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CORRELATION FOR KOVÁTS RETENTION INDEX OF C_9–C_{26} MONOALKYL AND POLYMETHYL ALKANES AND ALKENES

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SUMMARY

Correlations based on graph theoretic indices are proposed for prediction of the Kováts retention index of high-molecular-weight monoalkyl and polymethyl alkanes and alkenes. As a test for the proposed correlations, the Kováts index of monoalkyl hexadecanes in the C_{18}–C_{27} range were experimentally measured and compared with predicted values. Agreement between experimental and predicted values were quite satisfactory with an average error of 8 index units.

INTRODUCTION

The Kováts retention index system[1] is a logarithmic system where the logarithmic retention of a substance is interpolated between those of two standard compounds. Although any homologous series of organic compounds can be used as standards, originally *n*-alkanes were used exclusively. The retention index, I, is defined as:

$$I = 100z + 100\frac{\log t_R(\text{substance}) - \log t_R(z)}{\log t_R(z+1) - \log t_R(z)} \qquad (1)$$

where t_R is the net retention time and z represents an *n*-alkane with z carbon atoms. For linear-temperature-programmed gas chromatography, I can be expressed as:

$$I = 100z + 100\frac{t_R(\text{substance}) - t_R(z)}{t_R(z+1) - t_R(z)} \qquad (2)$$

Because of the relationship between structure and retention index of organic compounds, Kováts retention index system can be used to identify a component based on its retention behavior. The retention index for a compound depends on the stationary phase, the column temperature, and the structure of the compound. The correlations between structure and retention index for various stationary phases and temperatures have been the subject of many investigations since the initial work by Kováts. All of the methods have one common approach; the retention index is predicted from one or more structural features of the compound.

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Some investigators have taken the group-additivity approach for the prediction of I from structural formula of the compound. Group-additivity methods have been extensively studied by Benson[2] for prediction of thermochemical properties. The main hypothesis is that a property of a compound can be expressed as the sum of additive contributions from every structural group of the molecule.

Takács and co-workers[3–7] in a series of publications developed a scheme for prediction of Kováts retention indexes based on additive index contributions from individual bonds. They gave the index contributions for some 125 different bond types involved in saturated hydrocarbons, 118 bond types involving double bonds, and some 50 bonds involving aromatic and cyclic hydrocarbons. With such a large number of structural parameters, one would expect a high degree of accuracy for the predictive ability of Takács method. The approach of Takács and co-workers, however, has received critical reviews. Vanheertum[8] used the method of Takács to predict the Kováts index of some 80 paraffinic and olefinic compounds. For approximately 20% of the compounds, the error in predicted values was in excess of 10 index units (i.u.). He suggested that the method be expanded to include index contributions from a more complete set of bonds. Such an approach would give rise to even a larger number of structural parameters. Souter[9], on the other hand, criticized the validity of Takács approach. He suggested that predictive methods based on additivity assumption should involve as few groups as possible.

Spivakovskii *et al.*[10] used 28 structural groups for describing aliphatic alcohols and saturated hydrocarbons. The groups considered were structural "fragments" involving several types of bonds rather than a unique bond. The retention index was expressed as the summation of additive index contributions from individual fragments. The individual group contributions were obtained from experimental retention indices of some 97 C_6–C_9 aliphatic alcohols and alkanes on squalane using a least squares regression analysis. They reported a mean square error of 7 i.u. between calculated and experimental values.

Other than additivity schemes, empirical correlations, have been developed, for example by Dimov and Papazova[11–13], for prediction of I for various classes of organic compounds. A detailed list of these investigations is included in ref. 3.

Some investigators, for example Castello *et al.*[14], Schomburg and Dielmann[15] and Kissin and co-workers[16–19], have found it more useful to use group additivity methods for prediction of δI, *i.e.* the difference between the retention index of a compound and that for the corresponding *n*-alkane. Each structural group has an additive contribution to δI. These methods also require a significant number of structural parameters to accurately predict δI.

Many authors who have published structure–retention relationships, do not claim the correlation to be the only means of identification. Rather, it should be complementary to other identification methods such as gas chromatography–mass spectrometry. The recommendation of Souter[9] is thus reasonable that a predictive method for calculation of Kováts index should include as few structural parameters as possible.

The idea of using a few structural parameters for prediction of physical and thermodynamic properties of organic compounds has been studied by many investigators who have developed property–structure relationships based on graph-theoretic approaches.

GRAPH-THEORETIC APPROACH FOR PREDICTION OF KOVÁTS INDEX

Chemical graphs allow for mathematical representation of molecular structures. A graph is a set of vertices or points which are connected to each other by edges or lines. In a chemical graph, atoms other than hydrogen represent vertices and bonds represent edges. In terms of matrices, a graph can be represented by either an adjacency matrix, $\boldsymbol{A}$, or by a distance matrix, $\boldsymbol{D}$. These matrices are square matrices where rows (or columns) represent the atoms (vertices) of a chemical graph. The entries of the distance matrix, d_{ij}, represent the bond distance between vertices i and j. The entry a_{ij} of the adjacency matrix is 1 if i and j are connected by a bond, or 0 if i and j are not connected.

One graph-theoretic approach for prediction of Kováts index is based on topology–information correlations as proposed by Chrétien and co-workers[20–24]. In this approach, molecular structure for a compound in a family of compounds, for example alkenes, is represented by a graph which is generated from a focus point, for example the double bond in alkenes, based on the concept of ELCO (an Environment which is Limited, Concentric and Ordered). Superposition of these graphs gives the characteristic "imprint" for that particular family of compounds. Associated with this "imprint" are topological sites for which perturbation parameters are obtained from regression analysis of the available experimental Kováts indices. Kováts index for a particular compound can thus be predicted based on its structure (topological sites) and the associated perturbation parameters.

The topology–information correlation approach is quite a powerful technique for prediction of retention index. It utilizes a rather small number of parameters (one for each site) and provides an accuracy comparable to the more traditional methods based on additivity principles which use numerous parameters. In the case of *n*-alkenes, for example Dubois *et al.*[20], the retention indices were predicted using a 25-parameter correlation. The correlation coefficient was 0.9999 and standard deviation of 1.64.

Another graph theoretic approach for prediction of retention index, which uses even fewer parameters (as few as one or two), is based on correlations using graph theoretic indices. A graph theoretic index is a single number which mathematically characterizes the pattern of interconnections between atoms. The application of graph indices for property estimation was first realized by Wiener[25] in 1947. Since then, many different indices were proposed and applied for property estimation. Most of these indices are either based on the properties of the adjacency matrix or on the properties of the distance matrix. A review of these indices and their application is given by Rouvray[26].

Randić's connectivity index, χ, and the Wiener index, W, have been used by some investigators for correlating the Kováts retention index of some classes of organic compounds. Such correlations depend on the stationary phase and the column temperature. The connectivity index of Randić[27] is defined as:

$$\chi = \Sigma(v_i v_j)^{-1/2} \tag{3}$$

where v_i and v_j are the degrees of vertices i and j, respectively, and the summation extends over all edges. The degree of vertex i is defined as the number of edges connected to vertex i. From a chemical viewpoint, the degree of vertex i represents the order of the corresponding carbon.

