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GENERAL CONTRIBUTION TO THE THEORY OF RETENTION INDEX SYSTEMS IN GAS-LIQUID CHROMATOGRAPHY***

I. PRE-CALCULATION OF RETENTION INDICES OF ALKANES ON THE BASIS OF THEIR MOLECULAR STRUCTURES AND THERMODYNAMICS IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Results of the examination of several important problems connected with retention index systems, such as the additivity and pre-calculation of retention indices, the polarity of stationary phases expressed by retention indices and interaction factors on mixed stationary phases, are considered. This is intended to stimulate further constructive discussion, as happened with the relationship between molecular structure and retention index. It is hoped that this work will provide opportunities for researchers to extend their activities to other types of compounds and stationary phases and to consider the theory more deeply.

INTRODUCTION

The retention index system developed by Kováts¹ is of great importance in gas-liquid chromatography (GLC). Many workers have dealt with various theoretical and practical problems of retention index systems and achieved significant results, and the relationship between retention index and molecular structure has been considered in detail. The work of more than 100 researchers who had obtained good results in this field was outlined in several of our publications²⁻⁶. Without aiming at completeness, the following papers can be mentioned as examples of work that gave excellent results: Schomburg⁷⁻¹¹, Chovin^{12,13}, Janák and co-workers^{14,15}, Tourres and Loewenguth¹⁶⁻¹⁸, Keulemans and co-workers^{19,20}, Evans and Smith²¹⁻²³, Landa

* A general research programme on retention index systems was started in 1964 under the inspiration of J. Janák (Brno, Czechoslovakia) with the assistance of his co-workers K. Tesářík, M. Krejčí and J. Novák.

** Parts I-IV of this series are published consecutively, and not according to the alphabetical sequence of the names of the authors.

and co-workers²⁴⁻²⁶, Soják and co-workers^{27,28}, Haken^{29,30}, Matukuma³¹, Ladon³², Hattox and McCloskey³³, Tóth and co-workers³⁴⁻³⁷, Kováts and co-workers³⁸⁻⁴⁰ and Ettre and co-workers⁴¹⁻⁴⁵.

From a critical evaluation of published work and an appraisal of the results of discussions⁴⁶⁻⁴⁹ dealing with some problems of the relationship between retention index and molecular structure, this relationship could be established more firmly on a thermodynamic basis by considering the additivity theory of Rohrschneider⁵⁰ and Kováts⁵¹ as well as the work of Szabó and co-workers^{52,53} on the additivity of theoretical bond energies.

Parallel with this, the code system that we developed has been improved, in spite of its complexity. Because of the change to a thermodynamic basis and of the increased consideration of the role of the effect of temperature on individual interactions, the former incremental values had to be modified. By doing so, a number of values were rendered more reliable, thus overcoming previous difficulties.

THEORETICAL

As discussed in our previous publications²⁻⁶, the retention index was divided into three components, namely:

$$I_{\text{substance}}^{\text{stationary phase}}(T) = I_a + I_b + I_t^{\text{st. ph.}}(T) \quad (1)$$

where

- I = retention index, in index units (i.u.), under isothermal conditions;
- T = column temperature ($^{\circ}\text{C}$ or $^{\circ}\text{K}$);
- I_a = atomic index contribution (i.u.);
- I_b = bond index contribution (i.u.);
- st. ph. = stationary phase;
- I_t = interaction index contribution (i.u.).

While the atomic and bond index contributions are independent of the stationary phase and of column temperature, and depend only on the quality of the substance examined, the interaction index contribution is dependent on the quality of the substance examined, the stationary phase and the column temperature.

The sum of the atomic and bond index contributions gives the molecular index contribution, I_m (i.u.):

$$I_a + I_b = I_m \quad (2)$$

The atomic index contribution is obtained by summing the atomic index values of the individual atoms:

$$I_a = ki_a(\text{C}) + li_a(\text{H}) + mi_a(\text{Y}) + \dots \quad (3)$$

where

- i_a = atomic index value (i.u.);
- k = number of carbon atoms in the molecule examined;

l = number of hydrogen atoms in the molecule examined;

m = number of varieties of atom (Y), in the molecule examined;

Y = general designation of an arbitrary variety of atom, e.g., O, N, S, P.

