3665	3	6
2-Methylpentane	32	9.0000	2.8313	1.8679	3	6
3-Methylpentane	31	9.0833	2.8159	1.8839	4	6
2,2-Dimethylbutane	28	9.5000	2.6721	2.4350	3	6
2,3-Dimethylbutane	29	9.3333	2.7319	2.3228	4	6

TABLE I (cont.)

Alkane	W	H	^{m}H	^{m}H(ob)	p_3	N
Heptane	56	11.1500	3.3036	1.3410	4	7
2-Methylhexane	52	11.4833	3.2123	1.8322	4	7
3-Methylhexane	50	11.6165	3.1935	1.8506	5	7
3-Ethylpentane	48	11.7498	3.1716	1.8783	6	7
2,2-Dimethylpentane	46	12.0832	3.0545	2.2054	4	7
2,3-Dimethylpentane	46	11.9998	3.0965	2.2923	6	7
2,4-Dimethylpentane	48	11.8332	3.1222	2.3040	4	7
3,3-Dimethylpentane	44	12.2498	3.0270	2.2292	6	7
2,3,3-Trimethylbutane	42	12.4998	2.9549	2.6120	6	7
Octane	84	13.7429	3.6622	1.3229	5	8
2-Methylheptane	79	14.1001	3.5746	1.8068	5	8
3-Methylheptane	76	14.2667	3.5555	1.8250	6	8
4-Methylheptane	75	14.3167	3.5517	1.8285	6	8
4-Ethylhexane	72	14.4831	3.5276	1.8601	7	8
2,2-Dimethylhexane	71	14.7665	3.4212	2.1756	5	8
2,3-Dimethylhexane	70	14.7331	3.4580	2.2621	7	8
2,4-Dimethylhexane	71	14.6498	3.4694	2.2868	6	8
2,5-Dimethylhexane	74	14.4665	3.4887	2.2810	5	8
3,3-Dimethylhexane	67	15.0331	3.3877	2.2056	7	8
3,4-Dimethylhexane	68	14.8664	3.4406	2.2766	8	8
3-Ethyl-2-methylpentane	67	14.9164	3.4328	2.2877	8	8
3-Ethyl-3-methylpentane	64	15.2497	3.3553	2.2361	9	8
2,2,3-Trimethylpentane	63	15.4164	3.3033	2.5912	8	8
2,2,4-Trimethylpentane	66	15.1665	3.3368	2.6225	5	8
2,3,3-Trimethylpentane	62	15.4997	3.2907	2.6004	9	8
2,3,4-Trimethylpentane	65	15.1664	3.3654	2.6797	8	8
2,2,3,3-Tetramethylbutane	58	15.9997	3.1657	2.8800	9	8
Nonane	120	16.4606	4.0064	1.3094	6	9
2-Methyloctane	114	16.8358	3.9218	1.7879	6	9
3-Methyloctane	110	17.0263	3.9034	1.8055	7	9
4-Methyloctane	108	17.1095	3.8986	1.8095	7	9
3-Ethylheptane	104	17.3000	3.8737	1.8426	8	9
4-Ethylheptane	102	17.3832	3.8667	1.8510	8	9
2,2-Dimethylheptane	104	17.5502	3.7731	2.1529	6	9
2,3-Dimethylheptane	102	17.5500	3.8081	2.2376	8	9

TABLE I (cont.)

Alkane	W	H	^{m}H	^{m}H(ob)	p_3	N
2,4-Dimethylheptane	102	17.5167	3.8156	2.2645	7	9
2,5-Dimethylheptane	104	17.4167	3.8213	2.2724	7	9
2,6-Dimethylheptane	108	17.2170	3.8388	2.2609	6	9
3,3-Dimethylheptane	98	17.8832	3.7389	2.1840	8	9
3,4-Dimethylheptane	98	17.7665	3.7865	2.2552	9	9
3,5-Dimethylheptane	100	17.6332	3.8016	2.2775	8	9
4,4-Dimethylheptane	96	17.9832	3.7318	2.1910	8	9
3-Ethyl-2-methylhexane	96	17.8497	3.7752	2.2707	9	9
4-Ethyl-2-methylhexane	98	17.7164	3.7912	2.2938	8	9
3-Ethyl-3-methylhexane	92	18.2330	3.6975	2.2240	10	9
3-Ethyl-4-methylhexane	94	17.9830	3.7597	2.2835	10	9
2,2,3-Trimethylhexane	92	18.3497	3.6535	2.5669	9	9
2,2,4-Trimethylhexane	94	18.1831	3.6737	2.6086	7	9
2,2,5-Trimethylhexane	98	17.9498	3.6932	2.6124	6	9
2,3,3-Trimethylhexane	90	18.4830	3.6375	2.5793	10	9
2,3,4-Trimethylhexane	92	18.2330	3.6973	2.6649	10	9
2,3,5-Trimethylhexane	96	17.9664	3.7269	2.6845	8	9
2,4,4-Trimethylhexane	92	18.3164	3.6579	2.6209	8	9
3,3,4-Trimethylhexane	88	18.6163	3.6217	2.5907	11	9
3,3-Diethylpentane	88	18.4996	3.6604	2.2589	12	9
2,2-Dimethyl-3-ethylpentane	88	18.5830	3.6264	2.5918	10	9
2,3-Dimethyl-3-ethylpentane	86	18.7496	3.6023	2.6064	12	9
2,4-Dimethyl-3-ethylpentane	90	18.3330	3.6846	2.6753	10	9
2,2,3,3-Tetramethylpentane	82	19.2497	3.4878	2.8742	12	9
2,2,3,4-Tetramethylpentane	86	18.8330	3.5660	2.9643	10	9
2,2,4,4-Tetramethylpentane	88	18.7498	3.5482	2.9288	6	9
2,3,3,4-Tetramethylpentane	84	18.9996	3.5442	2.9540	12	9

We tested the following QSPR models: (i) Linear model – P = a + b (TI), (ii) Model used by Wiener[14] – P = a + b (TI/N^2) + c p_3, and (iii) Multivariate model, where P = physical property, TI = topological index, N = number of vertices and p_3 = number of paths of length 3.

