

CHROM. 6697

## CONTRIBUTION TO THE THEORY OF THE RETENTION INDEX SYSTEM

### VI. CALCULATION OF THE RETENTION INDICES OF COMPOUNDS CONTAINING HALOGEN ATOMS OR HYDROXYL GROUPS, AMINES, KETONES, ESTERS, HETEROCYCLIC COMPOUNDS, ADAMANTANES, SILANES AND STEROIDS ON APOLAR AND POLAR STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY

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#### SUMMARY

In a previous paper, a method was described for calculating the retention indices of aliphatic hydrocarbons on the basis of their molecular structures, on squalane as stationary phase. This method was later extended to olefinic, alicyclic and aromatic hydrocarbons<sup>1,2</sup>.

In the present paper, the widespread application of the method to different compounds (adamantanes, silanes, steroids, etc.) on different stationary phases is described.

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#### INTRODUCTION

In the last few years, the examination of the relationship between retention indices and molecular structure has become important in gas chromatography. We have already described<sup>1,2</sup> a method for calculating the retention indices of various hydrocarbons on the basis of their molecular structures, on squalane as stationary phase. The papers of Hively and Hinton<sup>3</sup>, Šingliar<sup>4</sup>, Tóth and Borsodi<sup>5</sup>, Golovnya and Uraletz<sup>6</sup>, Schomburg<sup>7</sup>, Burkhard *et al.*<sup>8</sup>, Garzó *et al.*<sup>9</sup> and Brooks *et al.*<sup>10</sup> have been most useful in our work.

Although only the simplest questions involved in calculations on polar stationary phase have been answered (individual factors and members, their role, etc.), we have discussed our initial results for different groups of compounds (steroids, alcohols, etc.) as, because of the characteristics (chemical affinities, interaction forces and relationships, etc.) of these groups of compounds, variations in the individual properties can be neglected in the calculations.

## THEORETICAL

As shown in a previous paper<sup>2</sup>, the retention indices of some compounds can be calculated by means of simple relationships based on their molecular structures. As these equations are used in the calculations in this paper, they are repeated without any discussion:

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

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

$$I_{\text{substance}}^{\text{stationary phase}}(T) = \frac{I_m}{f_{ia}^{\text{st.ph.}}(T) + f_{ii}^{\text{st.ph.}}(T)} \quad (3)$$

where:

$I$  = the retention index of the substance on the given stationary phase (st.ph.) and constant column temperature (index units, i.u.);

$T$  = column temperature ( $^{\circ}\text{K}$  or  $^{\circ}\text{C}$ );

$I_a$  = atomic index contribution (i.u.);

$I_b$  = bond index contribution (i.u.);

$I_i$  = interaction index contribution (i.u.);

$I_m$  = molecular index contribution (i.u.);

$f_{ia}$  = average interaction factor;

$f_{ii}$  = individual interaction factor.

It must be noted that  $f_{ii}^{\text{squalane}}(T) = 0$ .

As the method relates the properties of one member of a group of compounds to those of other members of the same group, it can be postulated that the  $f_{ii}^{\text{st.ph.}}(T)$  values are constant for members of a particular group of compounds, especially for homologous series at a constant temperature and on the same stationary phase. For example:

$$f_{ii, \text{ethanol}}^{\text{PEG-1500}}(90.0^{\circ}\text{C}) = f_{ii, \text{propanol-1}}^{\text{PEG-1500}}(90.0^{\circ}\text{C}), \text{ and so on.}$$

Of course, this supposition can give rise to some errors, but in most instances the error affects the results only slightly, so that they can be used satisfactorily in practical work. Further research will probably sooner or later enable the calculations to be made more exact, especially by taking into account the individual interaction values.

## EXPERIMENTAL

Most of the data used in this work were taken from the specialized literature, and were completed with control measurements in only a few instances for compounds with very heterogenous characteristics —alcohols on squalane as stationary phase and amines on PEG-1500 as stationary phase, etc.

