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CORRELATIONS BETWEEN MOLECULAR STRUCTURE AND PHYSICAL PROPERTIES OF ALKYL IODIDES AND THEIR RETENTION INDICES

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SUMMARY

All the isomers of alkyl iodides with one to six carbon atoms were analysed by gas chromatography, and the retention indices relative to 1-iodoalkanes were calculated.

The relationship between molecular structure, iodine atom position, boiling point, density, molecular volume and retention index was investigated.

Correlations between the retention index and the boiling point were found, and a pronounced effect of the molecular volume was also observed for branched compounds with iodine substituted on the tertiary carbon atom or in the α position.

In these compounds the increase of molecular volume tends to compensate the decrease in the boiling point, giving very similar values of the retention index.

INTRODUCTION

The correlations between structure, physical properties and gas chromatographic (GC) retention data have considerable importance. In fact, if these relationships are known, the identification of unknown compounds can be made on the basis of the analytical parameters, without resorting to comparison with pure samples, which are often difficult to find.

The GC behaviour of several series of compounds was studied by us with different columns under carefully controlled conditions. The results were compared in order to obtain a general relationship. Here we shall describe the results obtained with all the isomeric alkyl iodides with 1–6 carbon atoms, and some longer straight-chain compounds, and the observed correlations between molecular structure, boiling point, molecular volume and retention index of these compounds.

EXPERIMENTAL

Many of the products analysed were prepared by synthesis[1].

The boiling points, at standard pressure, were determined by distillation and by the SIWOLOBOFF method[2]. When the determination of boiling points was not possible at atmospheric pressure, due to thermal decomposition, and reliable data

were not available in the literature, the values were calculated from the boiling points at reduced pressure by means of the equation

$$\Delta t = \frac{(273.1 + t)\,(2.8808 - \log p)}{\varphi + 0.15\,(2.8808 - \log p)} \qquad (1)$$

where Δt = °C to be added to the observed boiling point.
t = the observed boiling point.
$\log p$ = the logarithm of the observed pressure in torr.
φ = the entropy of vaporisation at 760 torr.

According to HASS AND NEWTON[3] the entropies of vaporisation were taken as equal to those of hydrocarbons with the same structure. Even if this assumption is not fully correct, the comparison between the values calculated in this manner, the boiling points determined at standard pressure, and the literature data was satisfactory in all the cases when these three values were available. The difference was never greater than 1°. The values obtained by means of eqn. 1 are indicated by* in Table I.

TABLE I

PHYSICAL CONSTANTS AND RETENTION INDICES OF ANALYSED COMPOUNDS

No.	*Compound*	*T_b (°C) at 760 torr*	*Density at 20° (g/ml)*	*Molecular volume (cm^3)*	*I_{nt}*
1	Iodomethane	42.5	2.28	62.3	100
2	Iodoethane	72	1.93	80.81	200
3	1-Iodopropane	102.45	1.74	97.69	300
4	2-Iodopropane	89.45	1.70	99.99	245
5	1-Iodobutane	130	1.60	114.39	400
6	2-Iodobutane	120	1.598	114.54	359.5
7	1-Iodopentane	155.7*,[a]	1.51	131.16	500
8	2-Iodopentane	144.5	1.53	129.44	444
9	3-Iodopentane	145.5	1.52	130.30	458
10	1-Iodohexane	177	1.44	147.27	600
11	2-Iodohexane	165.6*	1.427	148.61	540
12	3-Iodohexane	167	1.45	146.25	540.5
13	1-Iodoheptane	198*	1.37	165.04	700
14	2-Iodoheptane	186.2*	1.38	163.85	636
15	3-Iodoheptane	187.4*	1.38	163.85	633.5
16	4-Iodoheptane	185	1.39	162.76	619.5
17	1-Iodo-2-methylpropane	120	1.61	113.68	360
18	2-Iodo-2-methylpropane	91.6*	1.55	118.08	271
19	1-Iodo-2-methylbutane	148	1.53	129.44	467
20	1-Iodo-3-methylbutane	147	1.51	131.16	451
21	2-Iodo-2-methylbutane	124.5	1.49	132.92	445
22	2-Iodo-3-methylbutane	141	1.503	131.77	444
23	1-Iodo-2-methylpentane	168	1.44	147.26	556
24	1-Iodo-3-methylpentane	170	1.46	145.24	561
25	1-Iodo-4-methylpentane	173.2	1.43	148.30	559
26	2-Iodo-2-methylpentane	142	1.41	150.40	538
27	2-Iodo-3-methylpentane	160*	1.45	146.25	541.5
28	2-Iodo-4-methylpentane	160	1.47	144.26	537
29	3-Iodo-2-methylpentane	147	1.31	161.88	536
30	3-Iodo-3-methylpentane	147	1.37	154.79	542