Statistical parameters for the linear models are given in Table III, for the Wiener-like models in Table IV, and for the multivariate models in Table V.

TABLE II

Boiling points bp / °C, molar volumes mv / cm^3, molar refractions mr / cm^3, heats of vaporization hv / kJ, critical temperatures ct / °C, critical pressures cp / atm, surface tensions st / dyne cm^{-1} and melting points mp / °C of lower alkanes

Alkane	bp / °C	mv / cm^3	mr / cm^3	hv / kJ	ct / °C	cp / atm	st / dyne cm^{-1}	mp / °C
Ethane	–88.6				32.3	48.2		–183.3
Propane	–42.1				96.8	42.0		–187.7
Butane	–0.5				152.0	37.5		–138.4
2-Methylpropane	–11.7				135.0	36.0		–159.6
Pentane	36.1	115.2	25.27	26.4	196.6	33.3	16.00	–129.7
2-Methylbutane	27.9	116.4	25.29	24.6	187.8	32.9	15.00	–159.9
2,2-Dimethylpropane	9.5	122.1	25.72	21.8	160.6	31.6		–16.6
Hexane	68.7	130.7	29.91	31.6	234.7	29.9	18.42	–95.4
2-Methylpentane	60.3	131.9	29.95	29.9	224.9	30.0	17.38	–153.7
3-Methylpentane	63.3	129.7	29.80	30.3	231.2	30.8	18.12	–118.0
2,2-Dimethylbutane	49.7	132.7	29.93	27.7	216.2	30.7	16.30	–99.9
2,3-Dimethylbutane	58.0	130.2	29.81	29.1	227.1	31.0	17.37	–128.5
Heptane	98.4	146.5	34.55	36.6	267.0	27.0	20.26	–90.6
2-Methylhexane	90.1	147.7	34.59	34.8	257.9	27.2	19.29	–118.3
3-Methylhexane	91.9	145.8	34.46	35.1	262.4	28.1	19.79	–119.4
3-Ethytlpentane	93.5	143.5	34.28	35.2	267.6	28.6	20.44	–118.6
2,2-Dimethylpentane	79.2	148.7	34.62	32.4	247.7	28.4	18.02	–123.8
2,3-Dimethylpentane	89.8	144.2	34.32	34.2	264.6	29.2	19.96	–119.1
2,4-Dimethylpentane	80.5	148.9	34.62	32.9	247.1	27.4	18.15	–119.2
3,3-Dimethylpentane	86.1	144.5	34.33	33.0	263.0	30.0	19.59	–134.5
2,3,3-Trimethylbutane	80.9	145.2	34.37	32.0	258.3	29.8	18.76	–24.9
Octane	125.7	162.6	39.19	41.5	296.2	24.64	21.76	–56.8
2-Methylheptane	117.6	163.7	39.23	39.7	288.0	24.80	20.60	–109.0
3-Methylheptane	118.9	161.8	39.10	39.8	292.0	25.60	21.17	–120.5
4-Methylheptane	117.7	162.1	39.12	39.7	290.0	25.60	21.00	–121.0
3-Ethylhexane	118.5	160.1	38.94	39.4	292.0	25.74	21.51	
2,2-Dimethylhexane	106.8	164.3	39.25	37.3	279.0	25.60	19.60	–121.2
2,3-Dimethylhexane	115.6	160.4	38.98	38.8	293.0	26.60	20.99	
2,4-Dimethylhexane	109.4	163.1	39.13	37.8	282.0	25.80	20.05	–137.5
2,5-Dimethylhexane	109.1	164.7	39.26	37.9	279.0	25.00	19.73	–91.2
3,3-Dimethylhexane	112.0	160.9	39.01	37.9	290.8	27.20	20.63	–126.1

TABLE II (cont.)

