

CHROM. 5934

## CONTRIBUTION TO THE THEORY OF THE RETENTION INDEX SYSTEM

## IV. RETENTION INDEX AND MOLECULAR STRUCTURE.

## CALCULATION OF RETENTION INDICES OF OLEFINS, CYCLIC HYDROCARBONS AND HOMOLOGUES OF BENZENE HYDROCARBONS ON THE BASIS OF THEIR MOLECULAR STRUCTURES

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SUMMARY

In a previous paper, the fundamentals of the relation between the retention index and molecular structure were derived, and the additivity of retention indices was shown with the help of the gas chromatographic literature. In this paper, the same problem is discussed on squalane as stationary phase for olefins, cyclic hydrocarbons and homologues of benzene. Our investigations also extended the theoretical aspects of the problem, especially at the interaction connections.

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## INTRODUCTION

It is well known that one of the most important tasks is the critical discussion and evaluation of thousands of gas chromatographic (GC) data and the correlation of suitably systematized data from various international sources. Although very significant experiments have been carried out<sup>1,2</sup>, there is much that remains to be done in this field. As it is now quite clear that the retention index system developed by Kováts<sup>3</sup> is the most suitable for this purpose, many workers and research groups have dealt intensively with several problems of this system. The most important of these questions is the relation between retention index and molecular structure, and we dealt with this question in a previous paper by considering aliphatic hydrocarbons<sup>4</sup>. In the present paper, using the valuable retention index data from the papers of Loewenguth and Tourres<sup>5-7</sup> and Hively and Hinton<sup>8</sup>, the same question is discussed for olefins, cyclic hydrocarbons and homologues of benzene, extending the theoretical aspects of the problem with the solution of some new questions.

## THEORETICAL

We reduced the retention index into separate additive components, such as:

- (a) atomic index contribution ( $I_a$ )  
 (b) bond index contribution ( $I_b$ )  
 (c) interaction index contribution ( $I_i$ ).  
 } molecular index contribution ( $I_m$ )

On account of the additivity of index contributions, the retention index,  $I$ , is given by:

$$\begin{aligned} I_{\text{stationary phase}}^{\text{substance}}(T) &= I_a + I_b + I_i^{\text{stationary phase}}(T) \\ &= I_m + I_i^{\text{stationary phase}}(T) \end{aligned} \quad (1)$$

where  $I$  is the retention index of the substance on the given stationary phase and constant column temperature (index units, i.u.) and  $T$  is the column temperature ( $^{\circ}\text{K}$  or  $^{\circ}\text{C}$ ).

The atomic index contributions can be calculated from:

$$I_a = n \cdot i_{a,H} + m \cdot i_{a,C} \quad (2)$$

where  $n$  = number of hydrogen atoms and  $m$  = number of carbon atoms.

$$i_a \approx \frac{\text{atomic weight}}{10} \quad (\text{index units}) \quad (3)$$

where  $i_a$  = atomic index value (i.u.).

The symbol " $\approx$ " is used when certain factors are neglected in the different cases. The atomic index contribution is the sum of the index values of the atoms, in index units i.u., similarly as with molecular weights. The atomic index values used for the calculations are summarized in Table I.

The bond index contribution is the sum of the retention index values of the bonds between the atoms, whereas the interaction index contribution expresses the interactions between the substance studied and the stationary phase in index units.

Whereas the molecular index contribution (atomic and bond) is independent of the stationary phase and the column temperature and is determined only by the

TABLE I

ATOMIC INDEX VALUES USED IN THE CALCULATIONS

Atom	Atomic index value (i.u.)
C	1.21
H	0.10
O	1.60
Cl	3.55
N	1.40
Si	2.81
Br	8.00
F	1.90
P	3.10
I	12.70
S	3.21

quality of the substance under study, the interaction index contribution depends on the stationary phase and the column temperature.

In our work, some theoretical aspects of the relation between retention index and molecular structure were examined. It can be stated that for any compound, *e.g.*, stationary phase, the following equation is valid:

$$I_{\text{stationary phase substance}}(T) = \frac{I_m}{f_{ia}^{\text{st.ph.}}(T) + f_{ii}^{\text{st.ph.}}(T)} \quad (4)$$

where st.ph. = stationary phase;  $f_{ia}$  = average interaction factor;  $f_{ii}$  = individual interaction factor.

