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GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOMETALLIC COMPOUNDS AND THEIR CARBON ANALOGUES

IV. DETERMINATION, CALCULATION AND CORRELATION OF KOVÁTS RETENTION INDICES FOR TETRAALKYLSILANES

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SUMMARY

Equations for the calculation of retention indices for mixed tetraalkylsilanes are given. The significance of the sign of the charge on the terminal methyl carbon atom of the alkyl groups bonded to silicon in determining the magnitude of the retention index and the ΔI value is discussed. Rules for the estimation of the temperature dependence of retention indices for tetraalkylsilanes are given. Linear relationships are shown to exist between retention indices for homologous series of mixed tetraalkylsilanes on the one hand and retention indices of symmetrical tetraalkylsilanes or of various tetraalkoxysilanes on the other. The two-phase plot of I_{160}^{APL} *versus* I_{160}^{XE} for tetraalkylsilanes is shown to be completely different from that for tetraalkoxysilanes.

INTRODUCTION

The three previous papers[1–3] in this series dealt with Kováts retention indices for tetraalkoxysilanes. Methods for the calculation of retention indices were developed, and various interrelations between retention indices, as well as relationships between retention indices and certain physical constants, were established. In this paper, a similar study of tetraalkylsilanes, R_4Si, with normal alkyl groups is reported.

Tetraalkylsilanes belong to the types of organosilicon compounds most frequently investigated by gas chromatography. Thus, Semlyen and co-workers[4,5] measured the retentions of a considerable number of symmetrical and mixed tetraalkylsilanes relative to mesitylene on squalane, and Pollard *et al.*[6], in connection with redistribution studies on tetraalkylsilanes, determined retention volumes on silicone oil E-301. In similar work by Hailey and Nickless[7], specific retention volumes were given for some tetraalkylsilanes mainly containing branched alkyl groups. Garzó *et al.*[8] reported retention indices for several organosilicon compounds on Apiezon L, SE-30 and QF-1, including tetramethyl- and tetraethylsilane. Wurst and Churáček[9] measured a quantity called the silicon index (I_{Si}) for tetramethyl-, tetraethyl- and tetrapropylsilane. However, no data were given that permit the recalculation of the silicon index to Kováts retention index.

EXPERIMENTAL

Apparatus and columns

A Varian Model 1400 gas chromatograph with a flame ionization detector, and equipped with an auxiliary thermocouple and temperature gauge (Mettler TM 15), was used for the retention index measurements. The temperature could be read to ±0.1° and was constant within this range during a measurement. Any significant deviation of the observed temperature from the measurement temperature in the tables was corrected for.

Perkin-Elmer capillary steel columns (50 m × 0.25 mm) containing Apiezon L and cyanosilicone XE-60, respectively, as stationary phases were used throughout. For the determination of accurate retention indices, the recently described computer method[10] was utilized.

Materials

Most of the compounds investigated were synthesized in this laboratory. The symmetrical tetraalkylsilanes were prepared from alkyl-lithium and silicon tetrachloride. The same method was used for preparing some of the mixed compounds, starting from appropriate alkyl chlorosilanes and alkyl-lithium. However, the majority of the mixed tetraalkylsilanes were obtained by alkyl interchange between symmetrical tetraalkylsilanes using aluminium chloride (1 mole-%) as catalyst[6]. Depending on the boiling points of starting material and products, the reaction mixture was heated either under reflux or in a sealed tube to 150–175° for 2 h. Under these conditions, the formation of undesired by-products was generally limited.

The syntheses by alkyl interchange were performed on a small scale. No separations of the compounds formed were made prior to the gas chromatographic investigation. The peaks in a chromatogram could generally be unequivocally assigned, as the various tetraalkylsilanes resulting from the systematic exchange of one alkyl group for another appeared in order of increasing molecular weight on both stationary phases. In some doubtful cases, this was proved by comparison with model compounds obtained by the alkyl-lithium–chlorosilane method.