Alkane	bp / °C	mv / cm^3	mr / cm^3	hv / kJ	ct / °C	cp / atm	st / dyne cm^{-1}	mp / °C
3,4-Dimethylhexane	117.7	158.8	38.85	39.0	298.0	27.40	21.64	
3-Ethyl-2-methylpentane	115.7	158.8	38.84	38.5	295.0	27.40	21.52	–115.0
3-Ethyl-3-methylpentane	118.3	157.0	38.72	38.0	305.0	28.90	21.99	–90.9
2,2,3-Trimethylpentane	109.8	159.5	38.92	36.9	294.0	28.20	20.67	–112.3
2,2,4-Trimethylpentane	99.2	165.1	39.26	35.1	271.2	25.50	18.77	–107.4
2,3,3-Trimethylpentane	114.8	157.3	38.76	37.2	303.0	29.00	21.56	–100.7
2,3,4-Trimethylpentane	113.5	158.9	38.87	37.6	295.0	27.60	21.14	–109.2
2,2,3,3-Tetramethylbutane	106.5				270.8	24.50		
Nonane	150.8	178.7	43.84	46.4	322.0	22.74	22.92	–53.5
2-Methyloctane	143.3	179.8	43.88	44.7	315.0	23.60	21.88	–80.4
3-Methyloctane	144.2	178.0	43.73	44.8	318.0	23.70	22.34	–107.6
4-Methyloctane	142.5	178.2	43.77	44.8	318.3	23.06	22.34	–113.2
3-Ethylheptane	143.0	176.4	43.64	44.8	318.0	23.98	22.81	–114.9
4-Ethylheptane	141.2	175.7	43.49	44.8	318.3	23.98	22.81	
2,2-Dimethylheptane	132.7	180.5	43.91	42.3	302.0	22.80	20.80	–113.0
2,3-Dimethylheptane	140.5	176.7	43.63	43.8	315.0	23.79	22.34	–116.0
2,4-Dimethylheptane	133.5	179.1	43.74	42.9	306.0	22.70	21.30	
2,5-Dimethylheptane	136.0	179.4	43.85	42.9	307.8	22.70	21.30	
2,6-Dimethylheptane	135.2	180.9	43.93	42.8	306.0	23.70	20.83	–102.9
3,3-Dimethylheptane	137.3	176.9	43.69	42.7	314.0	24.19	22.01	
3,4-Dimethylheptane	140.6	175.3	43.55	43.8	322.7	24.77	22.80	
3,5-Dimethylheptane	136.0	177.4	43.64	43.0	312.3	23.59	21.77	
4,4-Dimethylheptane	135.2	176.9	43.60	42.7	317.8	24.18	22.01	
3-Ethyl-2-methylhexane	138.0	175.4	43.66	43.8	322.7	24.77	22.80	
4-Ethyl-2-methylhexane	133.8	177.4	43.65	43.0	330.3	25.56	21.77	
3-Ethyl-3-methylhexane	140.6	173.1	43.27	43.0	327.2	25.66	23.22	
3-Ethyl-4-methylhexane	140.4	172.8	43.37	44.0	312.3	23.59	23.27	
2,2,3-Trimethylhexane	133.6	175.9	43.62	41.9	318.1	25.07	21.86	
2,2,4-Trimethylhexane	126.5	179.2	43.76	40.6	301.0	23.39	20.51	–120.0
2,2,5-Trimethylhexane	124.1	181.3	43.94	40.2	296.6	22.41	20.04	–105.8
2,3,3-Trimethylhexane	137.7	173.8	43.43	42.2	326.1	25.56	22.41	–116.8
2,3,4-Trimethylhexane	139.0	173.5	43.39	42.9	324.2	25.46	22.80	
2,3,5-Trimethylhexane	131.3	177.7	43.65	41.4	309.4	23.49	21.27	–127.8
2,4,4-Trimethylhexane	130.6	177.2	43.66	40.8	309.1	23.79	21.17	–113.4

TABLE II (cont.)

Alkane	bp / °C	mv / cm^3	mr / cm^3	hv / kJ	ct / °C	cp / atm	st / dyne cm^{-1}	mp / °C
3,3,4-Trimethylhexane	140.5	172.1	43.34	42.3	330.6	26.45	23.27	–101.2
3,3-Diethylpentane	146.2	170.2	43.11	43.4	342.8	26.94	23.75	–33.1
2,2-Dimethyl-3-ethyl-pentane	133.8	174.5	43.46	42.0	338.6	25.96	22.38	–99.2
2,3-Dimethyl-3-ethyl-pentane	142.0	170.1	42.95	42.6	322.6	26.94	23.87	
2,4-Dimethyl-3-ethyl-pentane	136.7	173.8	43.40	42.9	324.2	25.46	22.80	–122.2
2,2,3,3-Tetramethyl-pentane	140.3	169.5	43.21	41.0	334.5	27.04	23.38	–9.9
2,2,3,4-Tetramethyl-pentane	133.0	173.6	43.44	41.0	319.6	25.66	21.98	–121.1
2,2,4,4-Tetramethyl-pentane	122.3	178.3	43.87	38.1	301.6	24.58	20.37	–66.5
2,3,3,4-Tetramethyl-pentane	141.6	169.9	43.20	41.8	334.5	26.85	23.31	–102.1

In the case of multivariate models, we used six descriptors given in Table I, their logarithmically transformed values (six descriptors), and squares and crossproducts of the initial descriptors (21 descriptors). Thus, the total number of descriptors used was 33. In modeling, we considered all possible combinations of these descriptors with up to five descriptors. In Table V only the best multivariate models are reported for a given number of descriptors. These models were selected by using the CROMRsel algorithm[23] for the selection of the best possible sub-set of I descriptors from the initial set of N descriptors into the multiregression models. The quality of models is expressed by fitted (descriptive) statistical parameters: the correlation coefficient (R), standard error of estimate (S) and F-test (F). In addition, models are internally validated by computation of the leave-one-out cross-validated correlation coefficient (R_{cv}) and standard error of estimate (S_{cv}).