[a] Values marked * are extrapolated from low pressure data by means of eqn. 1.

The GC analyses were made on tricresyl phosphate columns, with a 15% loading on Chromosorb W 80–110 mesh, silanised with DMCS, using columns with I.D. of 2 mm, and length ranging from 1 to 3 m.

A Varian Aerograph gas chromatograph A-600 equipped with an electron capture detector was used. This instrument had an "all glass" arrangement to prevent decomposition of alkyl iodides during the analysis, and the injection of samples was made directly on to the column.

The retention values were calculated as adjusted retention times, by subtracting the gas hold-up time from the retention time of every substance.

RESULTS AND DISCUSSION

The compounds analysed, together with their physical constants and the retention indices relative to 1-iodoalkanes (I_{nI}) are listed in Table I. The use of the I_{nI} instead of the retention indices relative to normal paraffins (I_{np}) (ref. 4) is very convenient when analysing products with an electron capture detector, which is insensitive to saturated hydrocarbons[1,5].

The I_{nI} can easily be used instead of the I_{np}, due to the fact that the plots of log t_a as a function of the number of carbon atoms are parallel for n-paraffins and for 1-iodoalkanes, with the same column length and at the same temperature[5]. This parallel behaviour gives a linear relationship between the I_{nI} and the I_{np}.

TABLE II

COEFFICIENTS OF THE EQUATION $I_{np} = A_0 + A_1 \cdot I_{nI}$

	120-cm column			*300-cm column*	
	60 °C	*100 °C*	*120 °C*	*100 °C*	*120 °C*
A_0	573.23	573.53	561.99	579.56	564.12
A_1	0.9928	1.0208	1.0519	1.0135	1.0371

Table II gives the coefficients of the equation $I_{np} = A_0 + A_1 \cdot I_{nI}$ obtained by the least squares method from the values of I_{nI} and I_{np} for different analytical parameters.

The differences between the values of the angular coefficient A_1 are so small, and this coefficient is so close to 1, that for practical purposes one can calculate the I_{np} of every compound simply by adding A_0 to the value of I_{nI}. The A_0 can easily be determined for any column and analytical condition, by simultaneous injection of a few n-paraffins and 1-iodoalkanes.

An important characteristic of the I_{nI} is that δI_{nI} (*i.e.* the difference between the I_{nI} of the 1-iodoalkane and the I_{nI} of a branched isomer) is exactly the same as the δI_{np} (ref. 4) and can therefore be compared with the values of δI_{np} given by some authors for paraffins and other compounds[4,6].