The measurements were made on a Pye-Unicam, Model 104, and Carlo Erba

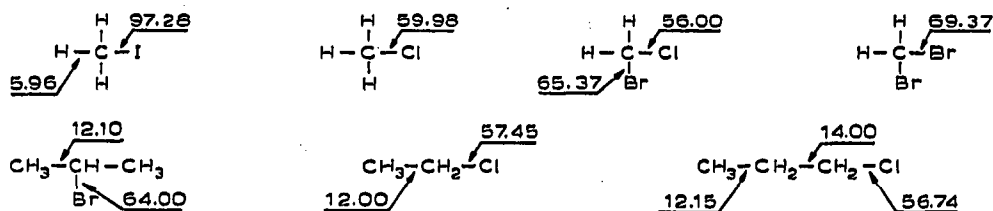


Fig. 1. Bond index contributions of some bond types in halogenated aliphatic hydrocarbons. The individual values are not repeated when they occur again in compounds in the later figures.

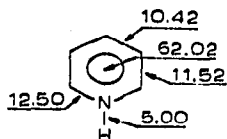


Fig. 2. Bond index values of pyridine.



Fig. 3. Bond index values of consecutive homologous ketones (methyl *n*-propyl ketone and methyl *n*-butyl ketone).

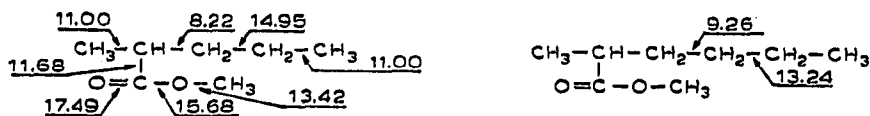


Fig. 4. Bond index values of consecutive homologous esters (methyl pent-2-anoate and methyl hex-2-anoate).

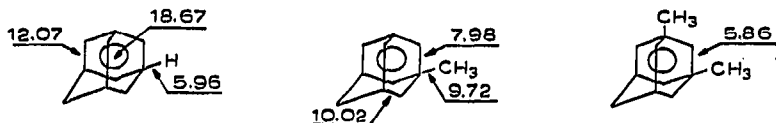


Fig. 5. Bond index values of some adamantanes.

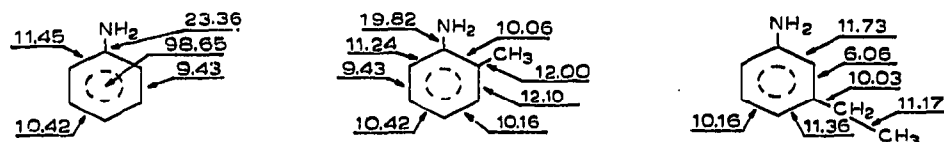


Fig. 6. Bond index values of some amines.

Fractovap, Models C and G, gas chromatographs. Thermal conductivity and flame ionization detectors, various types of columns (metallic and glass), different stationary phases, 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 air were used as auxiliary gases. All ex-

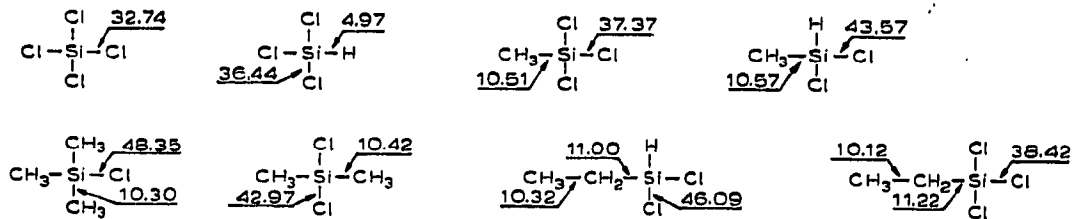


Fig. 7. Bond index values of some chlorosilanes.

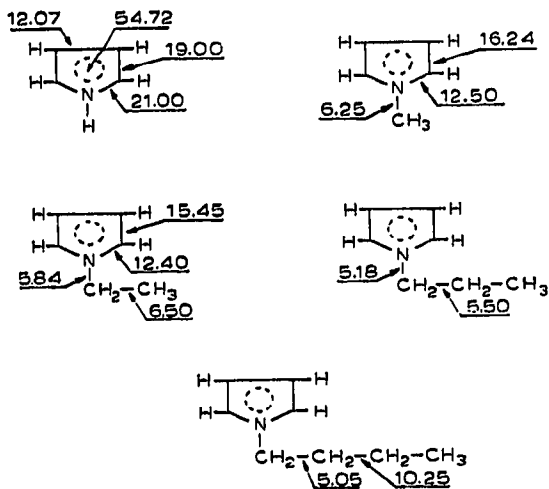


Fig. 8. Bond index values of some pyrroles.