From the statistical results, presented in Tables III-V, we learn:

(i) Comparison between linear models (see Table III) indicates the following: (1) The modified Harary index produced the best models for boiling points, heats of vaporization and critical pressures; (2) The number of carbon atoms gives the best statistical parameters for models of molar volumes, molar refractions, critical temperatures and surface tensions. Addi-

TABLE III

Statistical parameters of linear models[a]

Descriptors	R	R_{cv}	S	S_{cv}	F-test
			bp – 74		
W	0.9170	0.9057	18.341	19.495	380.7
H	0.9564	0.9502	13.426	14.333	772.9
${}^{m}H$	0.9863	0.9858	7.575	7.737	2582.2
${}^{m}H$(ob)	0.4369	0.3455	41.369	43.340	17.0
p_3	0.8342	0.8154	25.363	26.631	164.7
N	0.9855	0.9835	7.808	8.324	2425.8
			mv – 69		
W	0.9720	0.9693	4.027	4.213	1145.2
H	0.9586	0.9562	4.877	5.012	759.6
${}^{m}H$	0.9638	0.9608	4.567	4.752	875.7
${}^{m}H$(ob)	0.3313	0.2430	16.163	16.689	8.3
$480p_3$	0.6851	0.6587	12.478	12.897	59.3
N	0.9868	0.9860	2.775	2.859	2485.6
			mr – 69		
W	0.9616	0.9581	1.430	1.494	822.7
H	0.9817	0.9805	0.993	1.024	1777.5
${}^{m}H$	0.9612	0.9588	1.438	1.481	813.0
${}^{m}H$(ob)	0.3641	0.2879	4.855	5.008	10.2
p_3	0.7671	0.7485	3.344	3.458	95.8
N	0.9992	0.9992	0.206	0.212	42968.3
			hv – 69		
W	0.9642	0.9609	1.412	1.476	887.0
H	0.9097	0.9033	2.212	2.286	321.7
${}^{m}H$	0.9870	0.9864	0.856	0.874	2531.1
${}^{m}H$(ob)	0.1260	0.1091	5.285	5.449	1.1
p_3	0.7444	0.7224	3.557	3.686	83.3
N	0.9580	0.9550	1.527	1.579	748.1
			ct – 74		
W	0.8832	0.8682	26.666	28.221	255.3
H	0.9560	0.9489	16.672	17.945	765.4
${}^{m}H$	0.9653	0.9635	14.838	15.231	985.1

TABLE III (cont.)

Descriptors	R	R_{cv}	S	S_{cv}	F-test
^{m}H(ob)	0.4881	0.4100	49.623	52.022	22.5
p_3	0.8673	0.8509	28.303	29.878	218.6
N	0.9766	0.9734	12.224	13.034	1485.7
			cp – 74		
W	0.8729	0.8532	2.100	2.246	230.5
H	0.8730	0.8524	2.099	2.251	230.7
^{m}H	0.9610	0.9548	1.190	1.281	869.7
^{m}H(ob)	0.3926	0.2612	3.959	4.190	13.1
p_3	0.6233	0.5694	3.366	3.545	45.7
N	0.9291	0.9167	1.593	1.720	454.1
			st – 68		
W	0.8109	0.7965	1.120	1.158	126.7
H	0.8687	0.8594	0.948	0.979	202.9
^{m}H	0.8534	0.8451	0.998	1.023	177.0
^{m}H(ob)	0.2371	0.1055	1.860	1.921	3.9
p_3	0.8796	0.8697	0.911	0.945	225.6
N	0.8801	0.8726	0.909	0.935	226.9
			mp – 56		
W	0.3675	0.2536	31.866	33.361	8.4
H	0.4363	0.3456	30.832	32.269	12.7
^{m}H	0.4252	0.3330	31.012	32.412	11.9
^{m}H(ob)	0.2546	0.0735	33.135	34.764	3.7
p_3	0.3819	0.2384	31.666	33.632	9.2
N	0.4457	0.3614	30.672	32.040	13.4

[a] Abbreviations for properties considered are the same as in Table II. The number after each abbreviation corresponds to the number of alkanes with a known property.

tionally, the structure-boiling point model based on the number of carbon atoms is only slightly worse (R = 0.9855, R_{cv} = 0.9835, S = 7.8, S_{cv} = 8.3, F = 2426) than the model based on the modified Harary index (R = 0.9863, R_{cv} = 0.9858, S = 7.6, S_{cv} = 7.7, F = 2582). Therefore, it seems that the number of carbon atoms is a good descriptor for QSPR of lower alkanes. However, it cannot distinguish isomers, producing the so-called 'comb'-type correlations. Thus, the modified Harary index is preferred because it can

TABLE IV

Statistical parameters of Wiener-like models[a]