Table II reports the boiling points at standard pressure for n-paraffins, 1-iodoalkanes and 2-iodoalkanes. As can be seen from the values of ΔT_b that decrease with

TABLE III

BOILING POINTS (T_b) OF *n*-PARAFFINS, 1-IODOALKANES AND 2-IODOALKANES WITH DIFFERENT NUMBER OF CARBON ATOMS (n) AND ΔT_b, THE DIFFERENCE BETWEEN THE T_b OF TWO MEMBERS OF HOMOLOGOUS SERIES

n	*n-Paraffins*		*1-Iodoalkanes*		*2-Iodoalkanes*		T_b (1-iodo-) − T_b (2-iodo-)
	T_b	ΔT_b	T_b	ΔT_b	T_b	ΔT_b	
1	−161.5	—	42.5	—	—	—	—
2	− 88.6	72.9	72.0	29.5	—	—	—
3	− 42.1	46.5	102.4	30.4	89.5	—	12.9
4	− 0.5	41.6	130	27.6	120	30.5	10
5	36.1	36.6	155.7	25.7	144.5	24.5	11.2
6	68.7	32.6	177	21.3	165.6	21.1	11.4
7	98.4	29.7	198	21	186.2	20.6	11.8
8	125.7	27.3	224	24	210	23.8	12
9	150.8	25.1	243	21	234.2	24.2	9
10	174.1	23.3	261	18	250.5	16.3	10.5
11	195.3	21.2					
12	214.8	19.5					
13	234	19.2					
14	252.5	18.5					

an increase in the number of carbon atoms, the increment of boiling point due to the addition of a methylene group is smaller when the length of the chain increases.

The ΔT_b have very similar values for 1-iodoalkanes and for 2-iodoalkanes and the differences between the T_b for these two series of compounds (last column of Table III) are practically constant, within the limits of experimental error.

Fig. 1 shows that the general behaviour of the retention indices closely follows the behaviour of the boiling points and that the retention times and the boiling points are higher when the iodine is in the first position, in comparison to the corresponding values when iodine is substituted on a carbon atom inside the chain.

The ratio $\delta I_{nl}/\delta T_b$ for 2-iodo- and 3-iodoalkanes is reported in Table IV.

TABLE IV

RELATIONSHIP BETWEEN THE DIFFERENCE OF THE BOILING POINTS OF ISOMERS (δT_b) AND THE DIFFERENCES IN THEIR RETENTION INDICES (δI_{nl})

The δ values are calculated from the 1-iodoalkane.

	δI_{nl}	δT_b	$\delta I_{nl}/\delta T_b$
2-Iodopropane	55	13	4.23
2-Iodobutane	40.5	10	4.05
2-Iodopentane	66	11.2	5.89
2-Iodohexane	60	11.4	5.26
2-Iodoheptane	64	11.8	5.42
3-Iodopentane	42	9	4.66
3-Iodohexane	59.5	10	5.95
3-Iodoheptane	66.5	10.6	6.27
4-Iodoheptane	81.5	13	6.27

