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## TEMPERATURE DEPENDENCE OF THE RETENTION INDICES OF BRANCHED-CHAIN PARAFFINS ON NON-POLAR STATIONARY PHASES

### A METHOD FOR ITS CALCULATION ON THE BASIS OF MOLECULAR STRUCTURE\*

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#### SUMMARY

The temperature dependence,  $\Delta I/^\circ\text{C}$ , of the retention indices of many branched paraffins with six to eight carbon atoms was investigated using SF-96 columns, in the temperature range 80–120°.

Linear relationships were observed for all the compounds examined, and the calculation of the correct analysis temperature for the separation of interesting pairs of isomers was therefore possible. The dependence of  $\Delta I/^\circ\text{C}$  on the skeletal structure of the compounds permitted the determination of characteristic additive terms correlated with structural groups in the molecules, which could be added to give the overall temperature dependence of the index of any isomeric compound.

The effect of temperature programming on the separation of interesting pairs of isomers was also investigated.

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#### INTRODUCTION

In previous work, the relationships between the structures of branched-chain paraffins and their retention indices were investigated<sup>1</sup>. It was found that a constant value can be given to each structural group in the molecule, and that the retention index of every compound can be calculated by summing the values corresponding to these different groups. The terms to be added change as a function of the stationary phase and of the temperature of analysis, because the retention index,  $I$ ,<sup>2,3</sup> depends on temperature<sup>4,5</sup>.

The temperature dependence of the  $I$  values changes for different stationary phases and different series of compounds, and its behaviour for branched-chain alkanes was previously examined<sup>6</sup>. Over 50 compounds were analysed at different temperatures, on squalane and dinonylphthalate columns, and the results showed

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that the increase in the  $I$  values with temperature is typical for every compound, and depends on the dimensions of the molecule.

A comparison of the behaviour of alkanes and cycloalkanes on silicone columns has also been reported<sup>7</sup>, and an increase in the retention times of cycloalkanes with respect to alkanes was observed with increase in the analysis temperature. This difference was also suggested to be due to molecular dimensions. Hively and Hinton<sup>8</sup>, by studying the variation of retention index with temperature on squalane columns, suggested that only the cross-sectional area of the molecules has an effect on the difference in the retention indices, because, by definition, all  $n$ -alkanes have a  $\Delta I/^\circ\text{C}$  value of zero. Therefore, the increase in the molecular dimensions due to the chain-length cannot be considered, and only two dimensions have to be taken into account. The rigidity of the molecules also has an effect on their retention indices.

If the variation of  $I$  values with temperature depends on molecular structure, a theoretical calculation seems to be possible, as in the previously reported instance of the retention indices in isothermal analysis<sup>1</sup>. In the first stage of this calculation, we have taken into account those compounds that show a linear variation of  $I$  with temperature, having constant  $\Delta I/^\circ\text{C}$  throughout the interval considered, which corresponds to the useful temperature range of the stationary phase. A precise measurement of the  $\Delta I/^\circ\text{C}$  values was therefore necessary in order to check the linearity of the dependence and to obtain accurate values for calculations.

#### EXPERIMENTAL

In order to study the validity of our calculations over a wide temperature interval, a silicone liquid phase was used. GE-SF96 was preferred to SE-30 methyl silicone because of its better resolving power at relatively low temperatures.

A 20 % w/w concentration of liquid phase was loaded on Chromosorb P (DMCS), 60-80 mesh, and columns 4 m long and 1/4 in. O.D. were filled by the conventional technique.

It was found experimentally that both the dimensions of the column and the loading of stationary phase are not critical factors. Small variations in these two parameters change the absolute values of the retention times, but do not substantially influence the  $\bar{I}$  values.

A Varian Aerograph dual-column gas chromatograph, Model 1520, with a thermal conductivity detector and with fully proportional linear temperature programming was used. The temperature of the columns was monitored with precision thermometers (0.1°), in addition to the built-in thermocouple system.