Both the average and the individual interaction factors depend on the quality of the substance, *i.e.*, stationary phase as well as on the column temperature. It must be noted that  $f_{ii}^{\text{st.ph.}}$  is almost zero only for the squalane stationary phase, and, therefore:

$$I_{\text{squalane substance}}(T) = \frac{I_m}{f_{ia}^{\text{squalane}}(T)} \quad (5)$$

Therefore, the value of  $f_{ia}$  for the squalane stationary phase can be easily calculated. Some values of  $f_{ia}^{\text{squalane}}(T)$  are given in Table II for the most frequently used column temperatures.

TABLE II

$f_{ia}$  VALUES ON SQUALANE AS STATIONARY PHASE AT DIFFERENT COLUMN TEMPERATURES

Column temperature (°C)	$f_{ia}$
30.0	0.2569
50.0	0.2545
70.0	0.2526
90.0	0.2506
100.0	0.2500
120.0	0.2487

The value of  $f_{ii}$  can be calculated only with the help of the Rohrschneider concept and method, as stated in one of our previous papers<sup>9</sup>.

The bond index contributions were more difficult to define. To describe exactly the various bonds of olefins, the following codes are applied:

- (1) C-C saturated bonds are denoted by C.
- (2) C = C unsaturated bonds are denoted by C=.
- (3) On the right side of C are given, as superscript and subscript, the order of the two carbon atoms between which the double bond occurs, *e.g.*,  $C=\overset{4}{3}$  presents a double bond between a tertiary and a quaternary carbon atom. The index of the higher order is used as the superscript.

(4) If the neighbouring carbon atom is one of the carbon atoms of the double bond, this is represented by the symbol ". For example,  $\overset{3}{1}C''_{32}$  is a saturated bond between a tertiary and a secondary carbon atom. The tertiary carbon atom is at the

TABLE III

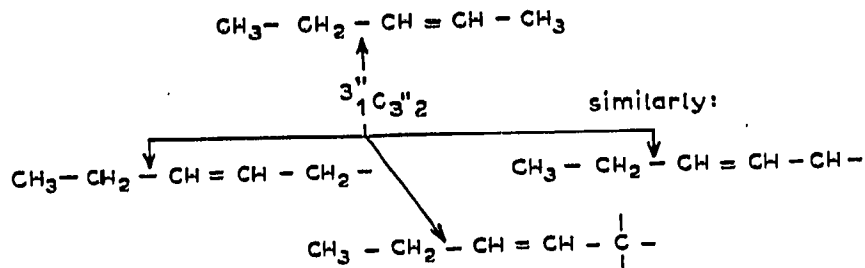
BOND INDEX CONTRIBUTIONS OBTAINED BY ITERATION

Bond code	Bond index contribution (i.u.)	Bond code	Bond index contribution (i.u.)
$3''C_{0\ 21}$	11.20	$4''C_{2\ 3''2}$	9.50
$4''C_{0\ 21}$	9.96	$4''C_{1\ 3''2}$	12.10
$4''C_{1\ 22}$	13.10	$4''C_{12\ 32}$	4.44
$4''C_{2\ 22}$	11.91	$33''C_{1\ 32}$	10.20
$3''C_{1\ 22}$	8.44	$4''C_{11\ 32}$	7.82
$3''C_{2\ 22}$	7.42	$4''C_{0\ 32}$	11.97
$3''C_{3\ 22}$	6.18	$3''C_{12\ 32}$	5.47
$3''C_{0\ 3''1}$	10.75	$3''C_{1\ 3''2}$	12.50
$4''C_{0\ 3''1}$	10.45	$3''C_{11\ 32}$	7.46
$13''C_{0\ 31}$	11.20	$3''C_{3\ 3''2}$	11.50
$14''C_{0\ 31}$	11.60	$2''C_{4\ 3''2}$	5.09
$23''C_{0\ 31}$	10.80	$13''C_{2\ 32}$	9.90
$24''C_{0\ 31}$	10.20	$14''C_{1\ 32}$	10.24
$33''C_{0\ 31}$	11.12	$14''C_{2\ 32}$	7.53
$2''C_{2\ 3''2}$	12.00	$2''C_{5\ 3''2}$	10.22
$3''C_{2\ 3''2}$	10.00	$3''C_{12\ 33''}$	9.20
$13''C_{1\ 32}$	11.70	$2''C_{11\ 33''}$	7.17
$2''C_{12\ 33''}$	8.80	$123''C_{0\ 41}$	8.00
$3''C_{11\ 33''}$	7.25	$33''C_{0\ 4''1}$	9.48
$4''C_{11\ 33''}$	9.13	$32''C_{1\ 4''2}$	10.60
$13''C_{11\ 33}$	8.69	$12''C_{1\ 4''2}$	6.36
$2''C_{13\ 33''}$	8.78	$14''C_{1\ 4''2}$	13.50
$2''C_{22\ 33''}$	11.59	$24''C_{1\ 4''2}$	10.50
$4''C_{0\ 4''1}$	6.25	$111C_{4''\ 42}$	5.60
$22''C_{0\ 4''1}$	8.70	$12''C_{4\ 4''2}$	2.00
$14''C_{0\ 4''1}$	9.70	$23''C_{1\ 4''2}$	10.70
$12''C_{0\ 41}$	6.25	$13''C_{2\ 4''2}$	7.20
$113''C_{0\ 41}$	7.60	$13''C_{1\ 4''2}$	7.40
$114''C_{0\ 41}$	7.80	$111C_{3''\ 42}$	5.50
$2''3C_{0\ 4''1}$	9.60	$22''C_{2\ 4''2}$	10.00
$2''4C_{0\ 4''1}$	9.80	$22''C_{3\ 4''2}$	9.98
$114''C_{0\ 41}$	13.84	$2''3C_{1\ 4''2}$	10.85