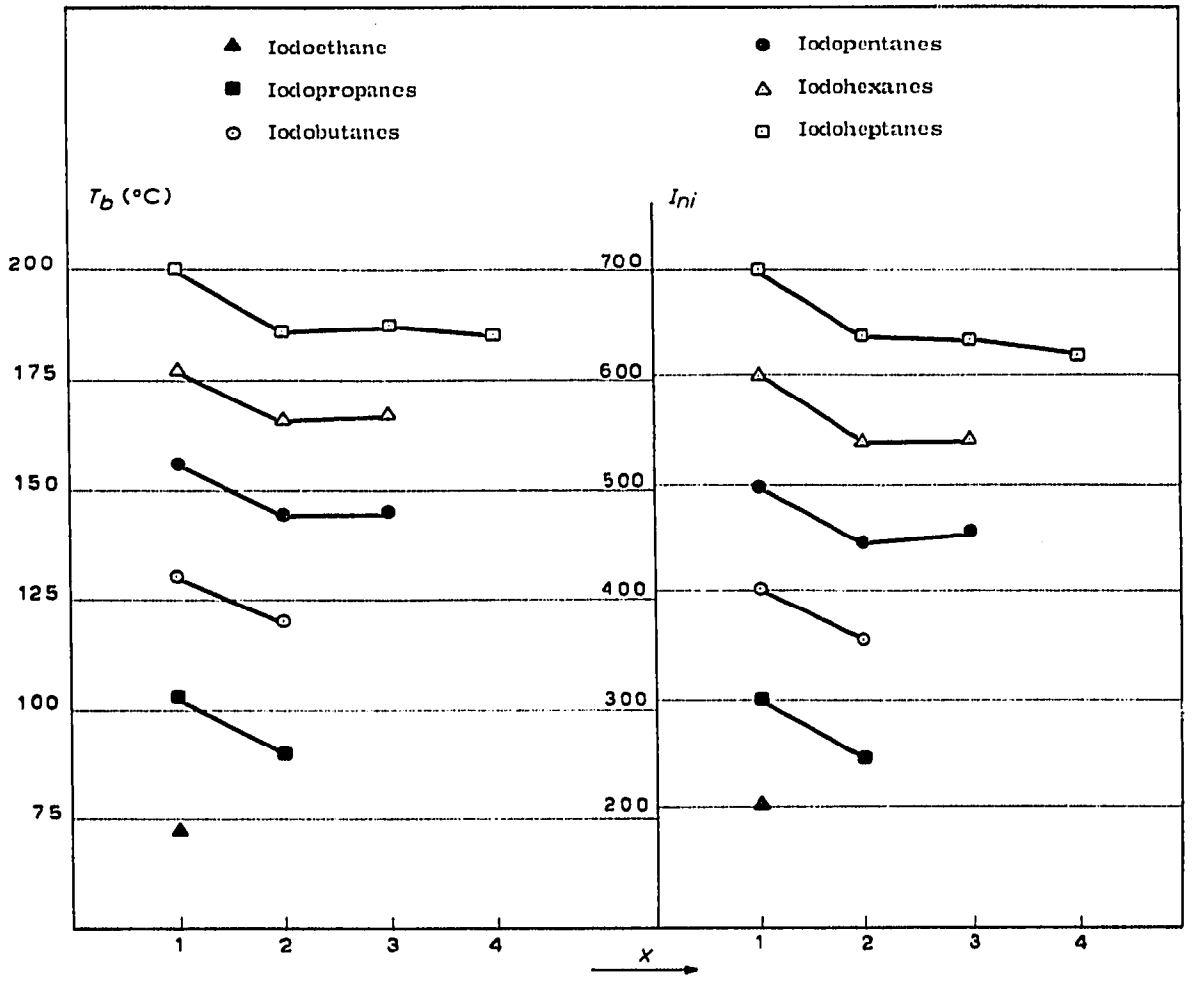

Fig. 1. Boiling point (T_b) and retention index (I_{ni}) of straight chain iodoalkanes as a function of the position of the iodine atom.

KOVATS[4] found that this ratio is approximately equal to 5, and the relationship was partially verified for straight-chain alkanes[6].

In this case the relationship seems to be verified for 2-iodoalkanes (an error of $\pm$ 0.3 units may be expected due to uncertainty in some boiling points) and this fact allows the calculation of the boiling points of higher homologues from the retention data. For 3-iodoalkanes the values of $\delta I_{ni}/\delta T_b$ show a slight increase with the number of C atoms in the molecule.

Molecular volumes for straight-chain iodoalkanes with 5, 6 and 7 carbon atoms have variations in the same sense as the boiling points and retention indices.

The molecular volumes given in Table I are obtained from the molecular weights divided by the density at 20°. Due to the dependence on temperature, these values are not valid at the temperature of analysis (100°) but it can be assumed that the increment is roughly proportional for all compounds and that the values are sufficiently exact for an indicative comparison.

When the iodoalkanes have a branched carbon chain, both retention indices and boiling points decrease with respect to the corresponding values for straight-chain compounds.