The atomic index value was established by definition:

$$i_a = \frac{\text{atomic weight}}{10} \quad (4)$$

i.e. the atomic index value of an arbitrary atom is equal to one tenth of its atomic weight expressed in index units. In one of our previous papers², the carbon atom was an exception to this definition as its atomic index value was 1.21 i.u. rather than 1.20 i.u. Because of the change to a thermodynamic basis, primarily because of the abandonment of the former fixed value for the C-H bond, this exception was eliminated. Because the alkanes considered here consist of carbon and hydrogen atoms only, it is very simple to calculate their atomic index contribution:

$$I_a(\text{C}_z\text{H}_{2z+2}) = 1.20z + 0.10(2z+2) \quad (5)$$

where z is the number of carbon atoms. The bond index contribution is given by the sum of the individual bond index values (increments). The determination of the individual bond index values was carried out in the following way:

(1) The ratio of the molecular and interaction index contributions was fixed by definition on squalane as stationary phase at 50.0°:

$$I_m : I_t = 1.00 : 2.93 \quad (6)$$

It should be noted that, on squalane as stationary phase at 50.0°, eqns. 1, 2 and 6 could be combined giving the following relationship:

$$I = I_m + I_t = I_m + 2.93 I_m = 3.93 I_m \quad (7)$$

where 3.93 = the interaction factor on squalane as stationary phase at 50.0°.

(2) The value of the bond index contribution was calculated by means of eqns. 1, 2 and 7.

(3) The full atomization energy of the molecule was taken from the thermodynamic literature, which in this case corresponds to I_b . The I_b value divided by the full atomization energy gives the index units/energy units factor. The energy values of the individual bonds known from thermodynamic papers⁵⁴⁻⁵⁶ multiplied by the index units/energy units factor give the bond index values of the individual bond increments, in index units. The values of some index units/energy units factors are given in Table I.

As an example of the steps in the calculation, the calculation of the bond index values for ethane is as follows. The empirical formula of ethane is C_2H_6 , and the atomic index contribution of ethane is therefore

$$I_a(\text{ethane}) = (2 \cdot 1.20) + (6 \cdot 0.10) = 3.00 \text{ i.u.} \quad (8)$$

TABLE I
VALUES OF INDEX UNITS/ENERGY UNITS FACTORS DETERMINED FOR ALKANES

Compound	Index units/energy units factor
Ethane	0.071
2-Methylpropane	0.070
2-Methylbutane	0.074
2-Methylpentane	0.075
2,2-Dimethylbutane	0.071
3-Methylpentane	0.077
2,3-Dimethylbutane	0.075
2-Methylhexane	0.076
2,2-Dimethylpentane	0.071
2,4-Dimethylpentane	0.072
2,2,3-Trimethylbutane	0.073

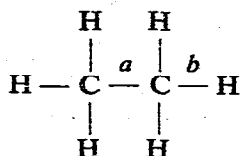
Its retention index, based on the original definition by Kováts¹, is 200.0 i.u. From eqn. 7:

$$I_m = \frac{200.0}{3.93} = 50.89 \text{ i.u.} \quad (9)$$

Thus, from eqn. 2:

$$I_b = 50.89 - 3.00 = 47.89 \text{ i.u.} \quad (10)$$

The atomization energy of ethane is 675.4 energy units (e.u.), so the index units/energy units factor of ethane is 0.071 (47.89/675.4). The energy of the bonds in the ethane molecule is as follows:



where $a = 87.0$ e.u. and $b = 97.9$ e.u. Thus, the increment value for the C-C bond in the ethane molecule is

$$87.0 \cdot 0.071 = 6.18 \text{ i.u.} \quad (11)$$

while that of the C-H bond is

$$97.9 \cdot 0.071 = 6.95 \text{ i.u.} \quad (12)$$

Thus, the value of I_b from the increments is

$$I_b = (6 \cdot 6.95) + (1 \cdot 6.18) = 47.88 \text{ i.u.} \quad (13)$$

The slight deviation (0.01 i.u.) between the results of eqns. 10 and 13 is due to the approximations that were made during the calculations.

Compared with the former ones, a significant deviation lies in the fact that the so-far² fixed value of the C-H bond was stopped at the change to a thermodynamic basis. By doing so, not only the criticism passed because of this was accepted but also the real situation was to a great extent approached. Namely, it succeeded in ensuring the thermodynamically permissible changes of these bonds. Because of the single valence of the hydrogen atom, however, this modification also necessitated, in the case of the C-H bond, the consideration of the order of carbon atoms bonded directly to the carbon atom. No change had to be made in the process developed previously for the C-C bonds², because it also met the thermodynamic requirements.