The temperature range from 50 to 250° was investigated, but, in order to avoid too long or too short retention times, 80, 90, 100, 110 and 120° ( $\pm 0.2^\circ$ ) were mainly used.

A constant flow-rate of helium of 43 ml/min was maintained by appropriate adjustment of the flow controller at every temperature change, in order to avoid the effect of the variation of the viscosity of the carrier gas with temperature<sup>9,10</sup>.

The high precision required for the calculation of the retention indices did not permit the measurement of the retention times on the recorder chart strip at standard speeds (30 or 60 in./h). Therefore, the true retention times were measured with as top-

watch to better than 1 sec, and each measurement was repeated at least four times. With this method, and by careful control of the temperature changes, retention indices were obtained that were accurate to the second decimal place.

The compounds (listed in Table I) mixed with *n*-paraffins for the calculation of the retention indices<sup>2</sup> were injected by means of a microsyringe. Pure compounds were obtained from various sources (Fluka AG, Phillips Petroleum, Chemical Samples Co., Carlo Erba). All the isomeric hexanes, all the heptanes (except 3-ethylpentane) and seven isomers of octane were analysed.

## RESULTS AND DISCUSSION

The retention indices obtained by the above method are listed in Table I and shown graphically in Fig. 1.

TABLE I  
RETENTION INDICES, *I*, AT DIFFERENT TEMPERATURES ON AN SF-96 COLUMN

Compound	80°	90°	100°	110°	120°
2-Methylpentane	570.12	570.28	571.04	571.13	570.85
3-Methylpentane	585.66	585.89	586.30	586.74	587.87
2,2-Dimethylbutane	542.16	543.36	544.75	545.80	547.42
2,3-Dimethylbutane	563.15	570.34	571.81	572.68	573.68
2-Methylhexane	668.35	668.68	669.01	669.50	669.95
3-Methylhexane	677.32	677.95	678.51	679.09	679.75
2,2-Dimethylpentane	627.79	628.51	629.70	630.40	631.70
2,3-Dimethylpentane	672.45	673.81	674.85	676.10	677.29
2,4-Dimethylpentane	632.42	632.98	633.19	633.65	633.57
3,3-Dimethylpentane	660.59	662.46	664.21	665.95	667.80
2,2,3-Trimethylbutane	642.14	644.23	646.10	648.87	650.77
3-Methylheptane	774.38	774.76	775.11	775.75	776.18
2,2-Dimethylhexane	723.77	724.77	725.75	726.42	727.80
2,3-Dimethylhexane	761.34	762.45	763.66	765.12	766.66
2,4-Dimethylhexane	736.07	736.54	737.36	738.19	738.90
3,3-Dimethylhexane	744.29	745.86	747.60	749.57	751.28
2,3,3-Trimethylpentane	759.95	762.11	764.53	767.27	769.65
2,2,3,3-Tetramethylbutane	727.21	730.14	733.28	736.21	739.23

For all the alkanes analysed, a linear dependence of the *I* values on temperature was observed. Only three compounds (2-methylpentane, 3-methylpentane and 2,4-dimethylpentane) showed slightly anomalous behaviour.

By using the least-squares method, the parameters  $F_0$  and  $F_1$  of the linear equation

$$I = F_0 + F_1 T \quad (1)$$

where *I* = retention index and *T* = analysis temperature (°C) were calculated and are reported in Table II. Table II also shows the average percentage error, *E*, which indicates the extent to which the theoretical values calculated by eqn. 1 differ from the experimental values. The agreement is very satisfactory, and confirms both the linearity of the plot of *I* against *T*, and the accuracy of the calculated constants.