TABLE V

RELATIONSHIP BETWEEN THE δI_{nt} AND THE δT_b OF 1-IODO-X-METHYLALKANES

	δI_{nt}	δT_b	$\delta I_{nt}/\delta T_b$
1-Iodo-1-methylpropane	40.5	10	4.05
1-Iodo-2-methylpropane	40	10	4.00
1-Iodo-1-methylbutane	66	11.2	5.89
1-Iodo-2-methylbutane	33	7.7	4.28
1-Iodo-3-methylbutane	49	8.7	5.63
1-Iodo-1-methylpentane	60	11.4	5.26
1-Iodo-2-methylpentane	44	9	4.89
1-Iodo-3-methylpentane	39	7	5.53
1-Iodo-4-methylpentane	41	7.3	5.85

The values of δI_{nt}, δT_b and the ratio $\delta I_{nt}/\delta T_b$ for 1-iodo-X-methylalkanes, where X indicates the position of the methyl group, are reported in Table V. The values of $\delta I_{nt}/\delta T_b$ differ more than in the case of straight-chain compounds, but, as can be seen from Fig. 2, the general behaviour of the retention indices still follows the behaviour of the boiling points.

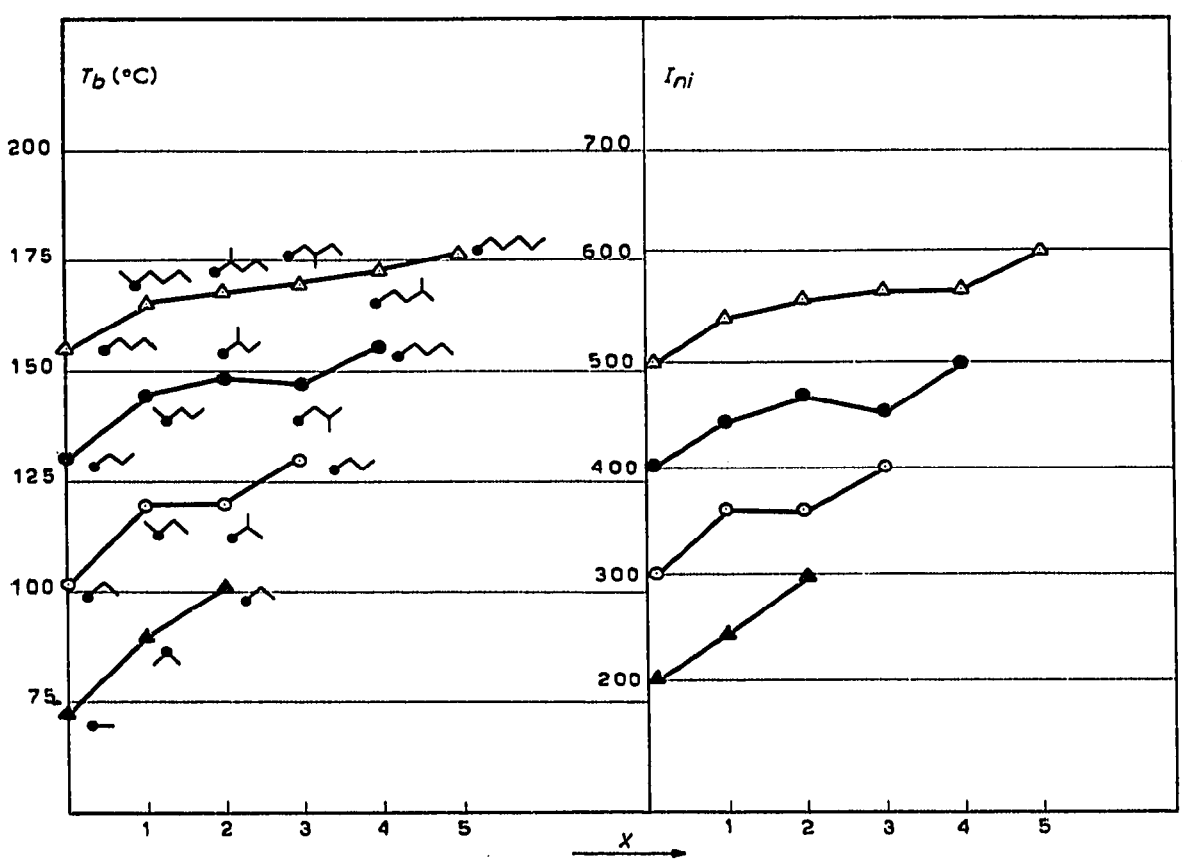

Fig. 2. Boiling point (T_b) and retention index (I_{nt}) of 1-iodo-X-methylalkanes, as a function of the value of X (position of the methyl group in the molecule).