Descriptors	R	R_{cv}	S	S_{cv}	F-test
			bp – 74		
W/N^2, p_3	0.9909	0.9882	6.199	7.057	1918.5
H/N^2, p_3	0.9405	0.9290	15.627	17.015	272.0
${}^mH/N^2$, p_3	0.9581	0.9421	13.172	15.424	397.3
${}^mH(\mathrm{ob})/N^2$, p_3	0.9685	0.9574	11.445	13.281	537.8
			mv – 69		
W/N^2, p_3	0.9361	0.9286	6.025	6.356	233.8
H/N^2, p_3	0.9289	0.9192	6.344	6.745	207.6
${}^mH/N^2$, p_3	0.9621	0.9549	4.671	5.088	410.8
${}^mH(\mathrm{ob})/N^2$, p_3	0.8667	0.8430	8.546	9.213	99.6
			mr – 69		
W/N^2, p_3	0.9563	0.9515	1.524	1.603	353.1
H/N^2, p_3	0.9511	0.9449	1.609	1.707	313.2
${}^mH/N^2$, p_3	0.9705	0.9649	1.256	1.370	535.0
${}^mH(\mathrm{ob})/N^2$, p_3	0.9066	0.8905	2.200	2.372	152.3
			hv – 69		
W/N^2, p_3	0.9972	0.9969	0.399	0.422	5861.5
H/N^2, p_3	0.9953	0.9943	0.514	0.568	3518.1
${}^mH/N^2$, p_3	0.9037	0.8910	2.281	2.419	147.0
${}^mH(\mathrm{ob})/N^2$, p_3	0.9605	0.9513	1.483	1.641	392.8
			ct – 74		
W/N^2, p_3	0.9822	0.9769	10.687	12.146	969.3
H/N^2, p_3	0.9368	0.9250	19.892	21.601	254.5
${}^mH/N^2$, p_3	0.9760	0.9688	12.369	14.090	714.6
${}^mH(\mathrm{ob})/N^2$, p_3	0.9830	0.9787	10.431	11.679	1019.2
			cp – 74		
W/N^2, p_3	0.9396	0.9251	1.473	1.634	267.6
H/N^2, p_3	0.8245	0.7891	2.436	2.645	75.4
${}^mH/N^2$, p_3	0.9330	0.9065	1.549	1.818	238.5
${}^mH(\mathrm{ob})/N^2$, p_3	0.9205	0.9074	1.682	1.810	197.0

TABLE IV (cont.)

Descriptors	R	R_{cv}	S	S_{cv}	F-test
		st – 68			
W/N^2, p_3	0.9764	0.9740	0.413	0.434	664.5
H/N^2, p_3	0.9769	0.9744	0.410	0.430	677.8
${}^mH/N^2$, p_3	0.9208	0.9128	0.747	0.782	181.1
${}^mH(\mathrm{ob})/N^2$, p_3	0.9863	0.9847	0.316	0.333	1159.9
		mp – 56			
W/N^2, p_3	0.4285	0.2432	30.959	33.236	6.0
H/N^2, p_3	0.3836	0.1499	31.643	33.877	4.6
${}^mH/N^2$, p_3	0.4978	0.3784	29.717	31.717	8.7
${}^mH(\mathrm{ob})/N^2$, p_3	0.4772	0.3536	30.111	32.051	7.8

[a]See footnote to Table III.

distinguish most isomers. The same is true of the Harary index. It should be noted that although both the Harary index and modified Harary index possess a fair discriminating power, they are not unique; (3) Comparison between the original Harary index and its modification reveals that the H index produced better models only in two cases (QSPR models of molar refractions and surface tensions); (4) Surprisingly poor models were obtained with ${}^mH(\mathrm{ob})$. Apparently, this index is much more potent in combination with other kinds of topological indices, and (5) All linear models for melting points are poor.

(ii) In the case of the Wiener-like models (see Table IV), the *reduced* Wiener index (W/N^2) (Ref. 24) produced the best models for boiling points, heats of vaporization and critical pressures, the *reduced* modified Harary (${}^mH/N^2$) led to the best models for molar volumes and molar refractions, ${}^mH(\mathrm{ob})/N^2$ gave the best models for critical temperatures and surface tensions, and all indices produced poor models for melting points. It is not surprising that the Wiener index is doing so well because this type of modeling was tailor-made for this index. Apparently, the Wiener index, which is a sterically deficient index, is augmented in modeling by the steric corrections in terms of the p_3 index. Since the Harary-type indices are sterically sensitive, they do not depend much on the p_3 index in modeling.

(iii) Comparison between the best linear models and the best Wiener-like models reveals the following: (1) The former are better in the case of molar volumes, molar refractions and critical pressures, and (2) The latter are su-

TABLE V

Statistical parameters of multivariate models[a]