The slopes  $F_1$  correspond to the increments in *I* per degree ( $\Delta I/^\circ\text{C}$ ), and the re-

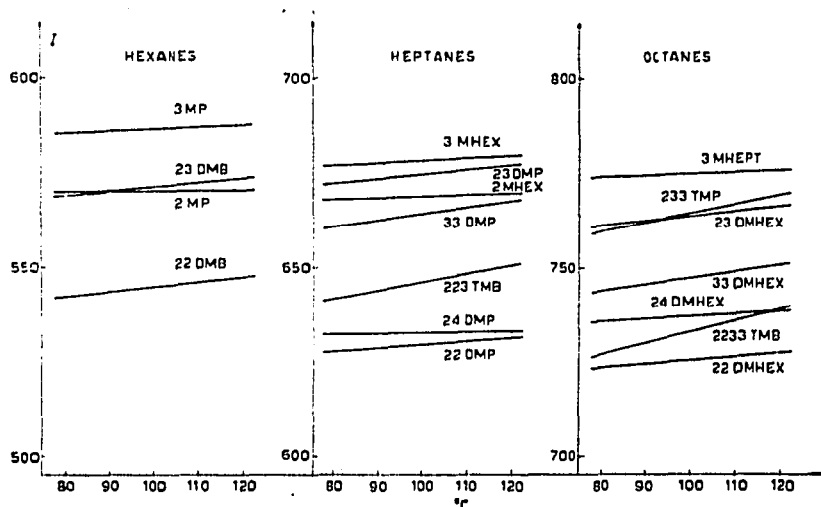


Fig. 1. Retention indices of branched-chain hexanes, heptanes and octanes on an SF-96 column as a function of temperature.

tion index of every compound at every temperature can therefore be calculated from the reported values.

By comparing the values in Tables I and II, no correlation can be seen between the values of  $I$  and the values of  $\Delta I/^\circ\text{C}$ . Isomers with high retention indices do not necessarily show a strong variation of retention index with temperature. Compounds that have the same characteristic groups, and differ only in the length of the main carbon chain, have similar temperature increments (see Table II).

TABLE II

CONSTANTS OF THE EQUATION  $I = F_0 + F_1T$  AND MEAN PERCENTAGE ERROR,  $E$

Compound	$F_0$	$F_1$	$E$
2-Methylpentane	567.06	0.0379	0.022
3-Methylpentane	581.23	0.0528	0.038
2,2-Dimethylbutane	531.74	0.1296	0.017
2,3-Dimethylbutane	560.14	0.1140	0.020
2-Methylhexane	665.08	0.0402	0.006
3-Methylhexane	672.53	0.0598	0.003
2,2-Dimethylpentane	619.93	0.0970	0.021
2,3-Dimethylpentane	662.94	0.1196	0.007
2,4-Dimethylpentane	629.38	0.0387	0.010
3,3-Dimethylpentane	646.31	0.1788	0.005
2,2,3-Trimethylbutane	624.53	0.2188	0.022
3-Methylheptane	770.69	0.0460	0.003
2,2-Dimethylhexane	716.00	0.0970	0.014
2,3-Dimethylhexane	750.79	0.1310	0.016
2,4-Dimethylhexane	730.12	0.0728	0.011
3,3-Dimethylhexane	730.04	0.1768	0.011
2,3,3-Trimethylpentane	740.16	0.2454	0.016
2,2,3,3-Tetramethylbutane	703.12	0.3010	0.005

By selecting appropriate compounds with characteristic groupings, and by using a calculation similar to the "comparison" method previously used for the theoretical calculation of the retention indices<sup>1</sup>, characteristic values of the temperature increment can be correlated with every structural grouping in the molecules. The temperature dependence of the retention index of any compound with known structure can therefore be predicted by summing these contributions from the individual groupings in the molecule.

An example of the calculation of the characteristic values of  $\Delta I/^\circ\text{C}$  is now given, referring to some of the compounds examined.

The effect of a characteristic grouping is more "free" from other effects when the main carbon chain is longer, and therefore from 2,2-dimethylhexane a value of  $\Delta I/^\circ\text{C} = 0.097$  index units (i.u.) can be attributed to the quaternary carbon atom (Q). From 2-methylhexane, a value of  $\Delta I/^\circ\text{C} = 0.040$  can be attributed to the tertiary carbon atom (T) (for these calculations, the  $F_1$  values are rounded up to the third decimal figure).