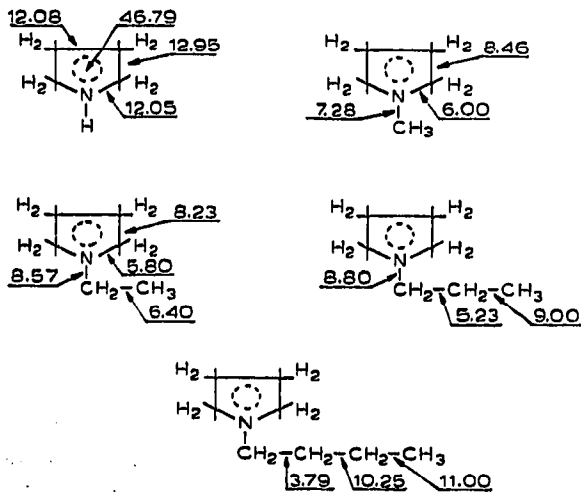


Fig. 9. Bond index values of some tetrahydropyrroles.

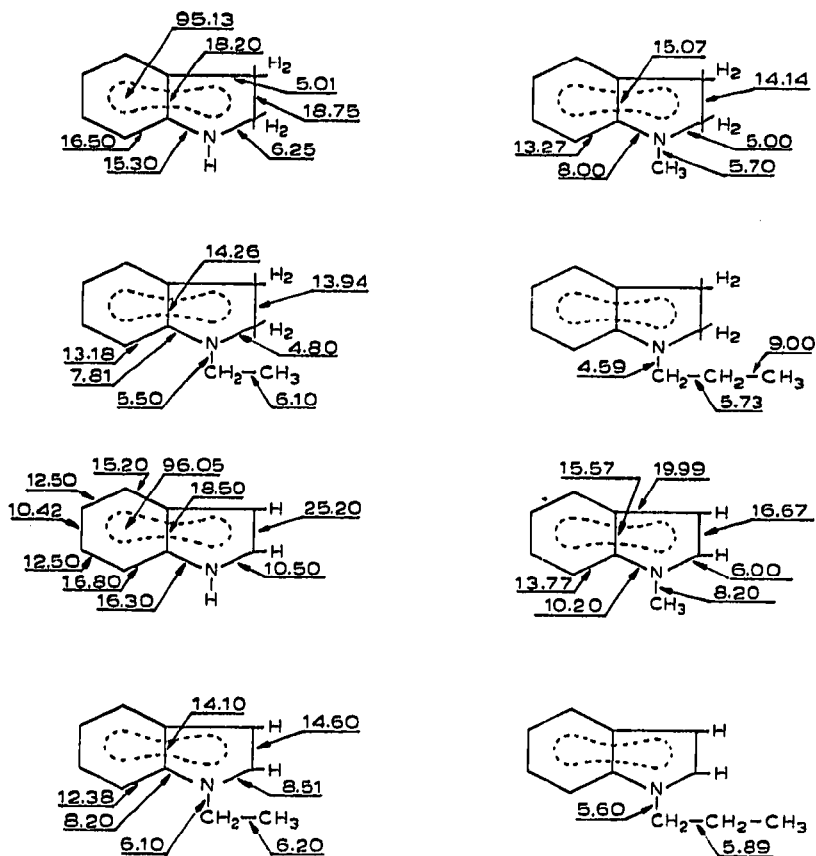


Fig. 10. Bond index values of some dihydroindoles and indoles.