I[b]	Descriptors	R	R_{cv}	S	S_{cv}	F-test
		bp – 74				
1	${}^{m}H$	0.9863	0.9858	7.575	7.736	2582.2
2	${}^{m}H$, p_3	0.9974	0.9968	3.320	3.666	6775.2
3	p_3, ln(W), ln(H)	0.9991	0.9984	1.991	2.591	12421.9
4	p_3, ln(W), ln(H), ln(${}^{m}H$)	0.9995	0.9994	1.503	1.638	16124.4
5	W, p_3, $W{\cdot}N$, ln(W), ln(${}^{m}H$(ob))	0.9997	0.9996	1.160	1.266	21378.1
		mv – 69				
1	${}^{m}H{\cdot}N$	0.9874	0.9864	2.713	2.816	2603.6
2	p_3, N	0.9990	0.9989	0.750	0.802	17197.1
3	p_3, N, ln(${}^{m}H$(ob))	0.9995	0.9993	0.554	0.625	20663.4
4	p_3, N, ${}^{m}H{\cdot}p_3$, ln(${}^{m}H$(ob))	0.9996	0.9995	0.464	0.528	21797.8
5	$W{\cdot}{}^{m}H$, $H{\cdot}H$, $H{\cdot}p_3$, $H{\cdot}N$, $p_3{\cdot}N$	0.9997	0.9996	0.403	0.487	22721.0
		mr – 69				
1	N	0.9992	0.9992	0.206	0.212	42968.3
2	p_3, N	0.9999	0.9999	0.054	0.058	305183.7
3	p_3, N, ${}^{m}H$(ob)$\cdot p_3$	1.0000	1.0000	0.047	0.051	263776.5
4	p_3, N, ${}^{m}H$(ob)$\cdot p_3$, ln(p_3)	1.0000	0.9999	0.044	0.070	221104.5
5	p_3, N, ${}^{m}H$(ob)$\cdot p_3$, $p_3{\cdot}p_3$, ln(p_3)	1.0000	0.9998	0.043	0.114	181288.1
		hv – 69				
1	${}^{m}H$	0.9870	0.9864	0.856	0.874	2531.1
2	${}^{m}H$, $p_3{\cdot}p_3$	0.9957	0.9953	0.496	0.518	3775.8
3	${}^{m}H$, ${}^{m}H$(ob)$\cdot N$, $p_3{\cdot}N$	0.9989	0.9988	0.246	0.264	10130.2
4	${}^{m}H$, $H{\cdot}H$, $H{\cdot}{}^{m}H$(ob), ${}^{m}H$(ob)$\cdot p_3$	0.9993	0.9992	0.204	0.219	10918.7
5	H, $H{\cdot}{}^{m}H$, ${}^{m}H{\cdot}{}^{m}H$(ob), ${}^{m}H$(ob)$\cdot p_3$, ln(N)	0.9993	0.9992	0.192	0.216	9663.5
		ct – 74				
1	ln(N)	0.9807	0.9778	11.117	11.915	1811.2
2	p_3, ln(W)	0.9960	0.9956	5.056	5.339	4453.5
3	p_3, ln(W), ln(${}^{m}H$(ob))	0.9971	0.9968	4.309	4.511	4038.8
4	p_3, ${}^{m}H{\cdot}p_3$, ln(W), ln(${}^{m}H$(ob))	0.9972	0.9967	4.278	4.619	3029.0
5	${}^{m}H$, p_3, $W{\cdot}{}^{m}H$(ob), $H{\cdot}{}^{m}H$, $H{\cdot}N$	0.9972	0.9966	4.252	4.655	2418.4

TABLE V (cont.)

I[b]	Descriptors	R	R_{cv}	S	S_{cv}	F-test
		cp – 74				
1	ln(W)	0.9717	0.9703	1.017	1.041	1219.1
2	p_3, ln(N)	0.9826	0.9790	0.800	0.877	992.5
3	p_3, ^mH·N, ln(N)	0.9876	0.9861	0.675	0.714	925.0
4	p_3, p_3·N, ln(H), ln(N)	0.9881	0.9861	0.663	0.716	709.4
5	p_3, N, W·p_3, ^mH·^mH, ^mH·N	0.9884	0.9858	0.655	0.723	573.9
		st – 68				
1	^mH·p_3	0.9213	0.9146	0.745	0.774	370.4
2	ln(^mH(ob)), ln(p_3)	0.9817	0.9800	0.365	0.381	863.2
3	p_3, ^mH·^mH(ob), ln(^mH)	0.9925	0.9908	0.234	0.259	1410.9
4	p_3·p_3, ln(^mH), ln(^mH(ob)), ln(p_3)	0.9951	0.9940	0.190	0.210	1585.3
5	p_3, N, ^mH·^mH(ob), ^mH(ob)·^mH(ob), ln(^mH)	0.9955	0.9937	0.181	0.214	1379.5
		mp – 56				
1	ln(H)	0.4868	0.4344	29.931	30.863	16.8
2	H, W·^mH(ob)	0.5593	0.4928	28.403	29.815	12.1
3	N, ^mH·^mH(ob), ^mH(ob)·^mH(ob)	0.7411	0.6667	23.004	25.538	21.1
4	H·^mH(ob), ^mH·^mH(ob), ^mH(ob)·N, ln(W)	0.7632	0.6884	22.140	24.854	17.8
5	H, H·p_3, ^mH·^mH(ob), ^mH(ob)·^mH(ob), p_3·p_3	0.8125	0.7391	19.974	23.081	19.4

[a] See footnote to Table III.
[b] Symbol I stands for the number of parameters used in the model.

perior for boiling points, heats of vaporization, critical temperatures and surface tensions. However, all of these models are inferior to the multivariate models.

(iv) In all the considered cases, the best models obtained are the multivariate models (see Table V). These models with three or more descriptors always contain ^mH and/or ^mH(ob) and p_3 and/or their ln values.

(v) Our four-parameter multivariate models are in all studied cases comparable to five-parameter models, based on a variety of connectivity indices, reported by Needham *et al*.[22] We compare our models to those of Needham *et al*. because they reported a very detailed study on modeling the physical

properties of lower alkanes. Thus, there is a set of good structure-property models, against which we compared our models. However, Needham *et al*. have reported only the fitted statistical parameters of their models. Therefore, we will discuss only the comparison between the fitted statistical parameters of our models and their models. We also carried out the leave-one-out cross-validation procedure to evaluate the quality of our models. Since in all cases the differences between fitted and cross-validated statistical parameters of models generated in this study are acceptable, we conclude that our models are significant and stable.