TABLE III (continued)

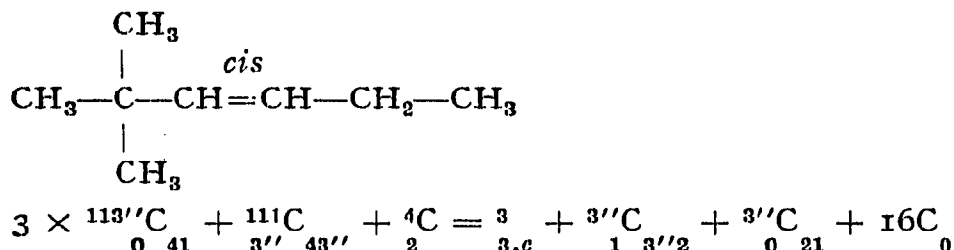
Bond code	Bond index contribution (i.u.)	Bond code	Bond index contribution (i.u.)
$^{23}_{0}C_{4''1}$	9.00	$^{12}_{2}C_{4''2}$	2.50
$^{24}_{0}C_{4''1}$	9.58	$^{12}_{3}C_{4''2}$	2.25
$^{13}_{0}C_{4''1}$	6.25	$^{113}_{1}C_{42}$	4.50
		$^{14}_{1}C_{42}$	13.50
$^{111}_{4''}C_{4''3}$	6.60	$^{23}_{0}C=4_3$	19.15
$^{111}_{3''}C_{43''}$	6.80	$^{14}_{0}C=4_3$	14.20
$^{12}_{11}C_{43}$	11.38	$^{13}_{0}C=4_3$	18.00
$^{14}_{11}C_{4''3}$	11.25	$^3C=3_{3,c}$	21.35
$^{111}_{3''}C_{43''}$	6.70	$^3C=3_{3,t}$	22.42
$^{12}_{12}C_{4''3}$	13.50	$^4C=3_{3,c}$	28.17
		$^4C=3_{3,t}$	22.86
$^{22}_{11}C_{4''3}$	11.46	$^{13}_{1}C=3_{3,c}$	31.24
$^{13}_{11}C_{4''3}$	13.40	$^{13}_{1}C=3_{3,t}$	28.48
$^{113}_{2''}C_{43''}$	16.60	$^2C=3_{3,c}$	23.39
$^{12}_{111}C_{44''}$	19.22	$^2C=3_{3,t}$	23.83
$^0C=2_2$	30.56	$^3C=3_{3,t}$	17.95
$^2C=3_2$	24.20	$^4C=3_{3,c}$	22.51
$^3C=3_2$	18.40	$^4C=3_{3,t}$	16.45
$^4C=3_2$	19.45	$^{11}_{1}C=4_3$	41.09
$^{12}_{0}C=4_2$	32.30	$^{13}_{1}C=4_{3,c}$	34.01
$^{22}_{0}C=4_2$	29.56	$^{12}_{1}C=4_{3,t}$	39.07
$^2C=3_{3,c}$	30.32	$^{13}_{1}C=4_{3,c}$	21.00
$^2C=3_{3,t}$	26.89	$^{13}_{11}C=4_4$	24.15
$^{22}_{1}C=4_3$	31.98	$^{22}_{11}C=4_4$	31.09
$^{11}_{2}C=4_3$	34.03	$^{12}_{12}C=4_{4,c}$	26.72
$^{12}_{2}C=4_{3,t}$	31.13	$^{12}_{12}C=4_{4,t}$	25.28
$^{11}_{3}C=4_3$	25.76		
$^{11}_{4}C=4_3$	33.45		
$^{11}_{11}C=4_4$	40.23		
$^{12}_{11}C=4_4$	33.14		