The behaviour of 2,2-dimethylbutane shows that an ethyl group directly connected to a terminal quaternary carbon atom (QE) makes a contribution to the temperature increment of  $(0.130 - 0.097) = 0.033$  i.u., while the propyl group in the same situation (2,2-dimethylpentane) does not have any effect.

However, a propyl group connected to an internal quaternary carbon atom (QP), as in 3,3-dimethylhexane, has a contribution of 0.033 i.u., equal to the QE arrangement above. No constant value, different from that given to the external tertiary carbon, can be attributed to the internal tertiary carbon atom, probably owing to the small size of the molecule considered, which does not permit the separation of the effects of this group from those of the two sides of the molecule.

Therefore, from 3-methylpentane, a contribution of 0.015 i.u. can be attributed to two ethyl groups connected to an internal tertiary carbon atom (dual ethyl: DE) and, as with the internal quaternary carbon atom, it can be assumed that the propyl-ethyl (PE) and dual propyl (DP) configurations also have approximately the same effect.

From 2,3-dimethylpentane, a value of 0.040 i.u. can be calculated for two adjacent tertiary carbon atoms (TT), in addition to the characteristic values of the two separated groups; from 2,2,3-trimethylbutane,  $\Delta I/^\circ\text{C} = 0.082$  is attributed to adjacent tertiary-quaternary (TQ) atoms, and from 2,2,3,3-tetramethylethylbutane,  $\Delta I/^\circ\text{C} = 0.107$  to a quaternary-quaternary (QQ) arrangement.

In Table III, the various structural groupings are listed, with the corresponding symbols and the calculated values that can be used to calculate the temperature increment of any branched hydrocarbon.

In Table IV, the compounds are listed in order of decreasing difference between experimental and calculated values in order to show systematic deviations. All the calculated increments are very close to the experimental values, except for 2,4-dimethylpentane, this discrepancy probably being due to the fact that the methylenic linkage between two tertiary carbon atoms makes a negative contribution to the temperature increment (as with the negative contribution of the linkage to the retention index value<sup>1</sup>).

Small deviations may be correlated with the presence of an internal tertiary carbon atom, which indicates that its effect is different from that of the terminal

TABLE III

CHARACTERISTIC GROUPINGS GIVING A CONSTANT INCREMENT TO THE  $\Delta I/^\circ\text{C}$  VALUES

Grouping	Symbol	$\Delta I/^\circ\text{C}$ (index units)
Quaternary C atom	Q	0.097
Tertiary C atom	T	0.040
Two tertiary C atoms in $\alpha$ -position	TT	0.040
Tertiary and quaternary C in $\alpha$ -position	TQ	0.082
Two-quaternary C in $\alpha$ -position	QQ	0.107
Ethyl group bonded to a quaternary C	QE	0.033
Propyl group bonded to an internal quaternary C	QP	0.033
Two ethyl groups on the same tertiary or quaternary C	DE	0.015
Ethyl and propyl groups on the same tertiary or quaternary C	PE	0.015
Two propyl groups on the same tertiary or quaternary C	DP	0.015

TABLE IV

CALCULATION OF THE TEMPERATURE DEPENDENCE OF THE  $I$  VALUES OF VARIOUS BRANCHED ALKANES BY MEANS OF THE ADDITIVE TERMS REPORTED IN TABLE III