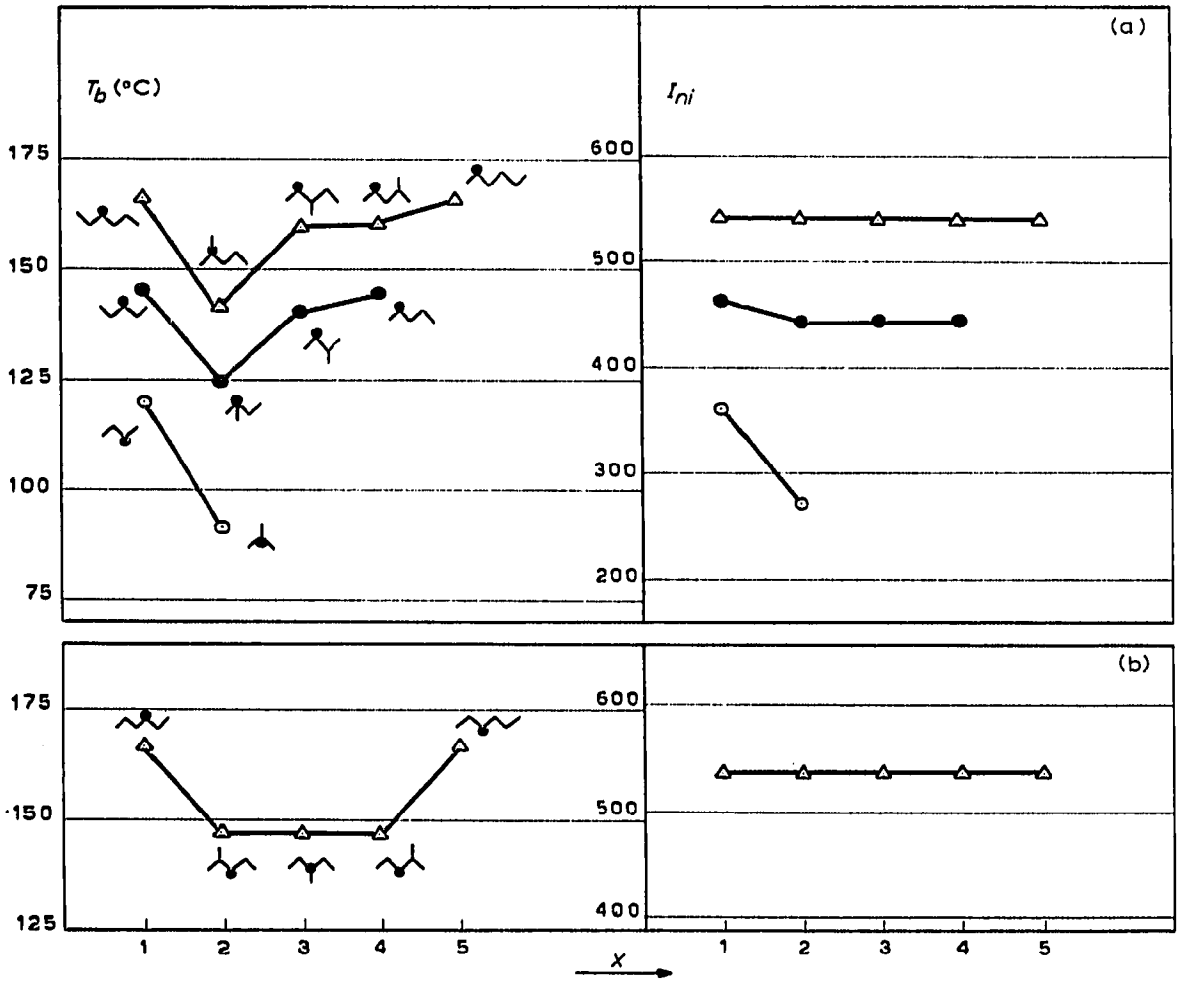

Fig. 3. Boiling point (T_b) and retention index (I_{ni}) of 2-iodo-X-methylalkanes (a) and 3-iodo-X-methylpentane (b), as a function of the position of the methyl group.