RESULTS AND DISCUSSION

Retention indices and ΔI values of tetraalkylsilanes

Table I summarizes retention indices and ΔI values of tetraalkylsilanes with R = methyl to pentyl, and in Table II the corresponding group values are given. These values were obtained by division of the indices and ΔI values for the symmetrical tetraalkylsilanes, SiR_4, in Table I by four. In Table I, I_{160}^{ApL} values are generally given to one decimal place, while I_{160}^{XE} values are generally given as integers, which is in agreement with the general rule that the retentions of non-polar compounds can be determined more accurately on non-polar than on polar stationary phases. As the XE-60 column has a recommended maximum temperature of 150°, I_{160}^{XE} values were obtained by extrapolation from I^{XE} values determined at lower temperatures. The ΔI values for *n*-alkyl groups bonded to silicon are strikingly low, and only 1/15th to 1/5th of the corresponding ΔI values for *n*-alkoxy groups[1]. This is a consequence of the low polarity of the Si–C bond compared with the Si–O–C bond.

TABLE I

EXPERIMENTAL AND CALCULATED RETENTION INDICES AND ΔI VALUES FOR TETRAALKYLSILANES

Compound	I_{160}^{ApL}			I_{160}^{XE}			$\Delta I_{160}=I_{160}^{XE}-I_{160}^{ApL}$		
	*Exptl.**	*Calcd.***	*Diff.*	*Exptl.****	*Calcd.***	*Diff.*	*Exptl.*	*Calcd.*§	*Diff.*
Me_4Si	420			437			17		
Et_4Si	922.2			948.1			25.9		
Pr_4Si	1192.9			1204.4			11.5		
Bu_4Si	1485.6			1508.7			23.1		
Pe_4Si	1820			1847			27		
Me_3SiEt	550	559	+ 9	569	578	+ 9	19	19	0
Me_2SiEt_2	676.9	688	+11	697	710	+13	20	22	+2
$MeSiEt_3$	800.1	810	+10	825	833	+ 8	25	23	−2
Me_3SiPr	634.0	638	+ 4	649	654	+ 5	15	16	+1
Me_2SiPr_2	838.8	841	+ 2	852	854	+ 2	13	13	0
$MeSiPr_3$	1026.0	1025	− 1	1037	1038	+ 1	11	13	+2
Me_3SiBu	722.7	724	+ 1	741	743	+ 2	18	19	+1
Me_2SiBu_2	1008.4	1003	− 5	1026	1023	− 3	18	20	+2
$MeSiBu_3$	1264.4	1257	− 7	1284	1279	− 5	20	22	+2
Me_3SiPe	814.0	820	+ 6	838	840	+ 2	24	20	−4
Me_2SiPe_2	1188.6	1187	− 2	1212	1209	− 3	23	22	−1
$MeSiPe_3$	1528.8	1520	− 9	1549	1545	− 4	20	25	+5
Et_3SiPr	994.1	996.5	+ 2.4	1020	1019	− 1	26	23	−3
Et_2SiPr_2	1064.4	1066.4	+ 2.0	1086	1085	− 1	22	19	−3
$EtSiPr_3$	1130.0	1131.8	+ 1.8	1145	1147	+ 2	15	15	0
Et_3SiBu	1076.3	1076.3	0.0	1103	1101	− 2	27	25	−2
Et_2SiBu_2	1222.1	1221.5	− 0.6	1247	1246	− 1	25	24	−1
$EtSiBu_3$	1358.7	1358.0	− 0.7	1382	1382	0	23	24	+1
Et_3SiPe	1164.0	1167	+ 3	1193	1193	0	29	26	−3
Et_2SiPe_2	1400.1	1397	− 3	1423	1424	+ 1	23	27	+4
$EtSiPe_3$	1618.0	1616	− 2	1640	1642	+ 2	22	26	+4

* The slope of the linear part of the *n*-alkane logt'_r–carbon number plot at 160° was 0.226.

** Calculated using eqn. 1; the k values on both columns are 4.2 and 2.2 for MeO and EtO, respectively.

*** The slope of the linear part of the *n*-alkane logt'_r–carbon number plot at 150° was 0.199.

§ Obtained by subtraction of I_{160}^{ApL} (calcd.) from I_{160}^{XE} (calcd.).