Randić[27,28] showed that Kováts retention index for alkanes can be correlated with the connectivity index. From the properties of the connectivity index and the definition of the Kováts index, such as correlation would be a linear relationship given by the following equation:

$$I = 200(\chi - 1.4142) + 300 \tag{4}$$

The factor of 200 converts the Kováts retention scale to that of the connectivity values while 1.4142 and 300 are connectivity and Kováts indices for propane, respectively. The above equation is exact for the n-alkane series, however, deviation from linearity is observed when considering isomeric compounds. Randić[28] suggested that such deviations from linearity were due to interactions between some methyl–methyl fragments in highly branched structures and improved the correlation by introducing a correction factor:

$$I = 200(\chi - 1.4142) + 300 + (T_3)^2 \tag{5}$$

where T_3 is the number of methyl–methyl fragments separated by 3 carbon atoms. With only two structural parameters, namely χ and T_3, the error in the predicted values of I was comparable with more sophisticated predictive methods based on numerous parameters. Several correlations between the retention index and the connectivity index were proposed by Gassiot-Matas and Firpo-Pamies[29] for various classes of compounds, and by Kaliszan and co-workers[30–32] for more complex structures such as pyrazine carbothioamide derivatives, polycyclic aromatics, and complex cyclic alcohols and methyl esters.

One difficulty in applying the Randić approach for alkyl substituted alkanes and alkenes is that the index does not have a high discriminating power for various isomers. For example the position of the alkyl substituent on the chain is not reflected in the index value. The index value for 4-methyl, 5-methyl, 6-methyl, ..., $n/2$-methyl isomers of methyl-n-alkane all have the same connectivity index. However, I is strongly affected by the position of branches with respect to the main chain.

Bonchev *et al.*[33] correlated the Kováts retention index of monoalkyl and o-dialkylbenzenes on squalane at 413 K with the Wiener index, W. The Wiener index for a structure is obtained from its distance matrix, $\boldsymbol{D}$, and is defined as:

$$W = 1/2\left(\sum_{i,j} d_{ij}\right) \tag{6}$$

W is the total number of bonds existing between all atoms in a molecular graph and it depends on the size and the shape of the skeletal network. The smaller the number is, the more compact is the corresponding structure.

Bonchev *et al.*[33] suggested the following equation for predicting the Kováts retention index, I, for monoalkyl and o-dialkylbenzenes in the C_9–C_{16} range:

$$I = 244\, W^{0.3} \tag{7}$$

With the above equation, the error between predicted and measured values of I was in the range of 1 to 20 i.u. with an average error of 7.5 i.u.

Unlike the connectivity index of Randić, the Wiener index has a high discriminating power for isomeric compounds. However, the Wiener index does not distinguish double or aromatic C–C bonds with the corresponding saturated or cyclic bonds. Hence the Wiener indices for alkenes and aromatics are identical to those for the corresponding alkanes and cycloalkanes, respectively. For a high discriminating power, in particular for isomeric compounds, Rouvray[26] suggests the design of so called superindices which are based on the combination of two or more indices.

Even with the problems associated with discrimination of isomeric compounds, a graph-theoretic approach for predicting Kováts retention index seems to be complementary to if not competitive with other emperical and additive methods. As pointed out by Bonchev *et al.*[33], such an approach is very simple to use, and most important, has an accuracy comparable with other approaches that require a significant number of structural parameters. In this study the graph theoretic approach for prediction of Kováts retention index has been extended to high-molecular-weight branched alkanes and alkenes.

RESULTS AND DISCUSSION

Correlations of the type given by eqns. 4 and 7 were developed using the experimental data of Kissin and co-workers[16–19] for the retention indices of monoalkyl and polymethyl alkanes and alkenes in the C_9–C_{26} range. Kissin and co-workers used a fused-silica capillary column coated with cross-linked methylsilicone. The temperature programming was from 40 to 300°C at 5°C/min.

The hydrocarbons considered by Kissin and co-workers can be divided into four categories. These include: (1) monoalkyl alkanes; (2) monoalkyl alkenes; (3) polymethyl alkanes; and (4) polymethyl alkenes.

Correlations of the form given by eqn. 4 for prediction of I from Randić connectivity index, χ, were obtained for each of the above classes of hydrocarbons. Eqn. 4, when rearranged, can be written as:

$$I = a_0 + a_1\chi \tag{8}$$

where a_0 and a_1 are 17.2 and 200, respectively. For the above classes of hydrocarbons, values of a_1 were found to be in the range of 183 to 198. Such correlations were found to be unsatisfactory with standard deviations ranging between 10 and 25 index units. It was thought that addition of a third term (a correction term such as that suggested by Randić[28]) containing the effect of the Wiener index on Kováts index would improve the correlation. However, correlations of the form given by eqns. 9 and 10 did not significantly improve the correlation given by eqn. 8.

$$I = a_0 + a_1\chi + a_2 W \tag{9}$$

$$I = a_0 + a_1\chi + a_2 \log W \tag{10}$$

Fig. 1 shows a plot of Kováts index *versus* Randić index for all hydrocarbons

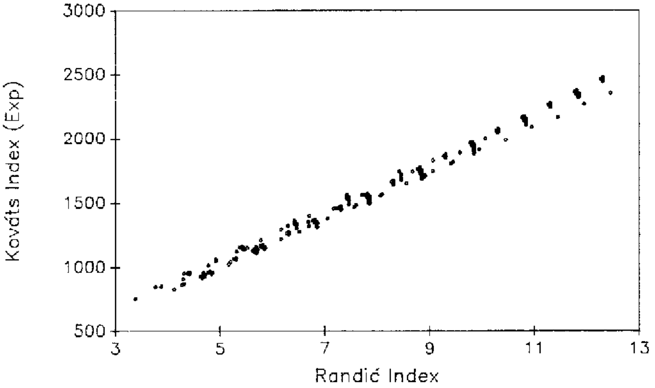

Fig. 1. Plot of Kováts index *versus* Randić index for C_{10} and higher alkanes and alkenes.

considered. Although a linear relationship exists over the entire range of χ values, deviations from linearity for isomeric compounds are significant. Fig. 2 shows the plot of Kováts index *versus* the Wiener index which suggests a smooth correlation in particular when one considers two classes of compounds; monoalkyl compounds and polymethyl compounds (see Figs. 3 and 4).