It must be mentioned that in Table V and in Fig. 2 and in all the following tables and figures, standard chemical nomenclature is not followed completely, in order to emphasise the fact that a compound belongs to a group with particular characteristics. For example, 2-iodohexane may be considered as 1-iodo-1-methylpentane, in order to compare its properties with those of similar products. For this reason, the straight-chain compounds with one less carbon atom are also reported in Fig. 3.

The behaviour of the 2-iodo- and 3-iodo-X-methylalkanes (see Table VI and Fig. 3) is quite different. The retention indices for isomeric compounds are very similar, but a sharp decrease is shown by the boiling points when both the iodine and the methyl groups are substituted along the chain. The minimum value is reached when the iodine and methyl group are on the same carbon atom in the 2-iodo-2-methylalkanes.

When the iodine atom is substituted in position 3, the methyl group in position 2 or 3 causes a sharp decrease of the boiling point without practically changing the retention index. It is very interesting to observe that the compounds which show this phenomenon and have a very low value of $\delta I_{ni}/\delta T_b$, such as 2-iodo-2-methyl-

TABLE VI

RELATIONSHIP BETWEEN THE δI_{nl} AND THE δT_b OF 2-IODO- AND 3-IODO-X-METHYLALKANES

	δI_{nl}	δT_b	$\delta I_{nl}/\delta T_b$
2-Iodo-1-methylpropane	40.5	10	4.05
2-Iodo-2-methylpropane	129	38.4	3.47
2-Iodo-1-methylbutane	42	9	4.66
2-Iodo-2-methylbutane	55	31.2	1.76
2-Iodo-3-methylbutane	56	16.7	3.35
2-Iodo-4-methylbutane	66	11.2	5.89
2-Iodo-1-methylpentane	59.5	10	5.95
2-Iodo-2-methylpentane	62	43	1.44
2-Iodo-3-methylpentane	53.5	17	3.15
2-Iodo-4-methylpentane	63	17	3.70
2-Iodo-5-methylpentane	60	11.4	5.26
3-Iodo-1-methylpentane	59.5	10	5.95
3-Iodo-2-methylpentane	64	30	2.13
3-Iodo-3-methylpentane	58	30	1.93

butane, 2-iodo-2-methylpentane, 3-iodo-2-methylpentane and 3-iodo-3-methylpentane, have molar volumes greater than those of the isomeric 1-iodoalkane (see Table I). In the case of 2-iodo-2-methyl and 3-iodo-3-methyl compounds this may be due to the steric hindrance of an iodine atom and three methyl groups on the same carbon atom.

In the case of 3-iodo-2-methylpentane a similar steric hindrance is given by two methyls on a carbon atom and an iodine atom plus an ethyl group on the next position. However, 2-iodo-3-methylpentane does not show the same behaviour notwithstanding the α position of the iodine atom with respect to a tertiary carbon atom.