For an accurate description of the bond increments, the following code system was introduced for the alkanes:

(1) C-C saturated bonds are denoted by C.

(2) A subscript on the right-hand side of the symbol C indicates the orders (primary, secondary, tertiary and quaternary) of the two carbon atoms between which the bond is formed, *e.g.*, C₂₁ represents a saturated bond between a primary and secondary carbon atom. The higher order is always placed first.

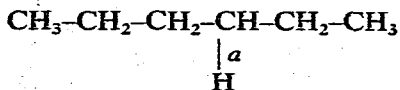
(3) The orders of the carbon atoms next to the higher-order carbon of the bond in question are given as a superscript on the left-hand side in increasing order, *e.g.*, ¹¹²C₄₁ represents a C-C saturated bond between a quaternary and primary carbon atom, and the quaternary carbon atom is bound to one secondary and two other primary carbon atoms.

(4) A subscript on the left-hand side indicates the order(s) of the carbon atom(s) attached to the lower-order carbon atom of the bond, *e.g.*, ₁₁¹¹¹C₄₃ denotes a saturated bond between a quaternary and a tertiary carbon atom, all of the neighbouring carbon atoms being primary.

(5) The C-H bond as designated by H.

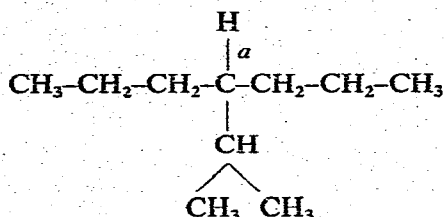
(6) The order of carbon atom to which the H atom is bound is given as a subscript on the right-hand side of the symbol. For ethane, this is H₁ because the hydrogen atoms of ethane are bound to the primary carbon atoms.

(7) The order of carbon atom(s) that is (are) immediately adjacent to the carbon atom of the C-H bond is (are) denoted subsequent to the first number of the subscript on the right-hand side of the symbol H in an increasing sequence of numbers. *E.g.*, for *n*-hexane, the C-H bond denoted by (a) is H₂₂₂:

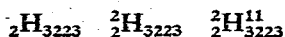


(8) The order of carbon atoms that are bound to the carbon atoms immediately adjacent to the carbon atom of a C-H bond is designated by a superscript and a subscript on the left-hand side of the symbol H and by a superscript on its right-hand side. When enumerating the order, the sequence of the subscripts on the right-hand side is followed clockwise on the one hand, and we keep an increasing order of number

on the order. As an example, the code for the C-H bond denoted by (*a*) in 4-isopropylheptane is ${}^2_2\text{H}_{3223}^{11}$:

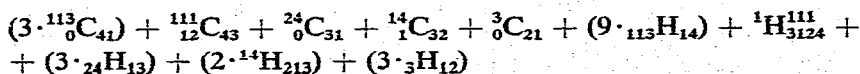
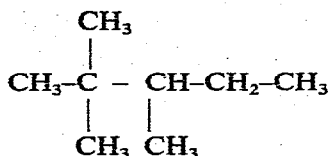


For this C-H bond, H_3 indicates that the H atom is bound to a tertiary carbon atom. To this tertiary carbon atom are immediately adjacent two secondary carbon atoms and one tertiary carbon atom, giving the symbol H_{3223} . The order of the carbon atoms bonding to the directly adjacent carbon atoms is designated clockwise in a sequence corresponding to the subscript on the right-hand side, starting from the subscript on the left-side and proceeding towards the superscript on the right-hand side:



For neighbouring bonds of various orders, an increasing sequence of numbers is observed.

As an example of the applicability of the code system, the structural formula and the bond code for 2,2,3-trimethylpentane are as follows:



The code system outlined may seem to be complicated, but after coding the bond increments for several compounds, it becomes a simple and rapid procedure. Also, its information content is maximal because it involves adjacent atoms.

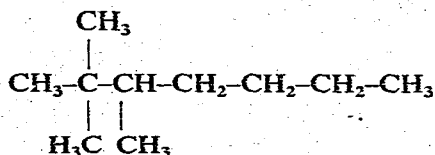
When examining the theoretical and practical implications of the code system, it is useful to find the causes of deviations, *e.g.*, for homologous series when applying the "roof-tile" effect.

An advantage of the new code system over previous systems is that it can be used for any type of compound, but each type of compound should be designated separately in order to give a uniform increment system from the increment values obtained by different workers. A few examples are given in Table II. The values of the bond increments for $\text{C}_1\text{-C}_{10}$ alkanes are given in Table III.