Correlations of the form suggested by Bonchev *et al.*[33], eqn. 11, were developed for each class of hydrocarbons.

$$I = b_0 W^{b_1} \tag{11}$$

The value of b_0 was found to be in the range of 172 to 192 with exponent b_1 ranging between 0.32 and 0.34. These values are in good agreement with those reported by Bonchev *et al.*[33] for alkyl-substituted benzenes. To distinguish between alkenes and corresponding alkanes, a third term was added to eqn. 11:

$$I = b_0 W^{b_1} \chi^{b_2} \tag{12}$$

The additional term resulted in an improved correlation. For polymethyl and

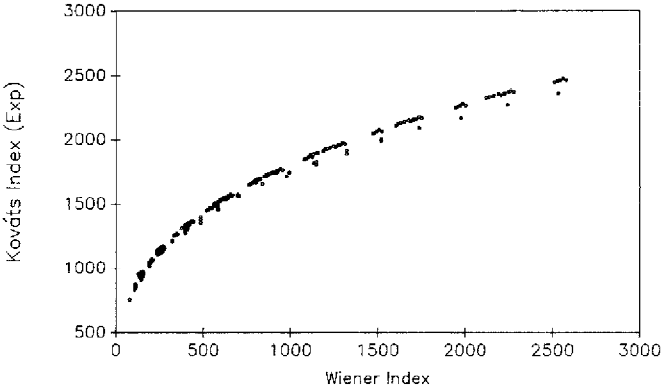

Fig. 2. Plot of Kováts index *versus* Wiener index for C_{10} and higher alkanes and alkenes.

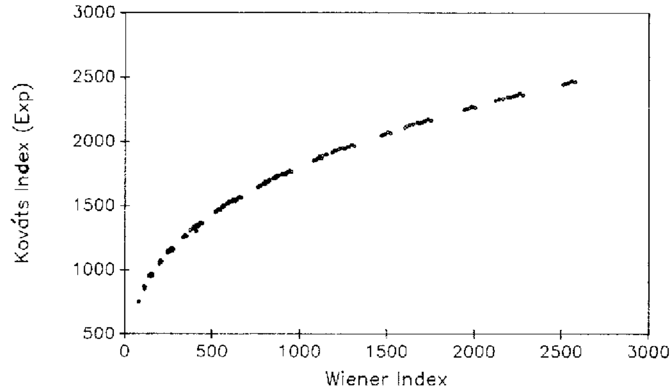

Fig. 3. Plot of Kováts index *versus* Wiener index for C_{10} and higher monoalkyl alkanes and alkenes.

monoalkyl hydrocarbons, the resulting correlations are given by eqns. 13 and 14, respectively.

$$I = 197 W^{0.258} \chi^{0.181} \tag{13}$$

$$I = 186 W^{0.276} \chi^{0.165} \tag{14}$$

The correlation coefficients for the above correlations were 0.998 and 1.000, respectively. For all the hydrocarbons considered, the experimental values of I are compared with those predicted by eqns. 13 and 14 in Table I. The correlation between experimental and predicted values is shown in Fig. 5.

For monoalkyl hydrocarbons, the error between predicted and experimental values was in the range of 0 to 26 i.u. with an average error of 5.1 i.u. For polymethyl hydrocarbons, the error was in the range of 1 to 29 i.u. with an average error of 10.9 i.u. For all hydrocarbons, the average error was 6.6 index units. The somewhat higher error for polymethyl hydrocarbons may indicate secondary effects (in particular for

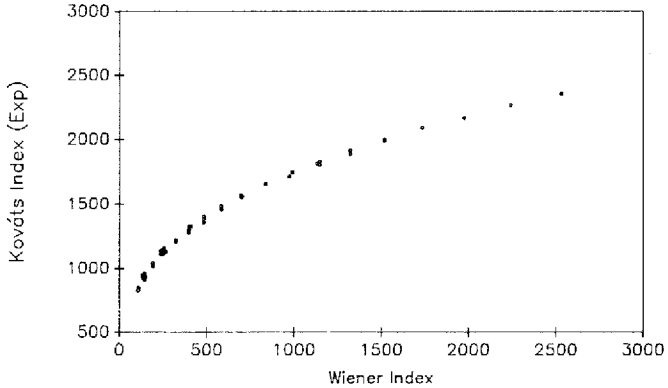

Fig. 4. Plot of Kováts index *versus* Wiener index for C_{10} and higher polymethyl alkanes and alkenes.

TABLE I

EXPERIMENTAL AND PREDICTED VALUES OF KOVÁTS INDEX

I = Kováts index; W = Wiener index; χ = Randić index; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl.

Compound	*I (Exp)*	*W*	χ	*I (Calc)*	*Difference*
2-Me-C_8	865.0	114	4.270	873.5	8.5
2-Me-C_9	964.0	158	4.770	973.4	9.4
2-Me-C_{10}	1065.0	212	5.270	1073.2	8.2
2-Me-C_{11}	1164.5	277	5.770	1172.8	8.3
2-Me-C_{12}	1265.0	354	6.270	1272.3	7.3
2-Me-C_{13}	1364.5	444	6.770	1371.6	7.1
2-Me-C_{14}	1465.0	548	7.270	1470.9	5.9
2-Me-C_{15}	1564.0	667	7.770	1570.0	6.0
2-Me-C_{16}	1664.5	802	8.270	1669.0	4.5
2-Me-C_{17}	1764.0	954	8.770	1767.9	3.9
2-Me-C_{18}	1864.5	1124	9.270	1866.8	2.3
2-Me-C_{19}	1964.0	1313	9.770	1965.6	1.6
2-Me-C_{20}	2064.5	1522	10.270	2064.3	−0.2
2-Me-C_{21}	2164.0	1752	10.770	2162.9	−1.1
2-Me-C_{22}	2263.5	2004	11.270	2261.5	−2.0
2-Me-C_{23}	2363.0	2279	11.770	2360.1	−2.9
2-Me-C_{24}	2463.0	2578	12.270	2458.6	−4.4
3-Me-C_8	872.0	110	4.308	866.2	−5.8
3-Me-C_9	971.0	153	4.808	966.1	−4.9
3-Me-C_{10}	1071.5	206	5.308	1066.0	−5.5
3-Me-C_{11}	1172.0	270	5.808	1165.8	−6.2
3-Me-C_{12}	1272.0	346	6.308	1265.6	−6.4
3-Me-C_{13}	1372.0	435	6.808	1365.2	−6.8
3-Me-C_{14}	1472.5	538	7.308	1464.7	−7.8
3-Me-C_{15}	1572.0	656	7.808	1564.0	−8.0
3-Me-C_{16}	1673.0	790	8.308	1663.3	−9.7
3-Me-C_{17}	1773.5	941	8.808	1762.5	−11.0
3-Me-C_{18}	1873.5	1110	9.308	1861.6	−11.9
3-Me-C_{19}	1973.7	1298	9.808	1960.6	−13.1
3-Me-C_{20}	2074.0	1506	10.308	2059.5	−14.5
3-Me-C_{21}	2174.0	1735	10.808	2158.4	−15.6
3-Me-C_{22}	2274.0	1986	11.308	2257.2	−16.8
3-Me-C_{23}	2373.7	2260	11.808	2355.9	−17.8
3-Me-C_{24}	2473.7	2558	12.308	2454.6	−19.1
4-Me-C_9	962.0	150	4.808	960.8	−1.2
4-Me-C_{10}	1061.5	202	5.308	1060.2	−1.3
4-Me-C_{11}	1161.0	265	5.808	1159.8	−1.2
4-Me-C_{12}	1261.0	340	6.308	1259.5	−1.5
4-Me-C_{13}	1360.0	428	6.808	1359.1	−0.9
4-Me-C_{14}	1460.5	530	7.308	1458.6	−1.9
4-Me-C_{15}	1560.0	647	7.808	1558.1	−1.9
4-Me-C_{16}	1660.5	780	8.308	1657.5	−3.0
4-Me-C_{17}	1760.0	930	8.808	1756.8	−3.2
4-Me-C_{18}	1860.2	1098	9.308	1856.0	−4.2
4-Me-C_{19}	1960.2	1285	9.808	1955.2	−5.0
4-Me-C_{20}	2060.5	1492	10.308	2054.2	−6.3
4-Me-C_{21}	2160.0	1720	10.808	2153.2	−6.8
4-Me-C_{22}	2259.5	1970	11.308	2252.1	−7.4
4-Me-C_{23}	2359.0	2243	11.808	2351.0	−8.0