same time a carbon atom of the unsaturated double bond. To the other side of the olefinic bond and to the secondary carbon atom, one methyl group is connected:



(5) The *cis* isomer is represented by *c* as the right-hand subscript, the *trans* isomer by *t*.

In this way, the bonds of all the olefins can be coded very easily. The bond code of 2,2-dimethyl-3-hexene is as follows<sup>4</sup>:



As a further step, the values (i.u.) of bonds occurring in olefins were determined by iteration. The values calculated this way are summarized in Table III.

It can easily be seen that the bonding code used for the olefins and aliphatic hydrocarbons<sup>4</sup> cannot be used immediately for other compounds investigated in our work (cyclic hydrocarbons and homologues of benzene).

The greatest hindrance in using the bonding code was the code system used to represent neighbouring atoms, which is why the graphic descriptions of the bonds were used in a similar manner to the structural formula. The values of bonds in the compounds examined are shown in Table IV.

## EXPERIMENTAL

The purpose of our experiments was the completion of available literature data, as most of the data necessary for studying retention indices and molecular structures can be found in the literature.

The measurements were made on Pye-Unicam Model 104 and 105 gas chromatographs and Carlo Erba Fractovap Model C and D. Thermal conductivity and flame ionization detectors, various types of packed and capillary columns, and Speedomax G and W recorders with sensitivities of 1.0 and 2.5 mV full-scale and a chart speed of 1.27 cm/min were used. Hydrogen and nitrogen were used as carrier gases and hydrogen, oxygen and in some cases air were used as auxiliary gases. Experiments were carried out in each instance under isothermal conditions. A semi-automatic device or a Hamilton syringe was used for the introduction of samples. The data for a squalane column are summarized in Table V together with the corresponding optimum GC conditions.

The effectiveness of the method developed was checked for a number of compounds with squalane as stationary phase. Some of the results are presented in Table VI.



TABLE V

DATA FOR OPTIMUM GC CONDITIONS FOR A STANDARD SQUALANE COLUMN

Gas chromatograph	Pye-Unicam Model 104
Detector	Flame ionization
Sample	0.1 $\mu$ l introduced with a Hamilton syringe
Column	Aluminium spiral, 3.0 m long and 3.0 mm I.D.
Packing	10.0% (w/w) of squalane on 60-80 mesh Chromosorb W
Carrier gas	Nitrogen
Inlet pressure of carrier gas	2.25 kp/cm <sup>2</sup>
Auxiliary gases	Hydrogen and air
Column temperatures (°C)	30.0, 50.0, 70.0, 90.0, 100.0, 110.0, and 120.0 $\pm$ 0.1°
Temperature of evaporator (°C)	Column temperature + 70-100°
Recorder	Speedomax W; 1.0 mV full-scale; 1.0 sec
Chart speed	1.27 cm/min

Experiments aimed at the extension of the method to compounds containing halogen atoms or hydroxyl groups are in progress.