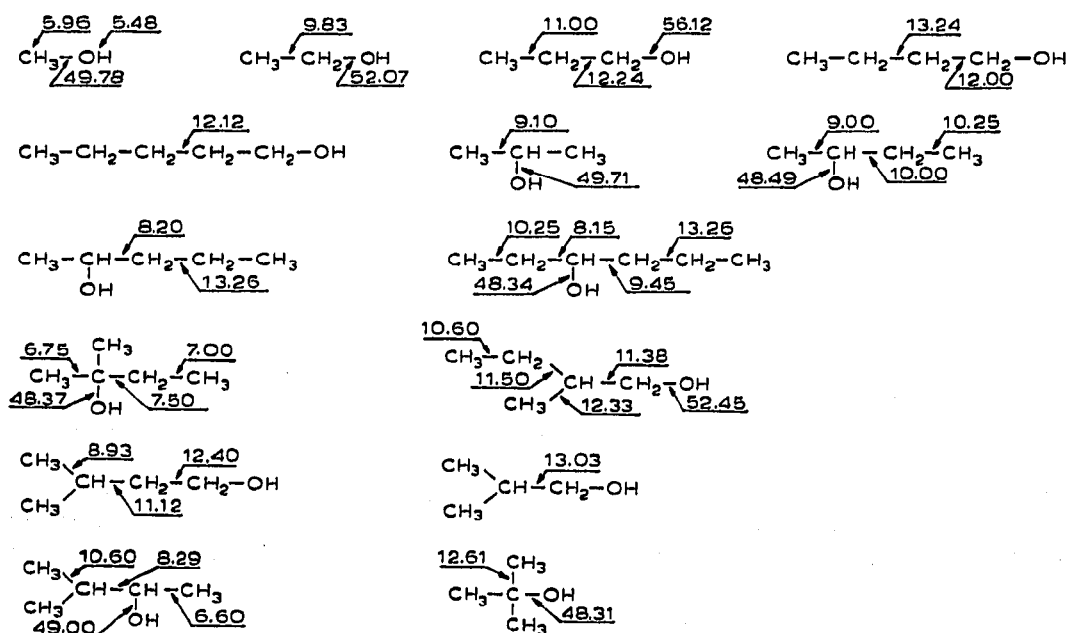


Fig. 11. Bond index values of some alcohols.

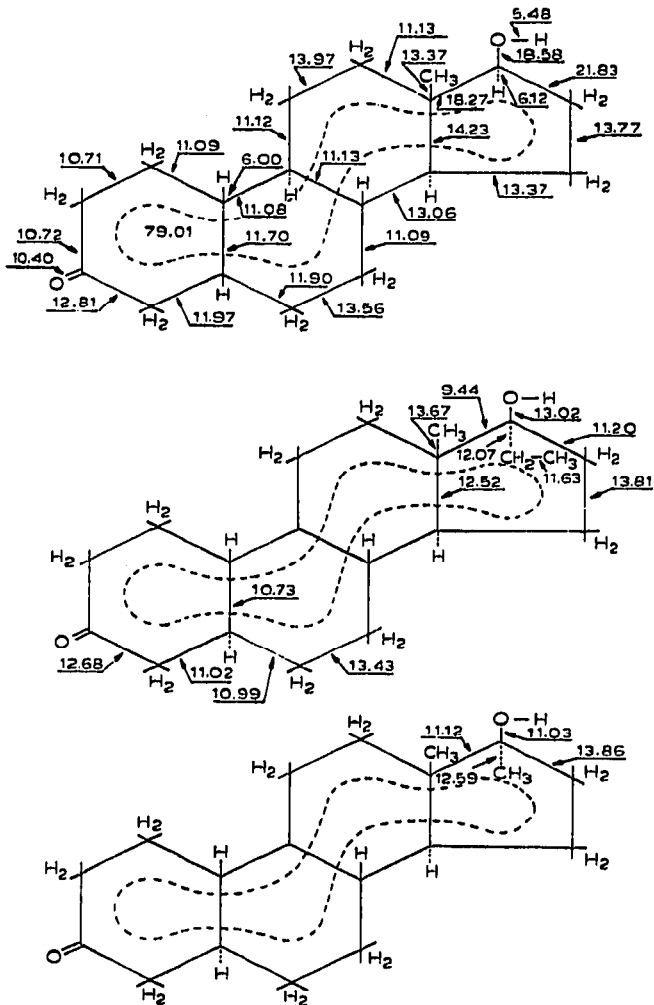


Fig. 12. Bond index values of some steroids.

periments were carried out under isothermal conditions. A semi-automatic device or Hamilton syringes were used for the introduction of samples.

Although we are developing a computer program for the investigation of the relationship between retention indices and molecular structure, in this work the computer was used only for making calculations (dependence of retention index on column temperature, calculation of substance-specific factors, etc.), as described in previous papers<sup>11,12</sup>.

Calculations of bond index contributions on squalane as stationary phase were made for halogen compounds, esters and alcohols, and the results are shown in Figs. 1–12. The results of some control calculations of retention indices are given in Tables I–VI.