TABLE I (*continued*)

Compound	*I (Exp)*	*W*	*χ*	*I (Calc)*	*Difference*
4-Me-C_{24}	2458.5	2540	12.308	2449.8	−8.7
5-Me-C_9	961.0	149	4.808	959.0	−2.0
5-Me-C_{10}	1058.0	200	5.308	1057.3	−0.7
5-Me-C_{11}	1156.0	262	5.808	1156.2	0.2
5-Me-C_{12}	1255.0	336	6.308	1255.4	0.4
5-Me-C_{13}	1354.0	423	6.808	1354.7	0.7
5-Me-C_{14}	1453.8	524	7.308	1454.0	0.2
5-Me-C_{15}	1553.6	640	7.808	1553.4	−0.2
5-Me-C_{16}	1653.4	772	8.308	1652.8	−0.6
5-Me-C_{17}	1753.2	921	8.808	1752.1	−1.1
5-Me-C_{18}	1853.0	1088	9.308	1851.3	−1.7
5-Me-C_{19}	1953.2	1274	9.808	1950.5	−2.7
5-Me-C_{20}	2053.0	1480	10.308	2049.7	−3.3
5-Me-C_{21}	2153.0	1707	10.808	2148.7	−4.3
5-Me-C_{22}	2252.0	1956	11.308	2247.7	−4.3
5-Me-C_{23}	2352.5	2228	11.808	2346.6	−5.9
5-Me-C_{24}	2453.0	2524	12.308	2445.5	−7.5
6-Me-C_{12}	1254.0	334	6.308	1253.3	− .7
6-Me-C_{14}	1451.0	520	7.308	1451.0	−0.0
6-Me-C_{16}	1650.0	766	8.308	1649.2	−0.8
6-Me-C_{17}	1749.0	914	8.808	1748.4	−0.6
6-Me-C_{18}	1848.0	1080	9.308	1847.6	−0.4
6-Me-C_{20}	2048.0	1470	10.308	2045.8	−2.2
6-Me-C_{21}	2147.5	1696	10.808	2144.9	−2.6
6-Me-C_{22}	2247.0	1944	11.308	2243.9	−3.1
6-Me-C_{24}	2446.5	2510	12.308	2441.8	−4.7
7-Me-C_{13}	1351.0	419	6.808	1351.1	0.1
7-Me-C_{14}	1450.0	518	7.308	1449.4	−0.6
7-Me-C_{15}	1548.0	632	7.808	1548.0	0.0
7-Me-C_{16}	1646.0	762	8.308	1646.8	0.8
7-Me-C_{17}	1745.0	809	8.808	1745.8	0.8
7-Me-C_{19}	1944.0	1258	9.808	1943.7	−0.3
7-Me-C_{21}	2143.0	1687	10.808	2141.7	−1.3
7-Me-C_{23}	2342.0	2204	11.808	2339.6	−2.4
3-Et-C_8	961.0	145	4.846	953.1	−7.9
3-Et-C_{10}	1157.0	258	5.846	1152.5	−4.5
3-Et-C_{12}	1355.0	419	6.846	1352.4	−2.6
3-Et-C_{14}	1554.0	636	7.846	1552.0	−2.0
3-Et-C_{16}	1753.0	917	8.846	1751.2	−1.8
3-Et-C_{18}	1952.0	1270	9.846	1950.1	−1.9
3-Et-C_{20}	2152.0	1703	10.846	2148.6	−3.4
3-Et-C_{22}	2351.5	2224	11.846	2346.7	−4.8
4-Et-C_8	954.0	141	4.846	945.8	−8.2
4-Et-C_{10}	1152.0	250	5.846	1142.6	−9.4
4-Et-C_{12}	1348.0	407	6.846	1341.6	−6.4
4-Et-C_{14}	1548.0	620	7.846	1541.1	−6.9
4-Et-C_{16}	1747.0	897	8.846	1740.6	−6.4
4-Et-C_{18}	1947.5	1246	9.846	1939.8	−7.7
4-Et-C_{20}	2148.0	1675	10.846	2138.8	−9.2
4-Et-C_{22}	2348.0	2192	11.846	2337.4	−10.6
5-Et-C_{10}	1146.0	246	5.846	1137.5	−8.5
5-Et-C_{12}	1341.0	399	6.846	1334.2	−6.8
5-Et-C_{14}	1538.0	608	7.846	1532.8	−5.2

(*Continued on p. 10*)

TABLE I (*continued*)