TABLE II
DESIGNATION OF SOME COMPOUND TYPES ACCORDING TO THE CODE SYSTEM

Code	Description
2a 2aC_2a_2a	Designates the C-C bond of benzene. The letter "a" refers to aromatic compounds. The carbon atom of the side-chain is not denoted by "a"
2c 2cC_2c_2c	The letter "c" designates cyclic compounds. The carbon atom of the side-chain is not denoted by "c"
2A 2AC_2A_2A	The letter "A" designates adamantane derivatives. The carbon atom of the side-chain is not denoted by "A"
2s_2s 2s_2sC_3s_2s	The letter "s" refers to steroids. The carbon atom of the side-chain is not denoted by "s"

As an example of the pre-calculation of retention indices, the calculation of that for of 2,2,3-trimethylheptane on squalane a stationary phase at 50.0° is shown below. The structural formula of 2,2,3-trimethylheptane is



The atomic index contribution is

$$10 \cdot \text{C} = 10 \cdot 1.20 = 12.00 \text{ i.u.}$$

$$22 \cdot \text{H} = 22 \cdot 0.10 = 2.20 \text{ i.u.}$$

$$I_a = 14.20 \text{ i.u.}$$

The bonds of the compound were coded and the corresponding bond increments were taken from Table III:

$$3 \cdot {}^{113}C_{41} = 3 \cdot 8.74 = 26.22 \text{ i.u.}$$

$${}^{111}_{12}C_{43} = 6.92 = 6.92 \text{ i.u.}$$

$${}^{24}_0C_{31} = 7.64 = 7.64 \text{ i.u.}$$

$${}^{14}_2C_{32} = 8.95 = 8.95 \text{ i.u.}$$

$${}^3_2C_{22} = 7.35 = 7.35 \text{ i.u.}$$

$${}^2_1C_{22} = 7.17 = 7.17 \text{ i.u.}$$

$${}^2_0C_{21} = 6.79 = 6.79 \text{ i.u.}$$

$$9 \cdot {}^{113}H_{14} = 9 \cdot 6.05 = 54.45 \text{ i.u.}$$

$${}^2H_{3124}^{111} = 5.53 = 5.53 \text{ i.u.}$$

$$3 \cdot {}^{24}H_{13} = 3 \cdot 7.11 = 21.33 \text{ i.u.}$$

$$2 \cdot {}^{14}_2H_{223} = 2 \cdot 6.36 = 12.72 \text{ i.u.}$$

$$2 \cdot {}^3_1H_{222} = 2 \cdot 7.46 = 14.92 \text{ i.u.}$$

$$2 \cdot {}^2H_{212} = 2 \cdot 7.77 = 15.54 \text{ i.u.}$$