(vi) Our four-parameter structure-boiling point model involves ln W, ln H, ln ${}^{m}H$ and p_3. Statistical parameters of this model (R = 0.9995, S = 1.5, F = 16124) are better than those of the five-parameter model of Needham *et al.* (R = 0.9995, S = 1.86, F = 9030). Our five-parameter model (R = 0.9997, S = 1.16, F = 21378) is much better than the same size model of Needham *et al*.

(vii) Our four-parameter structure-molar volume model involves ln ${}^{m}H$(ob), ${}^{m}H \cdot p_3$, N and p_3. Statistical parameters of this model (R = 0.9996, S = 0.46, F = 21797) are comparable to those of the five-parameter model reported by Needham *et al.* (R = 0.9995, S = 0.5, F = 14294). However, our five-parameter model is superior (R = 0.9997, S = 0.40, F = 22721).

(viii) Our four-parameter structure-molar refraction model involves ln p_3, ${}^{m}H$(ob)$\cdot p_3$, N and p_3. Statistical parameters of this model (R = 1.0, S = 0.04, F = 221104) are only slightly better than those of the five-parameter model reported by Needham *et al.* (R = 0.9999, S = 0.05, F = 152558).

(ix) Our four-parameter structure-heats of vaporization model involves ${}^{m}H$, $H \cdot H$, $H \cdot {}^{m}H$(ob) and ${}^{m}H$(ob)$\cdot p_3$. Statistical parameters of the model (R = 0.9993, S = 0.20, F = 10919) are comparable to those of the five-parameter model reported by Needham *et al.* (R = 0.9990, S = 0.2, F = 7849).

(x) Our four-parameter structure-critical temperature model involves ln W, ln ${}^{m}H$(ob), ${}^{m}H \cdot p_3$ and p_3. Statistical parameters of this model (R = 0.9972, S = 4.28, F = 3029) are comparable to those of the five-parameter model reported by Needham *et al.* (R = 0.9975, S = 4.1, F = 2795).

(xi) Our four-parameter structure-critical pressure model involves ln H, ln N, $N \cdot p_3$ and p_3. Statistical parameters of this model (R = 0.9881, S = 0.66, F = 709) are comparable to those of the five-parameter model reported by Needham *et al.* (R = 0.9889, S = 0.7, F = 594).

(xii) Our four-parameter structure-surface tension model involves ln ${}^{m}H$, ln ${}^{m}H$(ob), ln p_3 and $p_3 \cdot p_3$. Statistical parameters of this model (R = 0.9951, S = 0.19, F = 1585) are comparable to those of the five-parameter model reported by Needham *et al.* (R = 0.9945, S = 0.2, F = 1152).

(xiii) Our four-parameter structure-melting point model involves ln W, $H \cdot {}^{m}H$(ob), ${}^{m}H \cdot {}^{m}H$(ob) and $N \cdot {}^{m}H$(ob). Statistical parameters of this model (R = 0.7632, S = 22.14, F = 18) are poor. The same is true of the five-parameter model reported by Needham *et al.* (R = 0.7550, S = 23.8, F = 13). It is a well-known fact that the modeling of melting points is difficult. Actually, we could not find a good QSPR model for predicting melting points in literature.

(xiv) We also considered the intercorrelation between the indices given in Table I. The relationship between the pairs of indices is considered. The intercorrelation matrix reflecting the pairwise linear correlations between the

TABLE VI

Intercorrelation matrix

	W	H	${}^{m}H$	${}^{m}H$(ob)	p_3	N
W	1.0000	0.9244	0.9411	0.3084	0.7239	0.9428
H	0.9244	1.0000	0.9304	0.5987	0.8870	0.9877
${}^{m}H$	0.9411	0.9304	1.0000	0.3571	0.7458	0.9754
${}^{m}H$(ob)	0.3084	0.5987	0.3571	1.0000	0.6191	0.5176
p_3	0.7239	0.8870	0.7458	0.6191	1.0000	0.8394
N	0.9428	0.9877	0.9754	0.5176	0.8394	1.0000

six topological indices computed for 74 lower alkanes is given in Table VI.

The degree of the intercorrelation was appraised by the correlation coefficient R. Pairs of indices with R = 0.97 are considered highly intercorrelated, those with R between 0.90 and 0.97 appeciably intercorrelated, those with R = 0.90 weakly intercorrelated and, finally, those pairs of indices with R = 0.5 not intercorrelated.[11,25] Thus, two pairs of indices are highly intercorrelated: (H, N) and (${}^{m}H$, N), four pairs appreciably intercorrelated: (W, H), (W, ${}^{m}H$), (W, N) and (H, ${}^{m}H$), two pairs weakly intercorrelated: (H, p_3) and (p_3, N), and five pairs are not intercorrelated: (W, ${}^{m}H$(ob)), (W, p_3), (H, ${}^{m}H$(ob)), (${}^{m}H$, ${}^{m}H$(ob) and (${}^{m}H$(ob), N). It is interesting to note that the best multivariate models contain combinations of all indices, regardless of their intercorrelation status. This serves as a warning that it is not a good practice to eliminate, following the traditional views, highly intercorrelated indices from the modeling.

CONCLUDING REMARKS

Since its inception, the Harary index H has undergone several developments, such as the hyper-Harary index[3] HH and variable Harary index H^f.[19,26] Here, we have introduced the modified Harary index ${}^mH$ and we have also used the reduced Harary index H/N^2 and the reduced modified Harary index ${}^mH/N^2$. The modified Harary index gives greater contributions to outer bonds than to inner bonds in a molecule. This is opposite to the behavior of the original Harary index and complies with the chemists' understanding of the bond-bond interactions between molecules that are important for many physical properties. It is shown that ${}^mH$ has a great potential in the multivariate regression analysis since it was involved in all the best multivariate models obtained for eight properties of alkanes modeled in this study.