Compound	*I (Exp)*	*W*	χ	*I (Calc)*	*Difference*
5-Et-C_{16}	1736.0	881	8.846	1732.0	−4.0
5-Et-C_{18}	1937.0	1226	9.846	1931.2	−5.8
5-Et-C_{20}	2137.0	1651	10.846	2130.3	−6.7
5-Et-C_{22}	2335.0	2164	11.846	2329.1	−5.9
6-Et-C_{12}	1336.0	395	6.846	1330.5	−5.5
6-Et-C_{14}	1533.0	600	7.846	1527.2	−5.8
6-Et-C_{16}	1731.0	869	8.846	1725.4	−5.6
6-Et-C_{18}	1929.0	1210	9.846	1924.2	−4.8
6-Et-C_{20}	2129.0	1631	10.846	2123.1	−5.9
6-Et-C_{22}	2327.0	2140	11.846	2321.9	−5.1
7-Et-C_{14}	1530.0	596	7.846	1524.4	−5.6
7-Et-C_{16}	1727.0	861	8.846	1721.0	−6.0
7-Et-C_{18}	1924.0	1198	9.846	1918.9	−5.1
7-Et-C_{20}	2122.0	1615	10.846	2117.3	−4.7
7-Et-C_{22}	2320.0	2120	11.846	2315.9	−4.1
5-Pr-C_{13}	1516.0	584	7.846	1515.9	−0.1
5-Pr-C_{15}	1712.0	849	8.846	1714.4	2.4
5-Pr-C_{17}	1910.0	1186	9.846	1913.6	3.6
5-Pr-C_{19}	2108.0	1603	10.846	2113.0	5.0
7-Pr-C_{13}	1506.0	572	7.846	1507.2	1.2
7-Pr-C_{15}	1700.0	825	8.846	1700.9	0.9
7-Pr-C_{17}	1898.0	1150	9.846	1897.4	−0.6
5-Bu-C_{10}	1313.0	375	6.846	1311.6	−1.4
5-Bu-C_{12}	1505.0	568	7.846	1504.3	−0.7
5-Bu-C_{14}	1699.0	825	8.846	1700.9	1.9
5-Bu-C_{16}	1896.0	1154	9.846	1899.2	3.2
6-Bu-C_{12}	1498.0	560	7.846	1498.4	0.4
6-Bu-C_{14}	1691.0	809	8.846	1691.7	0.7
6-Bu-C_{16}	1887.0	1130	9.846	1888.2	1.2
7-Bu-C_{14}	1688.0	801	8.846	1687.1	−0.9
7-Bu-C_{16}	1880.0	1114	9.846	1880.8	0.8
6-Me-1-C_7=	752.6	79	3.380	759.5	6.9
7-Me-1-C_8=	853.1	114	3.880	859.7	6.6
5-Me-1-C_9=	951.6	149	4.418	945.7	−5.9
7-Me-1-C_9=	961.1	153	4.418	952.7	−8.4
8-Me-1-C_9=	954.7	158	4.380	959.8	5.1
4-Me-1-C_{10}=	1051.5	202	4.918	1047.0	−4.5
6-Me-1-C_{10}=	1048.1	200	4.918	1044.1	−4.0
8-Me-1-C_{10}=	1061.4	206	4.918	1052.6	−8.8
5-Me-1-C_{11}=	1147.8	262	5.518	1146.4	−1.4
7-Me-1-C_{11}=	1146.2	262	5.418	1143.0	−3.2
9-Me-1-C_{11}=	1161.0	270	5.418	1152.5	−8.5
10-Me-1-C_{11}=	1154.3	277	5.380	1159.3	5.0
4-Et-1-C_{10}=	1143.5	250	5.456	1129.6	−13.9
6-Et-1-C_{10}=	1136.1	246	5.456	1124.6	−11.5
8-Et-1-C_{10}=	1147.3	258	5.456	1139.5	−7.8
7-Me-1-C_{13}=	1340.9	419	6.418	1338.0	−2.9
9-Me-1-C_{13}=	1344.8	423	6.418	1341.5	−3.3
11-Me-1-C_{13}=	1362.2	435	6.418	1351.9	−10.3
4-Et-1-C_{12}=	1342.5	407	6.456	1328.6	−13.9
6-Et-1-C_{12}=	1328.1	395	6.456	1317.7	−10.4
8-Et-1-C_{12}=	1331.4	407	6.456	1328.6	−2.8
6-Bu-1-C_{10}=	1303.7	409	6.456	1330.4	26.7

TABLE I (*continued*)

Compound	*I (Exp)*	*W*	*χ*	*I (Calc)*	*Difference*
7-Me-1-C_{15}=	1539.2	632	7.418	1535.0	−4.2
9-Me-1-C_{15}=	1538.8	632	7.418	1535.0	−3.8
11-Me-1-C_{15}=	1544.4	640	7.418	1540.3	−4.1
13-Me-1-C_{15}=	1563.1	656	7.418	1550.9	−12.2
4-Et-1-C_{14}=	1538.3	620	7.456	1528.2	−10.1
8-Et-1-C_{14}=	1521.3	596	7.456	1511.6	−9.7
12-Et-1-C_{14}=	1542.8	636	7.456	1539.0	−3.8
6-Bu-1-C_{12}=	1490.7	560	7.456	1485.8	−4.9
8-Bu-1-C_{12}=	1494.8	568	7.456	1491.7	−3.1
13-Me-1-C_{17}=	1743.9	921	8.418	1739.0	−4.9
6-Et-1-C_{16}=	1722.1	869	8.456	1712.6	−9.5
10-Et-1-C_{16}=	1716.2	861	8.456	1708.3	−7.9
6-Bu-1-C_{14}=	1683.3	809	8.456	1679.1	−4.2
8-Bu-1-C_{14}=	1678.3	801	8.456	1674.5	−3.8
10-Bu-1-C_{14}=	1689.2	825	8.456	1688.2	−1.0
2,6-Me_2-1-C_7=	848.0	108	3.770	839.6	−8.4
2,6-Me_2-1-C_8=	954.5	146	4.308	929.7	−24.8
3,7-Me_2-1-C_8=	910.4	146	4.290	929.0	18.6
4,8-Me_2-1-C_9=	1015.0	194	4.774	1019.2	4.2
4,8-Me_2-1-C_{10}=	1120.4	249	5.312	1108.2	−12.2
6,10-Me_2-1-C_{11}=	1208.5	324	5.774	1204.1	−4.4
2,6-Me_2-2-C_{12}=	1324.9	408	6.298	1298.2	−26.7
2,6,10-Me_3-1-C_{11}=	1295.3	397	6.164	1284.1	−11.2
3,7,11-Me_3-1-C_{12}=	1354.1	484	6.684	1371.4	17.3
2,6,10-Me_3-1-C_{12}=	1400.8	484	6.702	1372.0	−28.8
4,8,12-Me_3-1-C_{13}=	1456.4	586	7.168	1459.0	2.6
3,7,11-Me_3-1-C_{13}=	1460.2	583	7.222	1459.1	−1.1
4,8,12-Me_3-1-C_{14}=	1562.1	698	7.706	1546.5	−15.6
7,11,15-Me_3-1-C_{16}=	1741.7	992	8.668	1729.8	−11.9
2,7,11,15-Me_4-1-C_{16}=	1828.8	1147	9.058	1810.2	−18.6
3,8,12,16-Me_4-1-C_{17}=	1888.6	1322	9.578	1896.8	8.2
4,9,13,17-Me_4-1-C_{18}=	2000.0	1518	10.062	1983.3	−16.7
2,3-Me_2-C_8	956.9	143	4.681	938.7	−18.2
2,4-Me_2-C_8	919.8	142	4.664	936.4	16.6
2,5-Me_2-C_8	926.6	143	4.664	938.1	11.5
2,6-Me_2-C_8	936.0	146	4.664	943.1	7.1
2,7-Me_2-C_8	930.6	151	4.626	950.0	19.4
3,5-Me_2-C_8	927.6	138	4.702	930.9	3.3
3,6-Me_2-C_8	942.3	141	4.702	936.1	−6.2
4,5-Me_2-C_8	947.8	135	4.718	926.2	−21.6
2,3-Me_2-C_{10}	1158.0	256	5.681	1129.8	−28.2
2,4-Me_2-C_{10}	1115.2	253	5.664	1125.8	10.6
2,5-Me_2-C_{10}	1118.5	252	5.664	1124.6	6.1
2,6-Me_2-C_{10}	1120.0	253	5.664	1125.8	5.8
2,7-Me_2-C_{10}	1125.7	256	5.664	1129.2	3.5
2,8-Me_2-C_{10}	1136.8	261	5.664	1134.8	−2.0
2,9-Me_2-C_{10}	1130.1	268	5.626	1141.2	11.1
3,5-Me_2-C_{10}	1118.4	245	5.702	1117.8	−0.6
3,6-Me_2-C_{10}	1128.8	246	5.702	1119.0	−9.8
3,7-Me_2-C_{10}	1132.6	249	5.702	1122.5	−10.1
3,8-Me_2-C_{10}	1143.6	254	5.702	1128.3	−15.3
4,5-Me_2-C_{10}	1138.0	238	5.719	1110.1	−27.9
4,6-Me_2-C_{10}	1111.2	239	5.702	1110.7	−0.5