$$3 \cdot {}^2H_{212} = 3 \cdot 7.63 = 22.89 \text{ i.u.}$$

Bond index contribution,

$$I_b = 218.42 \text{ i.u.}$$

TABLE III
 CODES AND BOND VALUES (INCREMENTS) OF BONDS IN C₁-C₂₀ ALKANES

Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)
³ ₃ C ₁₁	6.18	¹¹ ₁ C ₃₂	6.30	²² ₄ C ₃₂	4.56	²²⁴ ₀ C ₄₁	10.74
¹ ₃ C ₂₁	6.42	¹² ₁ C ₃₂	7.72	¹¹ ₁₁ C ₃₃	6.84	²³³ ₀ C ₄₁	9.52
² ₃ C ₂₁	6.79	¹³ ₁ C ₃₂	7.43	¹² ₁₁ C ₃₃	7.33	¹¹¹ ₁ C ₄₂	7.24
³ ₃ C ₂₁	6.78	¹⁴ ₁ C ₃₂	7.28	¹³ ₁₁ C ₃₃	7.10	¹¹¹ ₂ C ₄₂	6.31
⁴ ₃ C ₂₁	7.29	²² ₁ C ₃₂	7.51	¹⁴ ₁₁ C ₃₃	7.02	¹¹¹ ₃ C ₄₂	5.93
¹ ₁ C ₂₂	7.00	²³ ₁ C ₃₂	5.59	²³ ₁₁ C ₃₃	5.45	¹¹¹ ₄ C ₄₂	8.00
² ₁ C ₂₂	7.17	²⁴ ₁ C ₃₂	6.56	²³ ₁₁ C ₃₃	6.40	¹¹² ₁ C ₄₂	7.25
³ ₁ C ₂₂	8.22	³³ ₁ C ₃₂	6.60	²⁴ ₁₁ C ₃₃	6.08	¹¹² ₂ C ₄₂	6.40
⁴ ₁ C ₂₂	6.97	³⁴ ₁ C ₃₂	6.24	³³ ₁₁ C ₃₃	6.57	¹¹² ₃ C ₄₂	6.14
² ₂ C ₂₂	7.34	¹¹ ₂ C ₃₂	6.55	¹² ₁₂ C ₃₃	6.26	¹¹² ₄ C ₄₂	5.86
³ ₂ C ₂₂	7.35	¹² ₂ C ₃₂	7.39	¹³ ₁₂ C ₃₃	5.56	¹¹³ ₁ C ₄₂	8.42
⁴ ₂ C ₂₂	6.70	¹³ ₂ C ₃₂	6.04	²² ₁₂ C ₃₃	6.39	¹¹³ ₂ C ₄₂	5.88
³ ₃ C ₂₂	7.01	¹⁴ ₂ C ₃₂	8.95	²² ₁₃ C ₃₃	7.23	¹¹³ ₃ C ₄₂	6.08
⁴ ₃ C ₂₂	4.74	²² ₂ C ₃₂	7.06	²² ₂₁ C ₃₃	7.19	¹¹⁴ ₁ C ₄₂	9.67
⁴ ₄ C ₂₂	4.68	²³ ₂ C ₃₂	9.92	¹¹¹ ₀ C ₄₁	5.31	¹¹⁴ ₂ C ₄₂	7.51
¹¹ ₀ C ₃₁	5.91	²⁴ ₂ C ₃₂	6.77	¹¹² ₀ C ₄₁	6.87	¹²² ₁ C ₄₂	6.63
¹² ₀ C ₃₁	6.62	³³ ₂ C ₃₂	6.53	¹¹³ ₀ C ₄₁	8.74	¹²² ₂ C ₄₂	7.23
¹³ ₀ C ₃₁	7.20	¹¹ ₃ C ₃₂	5.78	¹¹⁴ ₀ C ₄₁	6.00	¹²² ₃ C ₄₂	5.98
¹⁴ ₀ C ₃₁	7.57	¹² ₃ C ₃₂	5.08	¹²² ₀ C ₄₁	7.53	¹²³ ₁ C ₄₂	6.39
¹² ₀ C ₃₁	6.97	¹⁴ ₃ C ₃₂	5.04	¹²³ ₀ C ₄₁	8.75	¹²³ ₂ C ₄₂	7.94
²³ ₀ C ₃₁	7.80	²² ₃ C ₃₂	7.00	²²² ₀ C ₄₁	6.97	¹²⁴ ₁ C ₄₂	10.22
²⁴ ₀ C ₃₁	7.64	²³ ₃ C ₃₂	5.79	¹²⁴ ₀ C ₄₁	10.05	¹³³ ₁ C ₄₂	9.04
³³ ₀ C ₃₁	7.65	¹¹ ₄ C ₃₂	6.21	¹³³ ₀ C ₄₁	9.88	²²² ₁ C ₄₂	6.69
³⁴ ₀ C ₃₁	7.56	¹² ₄ C ₃₂	4.90	¹³⁴ ₀ C ₄₁	7.95	²²² ₂ C ₄₂	7.08
⁴⁴ ₀ C ₃₁	9.49	¹³ ₄ C ₃₂	4.77	²²³ ₀ C ₄₁	6.72	²²³ ₁ C ₄₂	7.96

TABLE III (continued)

Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)
$^{111}_{11}C_{43}$	6.84	$^2H_{12}$	7.63	$^1H_{212}$	7.40	$^2_2H_{222}$	8.35
$^{111}_{12}C_{43}$	6.92	$^3H_{12}$	7.48	$^2H_{212}$	7.77	$^3_2H_{222}$	7.98
$^{111}_{13}C_{43}$	6.84	$^4H_{12}$	7.26	$^3H_{212}$	7.32	$^4_2H_{222}$	7.23
$^{111}_{14}C_{43}$	8.59	$^{11}H_{13}$	6.98	$^4H_{212}$	7.30	$^3_3H_{222}$	6.67
$^{112}_{11}C_{43}$	8.21	$^{12}H_{13}$	7.00	$^{11}H_{213}$	7.60	$^4_3H_{222}$	5.75
$^{112}_{12}C_{43}$	7.53	$^{13}H_{13}$	7.02	$^{12}H_{213}$	7.62	$^{11}_1H_{223}$	7.25
$^{112}_{13}C_{43}$	6.69	$^{14}H_{13}$	7.04	$^{13}H_{213}$	7.84	$^{12}_1H_{223}$	7.47
$^{112}_{22}C_{43}$	6.28	$^{22}H_{13}$	7.05	$^{14}H_{213}$	7.69	$^{13}_1H_{223}$	7.50
$^{111}_{22}C_{43}$	6.24	$^{23}H_{13}$	7.08	$^{22}H_{213}$	7.70	$^{14}_1H_{223}$	5.46
$^{111}_{23}C_{43}$	5.93	$^{24}H_{13}$	7.11	$^{23}H_{213}$	8.70	$^{22}_1H_{223}$	6.66
$^{113}_{11}C_{43}$	9.38	$^{33}H_{13}$	7.14	$^{24}H_{213}$	7.50	$^{23}_1H_{223}$	5.52
$^{113}_{12}C_{43}$	7.03	$^{34}H_{13}$	7.09	$^{33}H_{213}$	7.29	$^{24}_1H_{223}$	5.25
$^{114}_{11}C_{43}$	7.49	$^{44}H_{13}$	10.15	$^{34}H_{213}$	7.75	$^{33}_1H_{223}$	5.17
$^{122}_{11}C_{43}$	6.31	$^{111}H_{14}$	6.37	$^{111}H_{214}$	8.14	$^{11}_2H_{223}$	7.50
$^{122}_{12}C_{43}$	9.01	$^{112}H_{14}$	6.08	$^{112}H_{214}$	7.03	$^{12}_2H_{223}$	7.42
$^{123}_{11}C_{43}$	8.93	$^{113}H_{14}$	6.05	$^{113}H_{214}$	6.29	$^{13}_2H_{223}$	7.75
$^{222}_{11}C_{43}$	7.86	$^{114}H_{14}$	7.25	$^{114}H_{214}$	6.25	$^{14}_2H_{223}$	6.36
$^{111}_{111}C_{44}$	6.77	$^{122}H_{14}$	6.97	$^{122}H_{214}$	8.91	$^{22}_2H_{223}$	6.33
$^{112}_{111}C_{44}$	9.18	$^{123}H_{14}$	6.93	$^{123}H_{214}$	8.80	$^{23}_2H_{223}$	6.13
$^{113}_{111}C_{44}$	6.17	$^{124}H_{14}$	6.73	$^{124}H_{214}$	7.47	$^{11}_3H_{223}$	6.48
$^{112}_{112}C_{44}$	9.65	$^{133}H_{14}$	6.36	$^{133}H_{214}$	5.34	$^{12}_3H_{223}$	6.44
$^{122}_{112}C_{44}$	6.31	$^{222}H_{14}$	6.03	$^{222}H_{214}$	8.43	$^{13}_3H_{223}$	7.95
H_0	5.96	$^{223}H_{14}$	8.64	$^1_1H_{222}$	7.69	$^{11}_4H_{223}$	8.21
H_{11}	6.95	$^{224}H_{14}$	7.23	$^2_1H_{222}$	7.98	$^{12}_4H_{223}$	7.10
$^1H_{12}$	7.39	$^{134}H_{14}$	9.66	$^3_1H_{222}$	7.46	$^{111}_1H_{224}$	8.17
		H_{211}	7.37	$^4_1H_{222}$	7.33		

(Continued on p. 316)

TABLE III (continued)

Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)	Bond code	Bond value (i.u.)
$^{112}_1\text{H}_{224}$	6.45	$^{112}_{12}\text{H}_{234}$	4.85	$^1\text{H}_{3122}^1$	7.84	$^{11}\text{H}_{3133}^{22}$	4.98
$^{113}_1\text{H}_{224}$	8.00	$^{113}_{11}\text{H}_{234}$	4.08	$^1\text{H}_{3122}^2$	7.86	$^{11}\text{H}_{3134}^{111}$	8.09
$^{114}_1\text{H}_{224}$	4.87	$^{122}_{11}\text{H}_{234}$	6.17	$^1\text{H}_{3122}^3$	7.89	$^{11}\text{H}_{3134}^{112}$	6.65
$^{122}_1\text{H}_{224}$	7.22	$^{111}_{111}\text{H}_{244}$	8.61	$^1\text{H}_{3122}^6$	7.92	$^{111}\text{H}_{3144}^{111}$	5.03
$^{123}_1\text{H}_{224}$	5.29	$^{112}_{111}\text{H}_{244}$	7.30	$^2\text{H}_{3122}^2$	6.84	$^1_1\text{H}_{3222}^4$	8.03
$^{222}_1\text{H}_{224}$	5.85	H_{3111}	6.68	$^2\text{H}_{3122}^3$	6.53	$^1_1\text{H}_{3222}^2$	8.06
$^{211}_2\text{H}_{224}$	8.13	H_{3112}^1	7.43	$^2\text{H}_{3122}^4$	6.41	$^1_1\text{H}_{3222}^3$	7.96
$^{212}_2\text{H}_{224}$	6.02	H_{3112}^2	7.45	$^3\text{H}_{3122}^3$	4.49	$^1_1\text{H}_{3222}^4$	7.15
$^{122}_2\text{H}_{224}$	5.75	H_{3112}^3	7.47	$^1\text{H}_{3123}^{11}$	7.75	$^2_1\text{H}_{3222}^2$	7.38
$^{113}_2\text{H}_{224}$	5.31	H_{3112}^4	7.50	$^1\text{H}_{3123}^{12}$	7.86	$^2_1\text{H}_{3222}^3$	8.00
$^{111}_3\text{H}_{224}$	6.37	H_{3113}^{11}	7.96	$^1\text{H}_{3123}^{13}$	4.97	$^2_3\text{H}_{3222}^2$	7.22
$^{112}_3\text{H}_{224}$	4.11	H_{3113}^{12}	7.92	$^1\text{H}_{3123}^{22}$	6.20	$^1_1\text{H}_{3223}^{11}$	7.94
$^{111}_4\text{H}_{224}$	6.60	H_{3113}^{13}	7.90	$^2\text{H}_{3123}^{11}$	7.66	$^1_1\text{H}_{3223}^{12}$	6.28
$^{11}_1\text{H}_{233}$	6.82	H_{3113}^{14}	7.85	$^2\text{H}_{3123}^{12}$	7.47	$^1_1\text{H}_{3223}^{13}$	4.94
$^{12}_1\text{H}_{233}$	6.55	H_{3113}^{22}	8.01	$^2\text{H}_{3123}^{22}$	5.27	$^2_1\text{H}_{3223}^{11}$	6.15
$^{14}_1\text{H}_{233}$	6.17	H_{3113}^{23}	7.95	$^4\text{H}_{3123}^{13}$	7.18	$^3_1\text{H}_{3223}^{11}$	5.75
$^{22}_1\text{H}_{233}$	4.60	H_{3113}^{24}	7.42	$^1\text{H}_{3124}^{111}$	7.73	$^2_2\text{H}_{3223}^{11}$	4.06
$^{26}_1\text{H}_{233}$	4.91	H_{3113}^{33}	7.17	$^1\text{H}_{3124}^{112}$	6.70	$^1_1\text{H}_{3223}^{22}$	4.96
$^{22}_1\text{H}_{233}$	7.54	H_{3114}^{111}	7.14	$^1\text{H}_{3124}^{113}$	6.80	$^1_1\text{H}_{3224}^{111}$	7.90
$^{12}_1\text{H}_{233}$	6.38	H_{3114}^{112}	7.16	$^1\text{H}_{3124}^{122}$	1.94	$^1_1\text{H}_{3224}^{112}$	6.72
$^{111}_1\text{H}_{234}$	6.98	H_{3114}^{113}	7.18	$^2\text{H}_{3124}^{111}$	5.53	$^2_1\text{H}_{3224}^{111}$	7.18
$^{111}_1\text{H}_{234}$	6.84	H_{3114}^{114}	7.15	$^2\text{H}_{3124}^{112}$	5.40	$^{11}_1\text{H}_{3233}^{11}$	7.85
$^{111}_1\text{H}_{234}$	6.58	H_{3114}^{122}	7.67	$^3\text{H}_{3124}^{111}$	5.00	$^{11}_2\text{H}_{3233}^{11}$	7.03
$^{111}_1\text{H}_{234}$	6.11	H_{3114}^{123}	7.34	$^{11}\text{H}_{3133}^{11}$	8.38	$^{11}_1\text{H}_{3234}^{111}$	7.49
$^{122}_1\text{H}_{234}$	5.23	H_{3114}^{222}	8.33	$^{11}_1\text{H}_{3133}^{12}$	5.28	$^{11}_1\text{H}_{3233}^{111}$	7.13

The molecular index contribution (I_m) is

$$I_m = 14.20 + 218.42 = 232.62 \text{ i.u.} \quad (14)$$

The calculated retention index of 2,2,3-trimethylheptane on squalane at 50.0° from eqn. 7 is

$$I_{2,2,3-M_3C_7}^{sq}(50.0^\circ) = 3.93 \cdot 232.62 = 914.2 \text{ i.u.} \quad (15)$$

where sq = squalane, M = methyl and C₇ = heptane. The measured (913.0 i.u.), calculated (914.2 i.u.) and literature³¹ (912.7 i.u.) values were in good agreement.