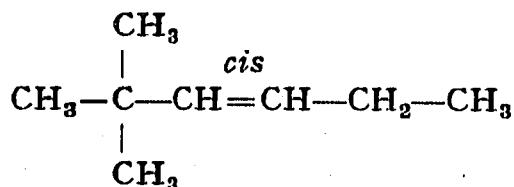
Finally, some examples will be presented to demonstrate the applicability of the method in analytical practice. A mixture of unknown composition was studied by GC on squalane as stationary phase at 50.0°C. One of the peaks, the retention index of which was found to be 716.8 i.u., was assumed to be due to 2,2-dimethyl-*cis*-3-hexene. However, the identification could not be made directly as no standard

TABLE VI

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF SOME COMPOUNDS AT 50.0°C WITH SQUALANE AS STATIONARY PHASE

Compound	Retention index		Deviation (i.u.)
	Measured (i.u.)	Calculated (i.u.)	
2-Methyl-2-butene	514.0	513.5	+0.5
2-Methyl-1-butene	487.0	487.1	-0.1
2,4,4-Trimethyl-2-pentene	715.0	715.1	-0.1
1-Methyl-cyclopentane	629.0	628.5	+0.5
1,1,3-Trimethylcyclopentane	724.6	723.8	+0.8
Benzene	640.0	640.2	-0.2
Toluene	747.0	745.3	+1.7

sample was available. Data similar to the index value measured we found in the literature<sup>7</sup>, which had to be checked. For this checking, the method described above was used. The structural formula of 2,2-dimethyl-*cis*-3-hexene is:



The bonds of the compound were coded and the corresponding bond index contributions were taken from Table III. These were:



Three $^{113}_{0}\text{C}_{41}$	bonds	$3 \times 7.60 \text{ i.u.}$	22.80 i.u.
$^{111}_{3}\text{C}_{43}$	bond	6.70 i.u.	6.70 i.u.
$^4_2\text{C}=\text{C}_{3,c}$	bond	22.51 i.u.	22.51 i.u.
$^{3'}_1\text{C}_{3''2}$	bond	12.50 i.u.	12.50 i.u.
$^{3''}_0\text{C}_{21}$	bond	11.20 i.u.	11.20 i.u.
Sixteen $\text{C}_0$	bonds <sup>4</sup>	$16 \times 5.96 \text{ i.u.}$	<u>95.76 i.u.</u>
			171.47 i.u.

The bond index contribution is therefore 171.47 i.u.

Then the atomic index contribution was calculated for  $\text{C}_8\text{H}_{16}$ :

Eight C atoms	$8 \times 1.21 \text{ i.u.}$	9.68 i.u.
Sixteen H atoms	$16 \times 0.10 \text{ i.u.}$	<u>1.60 i.u.</u>
		11.28 i.u.

The atomic index contribution is therefore 11.28 i.u.

The molecular index contribution was calculated as follows:

$$I_m = I_a + I_b = 171.47 + 11.28 = 182.75 \text{ i.u.}$$

$$f_{\text{squalane}}^{\text{ia}}(50.0^\circ\text{C}) = 0.2545 \text{ (Table II)}$$

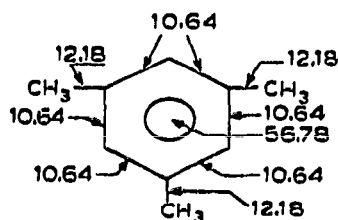
From eqn. 5:

$$I_{\text{squalane}}^{\text{2,2-dimethyl-}cis\text{-3-hexene}}(50.0^\circ\text{C}) = \frac{182.75}{0.2545} = 718.1 \text{ i.u.}$$

The measured (716.8 i.u.), calculated (718.1 i.u.) and literature (716.5 i.u.) index data were in good agreement (between +3 and -3 i.u.), and the unknown peak was therefore due to 2,2-dimethyl-*cis*-3-hexene.

The method of calculation is quite similar for different types of other compounds. As an example, the calculation of the retention index of 1,3,5-trimethylbenzene on squalane as stationary phase at 120.0°C is shown.

The structural formula of 1,3,5-trimethylbenzene is:



The bond index contribution is 228.92 i.u.

The atomic index contribution is 12.09 i.u. ( $\text{C}_9\text{H}_{12}$ )

The molecular index contribution is 241.01 i.u.

$$f_{\text{squalane}}^{\text{ia}}(120.0^\circ\text{C}) = 0.2487 \text{ (Table II)}$$

From eqn. 5:

$$I_{\text{squalane}}^{\text{3,3,5-trimethylbenzene}}(120^\circ\text{C}) = \frac{241.01}{0.2487} = 969.1 \text{ i.u.}$$

The retention index determined under the above experimental conditions was 968.0 i.u. Comparing this value to calculated 969.1 i.u., the agreement is good.

#### ACKNOWLEDGEMENT

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