(*Continued on p. 12*)

TABLE I (*continued*)

Compound	*I (Exp)*	*W*	χ	*I (Calc)*	*Difference*
4,7-Me$_2$-C$_{10}$	1120.8	242	5.702	1114.3	−6.5
2,6,10-Me$_3$-C$_{11}$	1276.8	397	6.521	1297.2	20.4
2,6,10-Me$_3$-C$_{12}$	1380.6	484	7.058	1384.9	4.3
2,6,10-Me$_3$-C$_{13}$	1466.6	586	7.558	1473.1	6.5
2,6,10-Me$_3$-C$_{15}$	1653.6	839	8.558	1652.8	−0.8
2,6,10,14-Me$_4$-C$_{15}$	1711.7	976	8.914	1731.3	19.6
2,6,10,14-Me$_4$-C$_{16}$	1816.2	1132	9.452	1818.0	1.8
2,6-Me$_2$-C$_7$	830.0	108	4.126	853.4	23.4
2,6-Me$_2$-C$_9$	1025.3	194	5.164	1033.8	8.5
3,7-Me$_2$-C$_9$	1042.2	192	5.202	1032.4	−9.8
2,6-Me$_2$-C$_{11}$	1216.7	324	6.164	1218.5	1.8
3,7-Me$_2$-C$_{12}$	1321.2	400	6.702	1306.2	−15.0
3,7,11-Me$_3$-C$_{13}$	1485.0	583	7.596	1472.5	−12.5
2,6,10-Me$_3$-C$_{14}$	1557.0	704	8.058	1562.5	5.5
3,7,11-Me$_3$-C$_{14}$	1570.0	698	8.096	1560.4	−9.6
2,6,10-Me$_3$-C$_{16}$	1746.9	992	9.058	1743.6	−3.3
2,6,10,15-Me$_4$-C$_{16}$	1806.0	1147	9.414	1822.8	16.8
2,6,10,15-Me$_4$-C$_{17}$	1913.8	1322	9.952	1910.0	−3.8
2,6,10,15-Me$_4$-C$_{18}$	1989.8	1518	10.452	1997.0	7.2
2,6,10,15-Me$_4$-C$_{19}$	2088.5	1736	10.952	2084.9	−3.6
2,6,10,15-Me$_4$-C$_{20}$	2165.5	1977	11.452	2173.5	8.0
2,6,10,15-Me$_4$-C$_{21}$	2268.0	2242	11.952	2262.6	−5.4
2,6,10,15-Me$_4$-C$_{22}$	2354.5	2532	12.452	2352.1	−2.4

adjacent branches and those in α position). These effects may be accounted for by methods such as that suggested by Randić[28].

To test the validity of the correlations, eqn. 14 was used to predict the Kováts retention index for a series of monoalkyl-substituted hexadecanes. The retention data for these compounds were not included in the parameter estimation for the correlations. *n*-Hexadecane was decomposed by thermal cracking at relatively mild

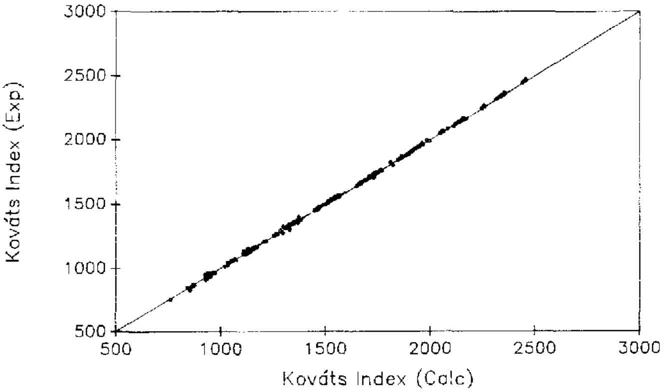

Fig. 5. Plot of experimental (Exp) *versus* predicted (Calc) Kováts index for C$_{10}$ and higher alkanes and alkenes.

temperatures, 400–440°C, and under relatively high pressure (14 MPa). Under the above conditions, the primary decomposition products were a complete series of *n*-alkanes and α-olefins ranging from C_2 to C_{15}. Also present in the products were significant amounts of monoalkyl hexadecanes. Under conditions of high pressure, the bimolecular reactions involving the addition of the parent *n*-hexadecyl radicals to the terminal carbon of the α-olefins become significant. These reactions lead to the formation of saturated alkanes containing a hexadecane backbone and a single branch ranging from ethyl to pentadecyl. Because of the symmetry of *n*-hexadecane, there are seven isomeric secondary *n*-hexadecyl radicals. The resulting monoalkyl hexadecanes have the alkyl branch at position 2–8. Only compounds up to C_{27}'s (undecylhexadecanes) were present in detectable amounts. C_{28^+} compounds were only present in trace amounts.

Liquid products were analyzed by a gas chromatograph equipped with a flame ionization detector using a DB-1 column. Temperature programming was as follows: initial temperature of 35°C for 3 min, up to 300°C at 3°C/min, and held at 300°C until complete elution.

Table II lists the high-molecular-weight compounds identified by gas chromatography–mass spectrometry and the corresponding experimental Kováts retention indices and those predicted by eqn. 14. The agreement between predicted and experimental values are quite satisfactory. The difference between experimental and predicted values were within ± 5 i.u. for over 40% of the compounds, and within ± 10 i.u. for over 70% of the compounds. The average error was 8.5 i.u. It is interesting to note that the predicted order of elution of compounds was identical to the experimental observation and, furthermore, the positions of peaks relative to the *n*-alkanes were accurately predicted. For example, among the C_{26} compounds (decylhexadecanes), the 2- and 3-isomers have retention times between those of *n*-C_{25} and *n*-C_{26}, whereas the 4-, 5-, 6-, 7- and 8-decylhexadecanes have retention times between those of *n*-C_{24} and *n*-C_{25}.