In Tables IV–VI, calculated retention index values are compared with measured values taken from the literature.

TABLE IV

COMPARISON OF MEASURED¹⁶ AND CALCULATED RETENTION INDICES OF SOME COMPOUNDS ON SQUALANE AT 50.0°

Compound	Retention index (i.u.)		Difference (i.u.)
	Measured ¹⁶	Calculated	
2,2-Dimethylheptane	815.4	815.4	0.0
4,4-Dimethylheptane	827.6	826.4	+1.2
2,6-Dimethylheptane	827.2	822.9	+4.3
3,3-Dimethylheptane	836.1	837.9	-1.8
3-Methyloctane	870.3	873.2	-2.9

TABLE V

COMPARISON OF MEASURED³¹ AND CALCULATED RETENTION INDICES OF SOME COMPOUNDS ON SQUALANE AT 50.0°

Compound	Retention index (i.u.)		Difference (i.u.)
	Measured ³¹	Calculated	
6-Methyl-3-ethylheptane	923.6	921.6	+2.0
2,5-Dimethyloctane	921.5	925.1	-3.6
2,7-Dimethyloctane	928.1	930.3	-2.2
3-Ethyloctane	963.8	964.0	-0.2
4-Ethyloctane	951.5	947.4	+4.1
2,2-Dimethyloctane	914.1	915.8	-1.7

It should be noted that in our previous work, the individual temperature dependence of the interaction factor on squalane was neglected. In some instances, this led to significant errors, ranging from 20 to 40 i.u., as shown by Engewald *et al.*⁴⁸ and Vanheertum⁴⁹, if the extrapolation interval was too high (50–60°). In this work, the individual temperature dependence of the interaction factor was taken into account, relying on literature data, $\partial I/\partial T$, if the measurements were different from 50.0° (Table VI).

TABLE VI

COMPARISON OF MEASURED^{5,6} AND CALCULATED RETENTION INDICES OF SOME COMPOUNDS ON SQUALANE AT 100.0°

Compound	Retention index (i.u.)		Difference (i.u.)
	Measured ^{5,6}	Calculated	
2-Methylundecane	1164.0	1164.4	-0.4
3-Methylundecane	1169.6	1171.6	-2.0
6-Methylundecane	1151.8	1152.8	-1.0
2,3-Dimethylundecane	1251.4	1253.0	-1.6
2,5-Dimethylundecane	1210.4	1211.6	-1.2
6,6-Dimethylundecane	1200.0	1199.0	+1.0
2,10-Dimethylundecane	1227.3	1229.0	-1.7
4,7-Dimethylundecane	1206.6	1210.1	-3.5

EXPERIMENTAL

The purpose of our experiments was to complete the available literature data, as most of the data that are necessary in studying retention indices and molecular structure can be found in the literature. The measurements were made with Carlo Erba Fractovap Model D, GV and GI-452, Pye Unicam Model 104-105, Perkin-Elmer Model 900, F-6 and F-11, instruments, with thermal conductivity and flame ionization detectors, various types of packed and capillary columns and Speedomax or Hitachi recorders with a sensitivity of 1.0 or 2.5 mV (full scale), and a chart speed of 1.27 or 5.08 cm/min. Hydrogen, argon and nitrogen were used as carrier gases and hydrogen, oxygen or air as auxiliary gases. All experiments were carried out under isothermal conditions. A semi-automatic device or a Hamilton syringe was used for sample introduction.

DISCUSSION

So far, the results obtained simply demonstrate the possibilities inherent in the method. The method will be suitable for peak identification and/or peak elimination, peak coincidence determinations and theoretical investigations only if the increment values are calculated by computer iteration relying on retention indices accurate to 0.1 i.u., based on exact thermodynamic bond energy data. In the latter case, it seems probable that bond energy and bond distance values can also be determined and/or calculated from gas chromatographic retention index data.

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