Compound	Characteristic groupings	$\Delta I/^\circ\text{C}$		Difference, exptl.-calc.
		Experimental	Calculated	
2,3-Dimethylhexane	T + T + TT	0.131	0.120	+0.011
3-Methylheptane	T	0.046	0.040	+0.006
3-Methylhexane	T + PE	0.060	0.055	+0.005
3,3-Dimethylpentane	Q + QE + QE + DE	0.179	0.178	+0.001
2,3-Dimethylpentane <sup>a</sup>	T + T + TT	0.120	0.120	0
2-Methylhexane <sup>a</sup>	T	0.040	0.040	0
2,2-Dimethylhexane <sup>a</sup>	Q	0.097	0.097	0
2,2-Dimethylpentane <sup>a</sup>	Q	0.097	0.097	0
2,2-Dimethylbutane <sup>a</sup>	Q + QE	0.130	0.130	0
2,2,3-Trimethylbutane <sup>a</sup>	Q + T + TQ	0.219	0.219	0
2,2,3,3-Tetramethylbutane <sup>a</sup>	Q + Q + QQ	0.301	0.301	0
3,3-Dimethylhexane <sup>a</sup>	Q + QE + QP + PE	0.177	0.178	-0.001
2-Methylpentane	T	0.038	0.040	-0.002
3-Methylpentane <sup>a</sup>	T + DE	0.053	0.055	-0.002
2,3-Dimethylbutane	T + T + TT	0.114	0.120	-0.006
2,3,3-Trimethylpentane	T + Q + TQ + QE	0.245	0.252	-0.007
2,4-Dimethylhexane	T + T	0.073	0.080	-0.007
2,4-Dimethylpentane	T + T	0.039	0.080	-0.041

<sup>a</sup> These compounds were used to calculate the characteristic values of  $\Delta I/^\circ\text{C}$ .

tertiary carbon atom. Measurements made with higher compounds will probably permit a better determination of the "internal tertiary" effect.

The calculation of the retention indices at any temperature gives satisfactory results, and also with the first approximation data reported in Table III. In fact, by starting from  $I_{81^\circ}$  (see Table I) and by calculating  $I_{121^\circ}$  by means of the calculated  $\Delta I/^\circ\text{C}$ , 2,3-dimethylpentane (which has the largest difference in Table III) shows a deviation of only 0.52 i.u. between the measured and the calculated retention indices. As a reproducibility of the order of 1 i.u. is considered to be normal in the experimental measurement of the retention indices, the calculated values are satisfactory even in the worst instance.

*Effect of the temperature dependence on the separation of isomers*

It can be seen from Tables I and II that the different temperature dependences of the retention indices will cause an inversion of the elution order of some isomers at different temperatures. By solving appropriate systems of equations of the type of eqn. 1, it is possible to determine the temperature at which the retention indices of two different compounds have the same value. In Table V these common points,  $I_c$  and  $T_c$ , are reported for various pairs of compounds that have an inversion point between 0 and 250°, which is the temperature range of the SF-96 column.

In Fig. 2 the various interferences of different compounds are shown graphically. With the column used, the mean peak width corresponds to about 5 i.u., so that partial interference between two peaks will take place in an  $I_c$  range of  $\pm 5$  i.u. and

TABLE V

PAIRS OF ISOMERS THAT EXHIBIT INTERSECTION OF THE  $I$  vs.  $T$  PLOTS, WITH TEMPERATURE  $T_c$  AND INDEX  $I_c$  OF THE COMMON POINTS

Pair of compounds	$T_c$ (°C)	$I_c$
2,4-Dimethylhexane + 3,3-dimethylpentane	1	730.20
2-Methylhexane + 2,3-dimethylpentane	27	666.16
2,2-Dimethylhexane + 2,2,3,3-tetramethylbutane	63	722.12
2,3-Dimethylhexane + 2,3,3-trimethylpentane	93	762.96
2,4-Dimethylhexane + 2,2,3,3-tetramethylbutane	118	738.73
2-Methylhexane + 3,3-dimethylpentane	136	670.52
3-Methylheptane + 2,3,3-trimethylpentane	153	777.73
3-Methylhexane + 2,3-dimethylpentane	160	682.12
3,3-Dimethylhexane + 2,2,3,3-tetramethylbutane	217	768.36
3-Methylhexane + 3,3-dimethylpentane	220	685.71
2-Methylhexane + 2,2,3-trimethylbutane	227	674.21
3-Methylheptane + 2,3-dimethylhexane	234	781.46