Data in Table I show that among isomeric monoalkyl alkanes of same carbon number and same alkyl group, the order of elution is correctly predicted. For example the retention index increases for 7-, 6-, 5-, 4-, 3- and 2-ethyl-C_{22}'s (2-ethyl-C_{22} = 3-methyl-C_{23}). The only exception is for methyl substituted alkanes where the 3-methylalkane has a higher retention index than the corresponding 2-methyl isomer. Also for the dimethyl compounds, the elution order is poorly predicted. In Table III, C_{10} and C_{18} compounds of Table I are listed in decreasing experimental retention index. C_{18} compounds are primarily monoalkyl compounds, for which the predicted order of elution is satisfactory. The C_{10} compounds, however, consist of monoalkyl and dimethyl compounds for which the predicted elution order is rather poor.

CONCLUSIONS

The graph-theoretic approach for estimation of Kováts index of organic compounds provides an easier alternative with same degree of accuracy to the more sophisticated methods based on additivity assumption. The approach of Bonchev *et al.*[33] was extended to high-molecular-weight monoalkyl and polymethyl alkanes and alkenes. Including two indices, W and χ, in the correlation resulted in an improved correlation. For approximately half of the compounds considered, the error in

TABLE II

EXPERIMENTAL AND PREDICTED KOVÁTS INDEX FOR ALKYL HEXADECANES

I = Kováts index; W = Wiener index, χ = Randić index.

Compound	*W*	χ	*I (Exp)*	*I (Calc)*	*Difference*
2-Ethyl-C_{16}	941	8.808	1774.8	1762.5	12.3
3-Ethyl-C_{16}	917	8.846	1769.5	1751.2	18.3
4-Ethyl-C_{16}	897	8.846	1749.3	1740.6	8.7
5-Ethyl-C_{16}	881	8.846	1739.6	1732.0	7.6
6-Ethyl-C_{16}	869	8.846	1733.2	1725.4	7.8
7-Ethyl-C_{16}	861	8.846	1728.0	1721.0	7.0
8-Ethyl-C_{16}	857	8.846	1726.6	1718.8	7.8
2-Propyl-C_{16}	1098	9.308	1859.1	1856.0	3.1
3-Propyl-C_{16}	1062	9.346	1846.9	1840.3	6.6
4-Propyl-C_{16}	1032	9.346	1823.4	1825.8	−2.4
5-Propyl-C_{16}	1008	9.346	1808.9	1813.9	−5.0
6-Propyl-C_{16}	990	9.346	1804.3	1804.9	−0.6
7-Propyl-C_{16}	978	9.346	1800.0	1798.9	1.1
8-Propyl-C_{16}	972	9.346	1798.6	1795.8	2.8
2-Butyl-C_{16}	1274	9.808	1952.7	1950.5	2.2
3-Butyl-C_{16}	1226	9.846	1936.5	1931.2	5.3
4-Butyl-C_{16}	1186	9.846	1911.4	1913.6	−2.2
5-Butyl-C_{16}	1154	9.846	1897.4	1899.2	−1.8
6-Butyl-C_{16}	1130	9.846	1889.7	1888.2	1.5
7-Butyl-C_{16}	1114	9.846	1884.6	1880.8	3.8
8-Butyl-C_{16}	1106	9.846	1883.1	1877.1	6.0
2-Pentyl-C_{16}	1470	10.308	2047.8	2045.8	2.0
3-Pentyl-C_{16}	1410	10.346	2028.3	2023.7	4.6
4-Pentyl-C_{16}	1360	10.346	2000.0	2003.6	−3.6
5-Pentyl-C_{16}	1320	10.346	1987.7	1987.1	0.6
6-Pentyl-C_{16}	1290	10.346	1979.6	1974.6	5.0
7-Pentyl-C_{16}	1270	10.346	1972.8	1966.1	6.7
8-Pentyl-C_{16}	1260	10.346	1971.3	1961.8	9.5
2-Hexyl-C_{16}	1687	10.808	2144.4	2141.7	2.7
3-Hexyl-C_{16}	1615	10.846	2122.9	2117.3	5.6
4-Hexyl-C_{16}	1555	10.846	2094.7	2095.3	−0.6
5-Hexyl-C_{16}	1507	10.846	2080.5	2077.3	3.2
6-Hexyl-C_{16}	1471	10.846	2071.7	2063.5	8.2
7-Hexyl-C_{16}	1447	10.846	2066.0	2054.1	11.9
8-Hexyl-C_{16}	1435	10.846	2064.2	2049.4	14.8
2-Heptyl-C_{16}	1926	11.308	2241.5	2238.1	3.4
3-Heptyl-C_{16}	1842	11.346	2218.4	2212.0	6.4
4-Heptyl-C_{16}	1772	11.346	2189.5	2188.5	1.0
5-Heptyl-C_{16}	1716	11.346	2174.8	2169.2	5.6
6-Heptyl-C_{16}	1674	11.346	2166.0	2154.4	11.6
7-Heptyl-C_{16}	1646	11.346	2160.1	2144.4	15.7
8-Heptyl-C_{16}	1632	11.346	2158.5	2139.3	19.2
2-Octyl-C_{16}	2188	11.808	2339.4	2334.9	4.5
3-Octyl-C_{16}	2092	11.846	2314.9	2307.4	7.5
4-Octyl-C_{16}	2012	11.846	2285.4	2282.7	2.7
5-Octyl-C_{16}	1948	11.846	2270.4	2262.5	7.9
6-Octyl-C_{16}	1900	11.846	2261.2	2246.9	14.3
7-Octyl-C_{16}	1868	11.846	2253.4	2236.4	17.0
8-Octyl-C_{16}	1852	11.846	2251.7	2231.1	20.6
2-Nonyl-C_{16}	2474	12.308	2436.6	2432.1	4.5

TABLE II (*continued*)

Compound	*W*	χ	*I (Exp)*	*I (Calc)*	*Difference*
3-Nonyl-C_{16}	2366	12.346	2411.6	2403.5	8.1
4-Nonyl-C_{16}	2276	12.346	2381.9	2377.9	4.0
5-Nonyl-C_{16}	2204	12.346	2366.3	2356.9	9.4
6-Nonyl-C_{16}	2150	12.346	2357.1	2340.8	16.3
7-Nonyl-C_{16}	2114	12.346	2349.3	2329.9	19.4
8-Nonyl-C_{16}	2096	12.346	2347.5	2324.4	23.1
2-Decyl-C_{16}	2785	12.808	2533.3	2529.4	3.9
3-Decyl-C_{16}	2665	12.846	2508.6	2500.1	8.5
4-Decyl-C_{16}	2565	12.846	2477.9	2473.8	4.1
5-Decyl-C_{16}	2485	12.846	2462.3	2452.3	10.0
6-Decyl-C_{16}	2425	12.846	2452.9	2435.8	17.1
7-Decyl-C_{16}	2385	12.846	2446.7	2424.6	22.1
8-Decyl-C_{16}	2365	12.846	2444.9	2419.0	25.9
2-Undecyl-C_{16}	3122	13.308	2631.7	2627.0	4.7
3-Undecyl-C_{16}	2990	13.346	2606.6	2597.1	9.5
4-Undecyl-C_{16}	2880	13.346	2574.3	2570.3	4.0
5-Undecyl-C_{16}	2792	13.346	2557.8	2548.4	9.4
6-Undecyl-C_{16}	2726	13.346	2547.9	2531.6	16.3
7-Undecyl-C_{16}	2682	13.346	2540.0	2520.3	19.7
8-Undecyl-C_{16}	2660	13.346	2538.4	2514.6	23.8

TABLE III

EXPERIMENTAL AND PREDICTED KOVÁTS INDEX

Me = Methyl; Et = ethyl; Pr = propyl; Bu = butyl.