From the point of view of the GC separation, it is clear that the increase of molar volume tends to compensate the decrease of boiling point, and the retention indices of isomeric compounds do not show such a large dependence on the structure. The phenomenon is probably complex, but it is interesting to observe that, by em-

TABLE VII

RELATIONSHIP BETWEEN THE δI_{nl} AND THE δT_b OF X-IODO-2-METHYLALKANES

	δI_{nl}	δT_b	$\delta I_{nl}/\delta T_b$
1-Iodo-2-methylbutane	33	7.7	4.28
2-Iodo-2-methylbutane	55	31.2	1.76
3-Iodo-2-methylbutane	56	16.7	3.35
4-Iodo-2-methylbutane	49	8.7	5.63
1-Iodo-2-methylpentane	44	9	4.89
2-Iodo-2-methylpentane	62	43	1.44
3-Iodo-2-methylpentane	64	30	2.13
4-Iodo-2-methylpentane	63	17	3.70
5-Iodo-2-methylpentane	41	7.3	5.85

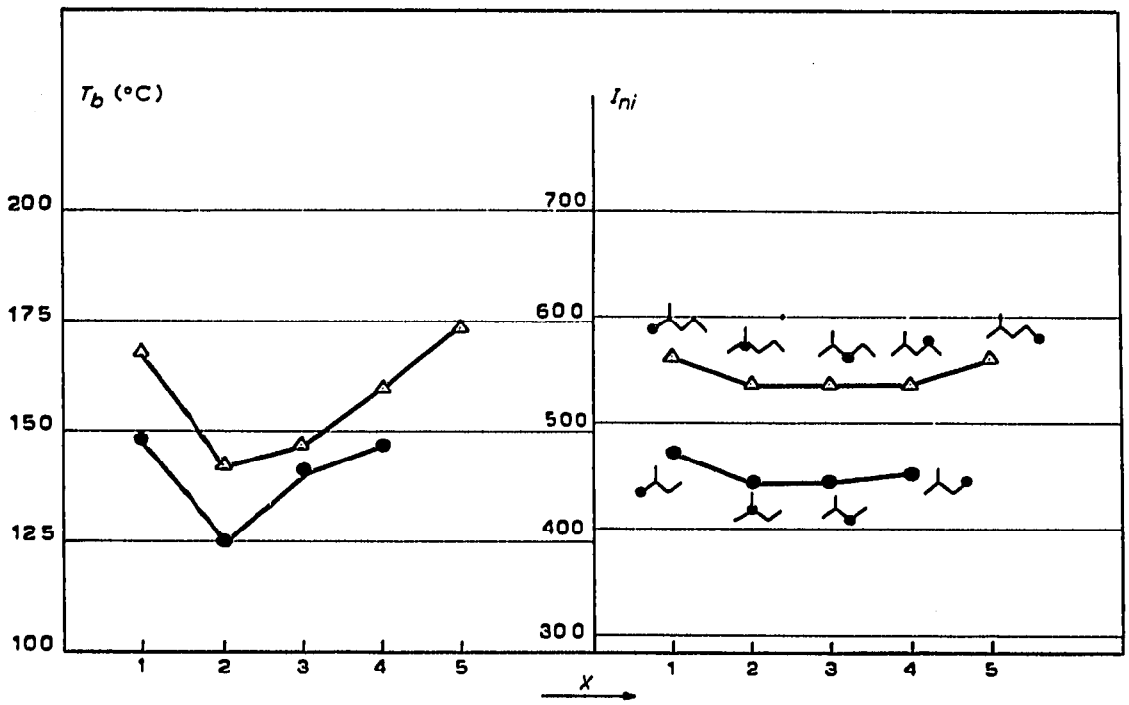

Fig. 4. Boiling point (T_b) and retention index (I_{ni}) of X-iodo-2-methylalkanes as a function of the position of the iodine atom.

pirically multiplying the boiling points by the molecular volume, values roughly proportional to the retention indices are obtained.

The retention index of 2-iodo-2-methylpropane decreases, according to its boiling point, and gives a higher value of $\delta I_{ni}/\delta T_b$. This behaviour may be due to its tetrahedral compact structure.

Table VII and Fig. 4 show the behaviour of compounds with a methyl group in position 2 and the iodine atom in different positions along the chain. It can be seen that the boiling points and the retention indices increase, when iodine is at the extremities of the chain and that boiling points reach their lowest value when the methyl group and the iodine atom are substituted on the same carbon atom or in an α position.

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