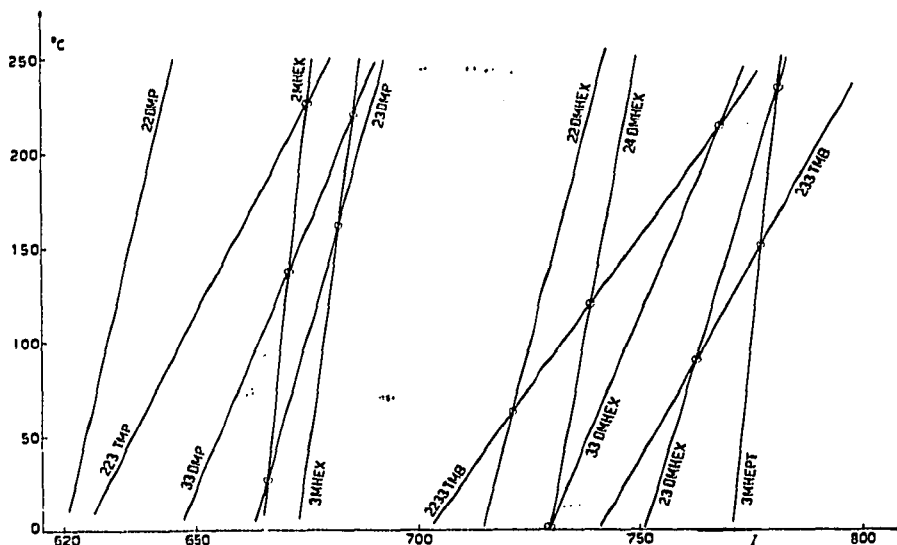


Fig. 2. Interference of various branched-chain alkanes on an SF-96 column at different temperatures.

a  $T_c$  range of  $\pm 10^\circ$ . Nevertheless, by knowing the retention indices of the compounds to be separated and their temperature increments, it is possible to predict the most suitable temperature for complete resolution of all of the peaks.

Taking into account the possibility of theoretically calculating both the retention index<sup>1</sup> and the temperature increment of a compound on the basis of its structure, as seen above, the possibility of both separating and identifying unknown compounds is greatly increased.

#### *Temperature-programmed analysis*

Some of the above interferences of peaks take place at low, and others at high temperatures. For example, 2,2,-dimethylhexane and 2,2,3,3-tetramethylbutane have the same retention indices at about  $65^\circ$ , while 3,3-dimethylhexane and 2,2,3,3-tetramethylbutane have the same retention indices at about  $215^\circ$ . Only two peaks will therefore be given in isothermal runs carried out at these two temperatures.

In addition, owing to the low number of theoretical plates of the column, the resolution of the first pair of isomers is not possible below  $80^\circ$ , while the latter pair cannot be separated above  $160^\circ$ . On the basis of the temperature dependence of the retention indices of these compounds, it can be deduced that isothermal analysis at  $120^\circ$  will separate the three substances considered (and this was experimentally checked), but it is more convenient to run a temperature-programmed analysis from the lowest to the highest interference temperature. In fact, the compounds separated at low temperature do not mix again when the temperature of the column increases. By suitable choice of the programming rate (between 6 and  $8^\circ/\text{min}$ ), all the examined compounds can be resolved with the described column.

The use of a suitable programming rate reduces the differences between the temperature increments of various compounds in such a way that the straight lines in Fig. 2 tend to become more parallel, thus giving fewer intersections.

The temperature-programmed analysis, therefore, in addition to the well known advantage of shortening the analysis time, gives a better resolution than all the possible isothermal runs in the temperature interval considered. In many instances, as in trace analysis and in the identification and measurement of radiolysis or thermal cracking products<sup>11,12</sup>, the use of packed columns and temperature programming has some advantages compared with isothermal capillary analysis.

A knowledge of the hypothetical retention indices and the temperature dependences for the expected compounds, calculated on the basis of their structures, permits the choice of the most suitable analysis temperature and programming rate, giving peaks that are well separated and narrow and therefore useful for accurate quantitative measurements.

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