Compound	*I (Exp)*	*I (Calc)*	*Compound*	*I (Exp)*	*I (Calc)*
C_{10} compounds			*C_{18} compounds*		
3-Me-C_9	971.0	966.1	3.Me-C_{17}	1773.5	1762.5
2-Me-C_9	964.0	973.4	2-Me-C_{17}	1764.0	1767.9
4-Me-C_9	962.0	960.8	4-Me-C_{17}	1760.0	1756.8
7-Me-1-C_9=	961.1	952.7	5-Me-C_{17}	1753.2	1752.1
3-Et-C_8	961.0	953.1	3-Et-C_{16}	1753.0	1751.2
5-Me-C_9	961.0	959.0	6-Me-C_{17}	1749.0	1748.4
2,3-Me_2-C_8	956.9	938.7	4-Et-C_{16}	1747.0	1740.6
8-Me-1-C_9=	954.7	959.8	7-Me-C_{17}	1745.0	1745.8
2,6-Me_2-1-C_8=	954.5	929.7	13-Me-1-C_{17}=	1743.9	1739.0
4-Et-C_8	954.0	945.8	5-Et-C_{16}	1736.0	1732.0
5-Me-1-C_9=	951.6	945.7	6-Et-C_{16}	1731.0	1725.4
4,5-Me_2-C_8	947.8	926.2	7-Et-C_{16}	1727.0	1721.0
3,6-Me_2-C_8	942.3	936.1	6-Et-1-C_{16}=	1722.1	1712.6
2,6-Me_2-C_8	936.0	943.1	10-Et-1-C_{16}=	1716.2	1708.3
2,7-Me_2-C_8	930.6	950.0	5-Pr-C_{15}	1712.0	1714.4
3,5-Me_2-C_8	927.6	930.9	7-Pr-C_{15}	1700.0	1700.9
2,5-Me_2-C_8	926.6	938.1	5-Bu-C_{14}	1699.0	1700.9
2,4-Me_2-C_8	919.8	936.4	6-Bu-C_{14}	1691.0	1691.7
3,7-Me_2-1-C_8=	910.4	929.0	10-Bu-1-C_{14}=	1689.2	1688.2
			7-Bu-C_{14}	1688.0	1687.1
			6-Bu-1-C_{14}=	1683.3	1679.1
			8-Bu-1-C_{14}=	1678.3	1674.5
			2,6,10-Me_3-C_{15}	1653.6	1652.8

predicted values of *I* was less than 5 i.u., and for approximately 80% of the compounds, the error was less than 10 index units. The correlation for monoalkyl alkanes was tested to predict the retention behavior of monoalkylhexadecanes in the range of C_{18} to C_{27}. Agreement between predicted and experimental Kováts indices was satisfactory.

REFERENCES

1 E. sz. Kováts, *Adv. Chromatogr.*, 1 (1965) 229.
2 S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1976.
3 J. M. Takács, C. Szita and G. Tarján, *J. Chromatogr.*, 56 (1971) 1.
4 C. Káplár, C. Szita, J. M. Takács and G. Tarján, *J. Chromatogr.*, 65 (1972) 115.
5 J. M. Takács, Zs. Tálas, I. Bernáth and Gy. Czakó, *J. Chromatogr.*, 67 (1972) 203.
6 J. M. Takács, E. Kocsi, E. Garmavolgyi, E. Eckhart, T. Lombosi, Sz. Nyiredy, I. Borbély and Gy. Krasznai, *J. Chromatogr.*, 81 (1973) 1.
7 J. M. Takács, *J. Chromatogr. Sci.*, 11 (1973) 210.
8 R. Vanheertum, *J. Chromatogr. Sci.*, 13 (1975) 150.
9 P. Souter, *J. Chromatogr. Sci.*, 12 (1974) 418.
10 G. I. Spivakovskii, A. I. Tishchenko, I. I. Zaslavskii and N. S. Wulfson, *J. Chromatogr.*, 144 (1977) 1.
11 N. Dimov, *J. Chromatogr.*, 119 (1976) 109.
12 D. Papazova and N. Dimov, *J. Chromatogr.*, 137 (1977) 259.
13 N. Dimov and D. Papazova, *J. Chromatogr.*, 137 (1977) 265.
14 G. Castello, M. Lunardelli and M. Berg, *J. Chromatogr.*, 76 (1973) 31.
15 G. Schomburg and G. Dielmann, *J. Chromatogr. Sci.*, 11 (1973) 151.
16 Y. V. Kissin, G. P. Feulmer and W. B. Payne, *J. Chromatogr. Sci.*, 24 (1986) 164.
17 Y. V. Kissin, *J. Chromatogr. Sci.*, 24 (1986) 278.
18 Y. V. Kissin and G. P. Feulmer, *J. Chromatogr. Sci.*, 24 (1986) 53.
19 Y. V. Kissin, *Ind. Eng. Chem. Res.*, 26 (1987) 1633.
20 J. E. Dubois, J. R. Chrétien, L. Soják and J. A. Rijks, *J. Chromatogr.*, 194 (1980) 121.
21 J. R. Chrétien and J. E. Dubois, *J. Chromatogr.*, 158 (1978) 43.
22 J. R. Chrétien and J. E. Dubois, *Anal. Chem.*, 49 (1977) 747.
23 J. E. Dubois and J. R. Chrétien, *J. Chromatogr. Sci.*, 12 (1974) 811.
24 J. R. Chrétien and J. E. Dubois, *J. Chromatogr.*, 126 (1976) 171.
25 H. Wiener, *J. Am. Chem. Soc.*, 69 (1947) 2636.
26 D. Rouvray, in R. B. King (Editor), *Chemical Applications of Topology and Graph Theory*, Elsevier, New York, 1983, pp. 159–177.
27 M. Randić, *J. Am. Chem. Soc.*, 97 (1975) 6609.
28 M. Randić, *J. Chromatogr.*, 161 (1978) 1.
29 M. Gassiot-Matas and G. Firpo-Pamies, *J. Chromatogr.*, 187 (1980) 1.
30 R. Kaliszan and H. Lamparczyk, *J. Chromatogr. Sci.*, 16 (1978) 246.
31 R. Kaliszan and H. Foks, *Chromatographia*, 10 (1977) 346.
32 R. Kaliszan, *Chromatographia*, 10 (1977) 529.
33 D. Bonchev, Ov. Mekenjan, G. Protić and N. Trinajstić, *J. Chromatogr.*, 176 (1979) 149.