TABLE I

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF ADAMANTANES AT DIFFERENT TEMPERATURES ON SQUALANE AS STATIONARY PHASE

Compound	110°		125°		Deviation (i.u.)	
	Measured <sup>a</sup> (i.u.)	Calculated (i.u.)	Measured <sup>a</sup> (i.u.)	Calculated i.u.	110°	125°
1,3,5-Trimethyl- adamantane	1153.0	1147.4	1161.0	1158.5	+5.6	+2.5
1,3,5,7-Tetra- methyladamantane	1169.0	1164.7	1176.0	1175.9	+4.3	+0.1

TABLE II

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF ESTERS AT 120° ON SQUALANE AS STATIONARY PHASE

Compound	Retention index (i.u.)		Deviation (i.u.)
	Measured <sup>13</sup>	Calculated	
Methyl heptan-2-oate	996.0	994.2	+1.8
Methyl octan-2-oate	1094.0	1093.0	+1.0
Methyl nonan-2-oate	1192.0	1194.9	-2.9

TABLE III

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF HALOGEN COMPOUNDS AT 49° ON SQUALANE AS STATIONARY PHASE

Compound	Retention index (i.u.)		Deviation (i.u.)
	Measured <sup>5</sup>	Calculated	
1-Chloropropane	520.6	520.5	+0.1
1-Bromopropane	601.4	601.4	0.0
1-Bromobutane	703.8	703.4	+0.4

TABLE IV

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF INDOLES AT 190° ON SE-30 AS STATIONARY PHASE

Compound	Retention Index (i.u.)		Deviation (i.u.)
	Measured <sup>5</sup>	Calculated	
Indole	1310.0	1312.1	-2.1
N-Methylindole	1301.0	1300.9	+0.1
N-Ethylindole	1356.0	1356.6	-0.6
N-n-Propylindole	1445.0	1448.8	-3.8

TABLE V

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF PYRROLES AT 110° ON SE-30 AS STATIONARY PHASE

Compound	Retention index (i.u.)		Deviation (i.u.)
	Measured <sup>5</sup>	Calculated	
Tetrahydropyrrole	688.0	687.7	+0.3
N-Ethyltetrahydropyrrole	774.0	771.9	+2.1
Pyrrole	740.0	743.5	-3.5
N-Methylpyrrole	739.0	735.3	+3.7

TABLE VI

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF STEROIDS AT 210° ON OV-17 AS STATIONARY PHASE

Compound	Retention index (i.u.)		Deviation (i.u.)
	Measured <sup>10</sup>	Calculated	
Estr-3-one-5 $\alpha$ -H-17 $\alpha$ -H-17 $\beta$ -ol	2790.0	2796.1	-6.1
17 $\alpha$ -Methylestr-3-one-5 $\beta$ -H-17 $\beta$ -ol	2820.0	2819.0	+1.0
17 $\alpha$ -Ethylestr-3-one-5 $\alpha$ -H-17 $\beta$ -ol	2915.0	2911.9	+3.1

The results obtained, which give only a limited demonstration of the method, indicate the great possibilities of the calculation procedure.

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## REFERENCES

- 1 J. Takács, C. Szita and G. Tarján, *J. Chromatogr.*, 56 (1971) 1.
- 2 J. Takács, Zs. Tálas, I. Bernát, Gy. Czakó and A. Fischer, *J. Chromatogr.*, 67 (1972) 203.
- 3 R. A. Hively and R. E. Hinton, *J. Gas Chromatogr.*, 6 (1968) 203.
- 4 M. Šingliar, *J. Chromatogr.*, 65 (1972) 311.
- 5 T. Tóth and A. Borsodi, *Magy. Kém. Foly.*, 77 (1971) 576.
- 6 R. V. Golovnya and V. P. Uraletz, *J. Chromatogr.*, 61 (1971) 65.
- 7 G. Schomburg, *Separ. Sci.*, 1 (1966) 339.
- 8 J. Burkhard, J. Vais, L. Vodička and St. Landa, *J. Chromatogr.*, 42 (1969) 207.
- 9 G. Garzó, J. Fekete and M. Blazsó, *Acta Chim. Acad. Sci. Hung.*, 51 (1967) 359.
- 10 C. J. W. Brooks, A. R. Thawley, P. Rocher, B. S. Middleditch, G. M. Anthony and W. G. Stillwell, *J. Chromatogr. Sci.*, 9 (1971) 35.
- 11 E. B. Molnár, P. Mórítz and J. Takács, *J. Chromatogr.*, 66 (1972) 205.
- 12 Zs. Szentirmay, G. Tarján and J. Takács, *J. Chromatogr.*, 73 (1972) 11.
- 13 G. Schomburg, *J. Chromatogr.*, 14 (1964) 157.