Acknowledgements. – This work was supported in part by the Ministry of Science and Technology of the Republic of Croatia through grants 00980606 (BL, AM, SN, NT). We thank the referees for helpful comments.

REFERENCES

1. These two lines are taken from Frank Harary's poem »Same Time Next Year in Dubrovnik, Croatia«, *Croat. Chem. Acta* **74** (2001) III.
2. D. Plavšić, S. Nikolić, N. Trinajstić, and Z. Mihalić, *J. Math. Chem*. **12** (1993) 235–250.
3. V. Diudea, *J. Chem. Inf. Comput. Sci*. **37** (1997) 292–299.
4. J. Devillers and A. T. Balaban, *Topological Indices and Related Descriptors in QSAR and QSPR*, Gordon & Breach Sci. Publ., Amsterdam, 1999.
5. R. Todeschini and V. Consonni, *Handbook of Molecular Descriptors*, Wiley-VCH, Weinheim, 2000.
6. O. Ivanciuc, T.-S. Balaban, and A. T. Balaban, *J. Math. Chem*. **12** (1993) 309–318.
7. O. Ivanciuc, T. Ivanciuc, and A. T. Balaban, *J. Chem. Inf. Comput. Sci.* **38** (1998) 395–401.
8. Z. Mihalić and N. Trinajstić, *J. Chem. Educ.* **69** (1992) 701–712.
9. O. Ivanciuc, *J. Chem. Inf. Comput. Sci*. **40** (2000) 1412–1422.
10. B. Lučić, I. Lukovits, S. Nikolić, and N. Trinajstić, *J. Chem. Inf. Comput. Sci*. **41** (2001) 527–535.
11. N. Trinajstić, S. Nikolić, S. C. Basak, and I. Lukovits, *SAR QSAR Environ. Res*. **12** (2001) 31–54.
12. F. Harary, *Graph Theory*, 2nd printing, Addison-Wesley, Reading, MA, 1971.
13. N. Trinajstić, *Chemical Graph Theory*, 2nd revised edition, CRC Press, Boca Raton, FL, 1992.
14. H. Wiener, *J. Am. Chem. Soc*. **69** (1947) 17–20.
15. H. Hosoya, *Bull. Chem. Soc. Jpn*. **44** (1971) 2332–2339.
16. S. Nikolić, N. Trinajstić, and Z. Mihalić, *Croat. Chem. Acta* **68** (1995) 105–129.
17. T. S. Balaban, P. A. Filip, and O. Ivanciuc, *J. Math. Chem*. **11** (1992) 79–105.

18. A. T. Balaban, D. Mills, O. Ivanciuc, and S. C. Basak, *Croat. Chem. Acta* **73** (2000) 923–941
19. M. Randić and J. Zupan, *J. Chem. Inf. Comput. Sci.* **41** (2001) 550–560.
20. S. Nikolić, N. Trinajstić, and M. Randić, *Chem. Phys. Lett.* **333** (2001) 319–321.
21. I. Gutman and J. Žerovnik, *Croat. Chem. Acta* **75** (2002) 603–612.
22. D. E. Needham, I.-C. Wei, and P. G. Seybold, *J. Am. Chem. Soc.* **110** (1988) 4186–4194.
23. B. Lučić and N. Trinajstić, *J. Chem. Inf. Comput. Sci*. **39** (1999) 121–132.
24. P. G. Seybold, M. May, and U. A. Bagal, *J. Chem. Educ*. **64** (1987) 575–581.
25. K. Kovačević, D. Plavšić, N. Trinajstić, and D. Horvat, in: A. Graovac (Ed.), *MATH/CHEM/COMP 1988*, Elsevier, Amsterdam, 1989, pp. 213–224.
26. M. Randić and M. Pompe, *J. Chem. Inf. Comput. Sci*. **41** (2001) 575–581.

SAŽETAK

Hararyjev indeks – 12 godina poslije

Bono Lučić, Ante Miličević, Sonja Nikolić i Nenad Trinajstić

Predložena je modifikacija Hararyjeva indeksa koji je uveden prije 12 godina i označen slovom H. Modificirani Hararyjev indeks, označen slovima ${}^{m}H$, moguće je podijeliti u doprinose vanjskih i unutarnjih veza u alkanima. Doprinosi vanjskih veza mnogo su veći nego doprinosi unutarnjih što je u skladu s predodžbom prema kojoj vanjske veze, zbog toga što se nalaze na površini molekule, pridonose fizikalnim i kemijskim svojstvima molekula znatno više nego unutarnje veze. U slučaju izvornoga Hararyjeva indeksa, odnos doprinosa vanjskih i unutarnjih veza bio je obrnut. Hararyjev indeks, njegova modifikacija i Wienerov indeks uspoređeni su u modeliranju osam reprezentativnih fizikalnih svojstava nižih alkana. Razmatrane su tri vrste modela: linearni modeli, modeli Wienerova tipa i multivarijatni modeli, koji su dobiveni pomoću postupka CROMsel (vidi ref. 23). Najboljima su se pokazali oni multivarijatni modeli koji sadrže modificirani Hararyjev indeks.