The increase in the group index per CH_2 group added is also given in Table II. The large increase for the first CH_2 group added is remarkable and it is concluded that the retention index of Me_4Si is abnormally low on both Apiezon L and XE-60. On the basis of refractometric studies, it has been proposed by Fajans[11] that in an alkyl chain bonded to silicon, the charge distribution is

$$\mathrm{Si}{-}\underset{\alpha}{\overset{-}{\mathrm{CH_2}}}{-}\underset{\beta}{\overset{+}{\mathrm{CH_2}}}{-}\underset{\gamma}{\overset{-}{\mathrm{CH_2}}}{-}\underset{\delta}{\overset{+}{\mathrm{CH_2}}}{-}\underset{\varepsilon}{\overset{-}{\mathrm{CH_2}}}{-}\ldots$$

where the magnitude of the charge diminishes with increasing distance from the silicon atom. Comparison with the $\delta I(CH_2)$ values in Table II shows that the high β-CH_2 value is connected with a positive charge and the low γ-CH_2 value with a

TABLE II

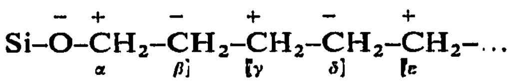
GROUP RETENTION INDICES AND GROUP ΔI VALUES FOR *n*-ALKYL GROUPS BONDED TO SILICON IN SYMMETRICAL TETRAALKYLSILANES

R	$I_{160}^{ApL}(RSi)$	$\delta I(CH_2)$	$I_{160}^{XE}(RSi)$	$\delta I(CH_2)$	$\Delta I_{160}(RSi)$
Me	105.0		109.3		4.3
Et	230.6	125.6	237.0	127.7	6.5
Pr	298.2	67.6	301.1	64.1	2.9
Bu	371.4	73.2	377.2	76.1	5.8
Pe	455.0	83.6	461.8	84.6	6.8

negative charge. From refractometric investigations, in which a similar change in the group refraction of CH_2 was demonstrated, it was concluded that the influence of the silicon atom did not reach appreciably beyond the δ-CH_2 group[12]. Although tetraalkylsilanes with alkyl groups larger than pentyl have not been investigated, there is reason to assume that the ε-$\delta I(CH_2)$ value is close to the normal one, just as was found for the refraction of the ε-CH_2 group.

Thus, on the basis of the Fajans' theory, the low retention index for Me_4Si should be attributed to the negatively charged methyl carbon atoms, which cause the solubility of the molecule in the stationary phase to be lower than expected for normal behaviour. Similarly, the high retention index of Et_4Si should be connected with the now positively charged terminal methyl carbon atoms, causing the solubility to be higher than expected.

For the previously investigated tetraalkoxysilanes, a similar variation in the $\delta I(CH_2)$ values in the vicinity of the silicon atom existed (see Table IV in ref. 1). In this instance, the charge distribution is assumed to be[12]



$$\mathrm{Si{-}\overset{-}{O}{-}\underset{\alpha}{\overset{+}{C}}H_2{-}\underset{\beta]}{\overset{-}{C}}H_2{-}\underset{[\gamma}{\overset{+}{C}}H_2{-}\underset{\delta]}{\overset{-}{C}}H_2{-}\underset{[\varepsilon}{\overset{+}{C}}H_2{-}\ldots}$$

The difference between I(EtOSi) and I(MeOSi) is strikingly small, which is mainly caused by the too high retention index for $(MeO)_4Si$. Accordingly, the positive charge on the methyl carbon atoms in $(MeO)_4Si$ renders the molecule more soluble in the stationary phase than expected for normal behaviour. Judging from the $\delta I(CH_2)$ values, the influence of the silicon (and oxygen) atom does not reach appreciably beyond the δ-CH_2 group in this instance either.

A comparison between the I(RSi) values and the corresponding I(ROSi) values (see Table III) shows a considerable variation in the differences with the size of the R group. On Apiezon L, I(ROSi) is about 60 index units higher than I(RSi) for R = methyl, which must be attributed to the opposite charges on the two methyl groups. For R = ethyl, I(ROSi) is about 18 index units lower than I(RSi), as a consequence of the now reversed charges of the terminal methyl groups. With increasing R, the group indices become more alike and are nearly identical for R = butyl and pentyl. Accordingly, we can conclude that on Apiezon L, for small R values, the charge of the terminal methyl group has a dominating influence on the retention, whereas for larger R groups, their size is the retention-determining factor, the charge in this instance

TABLE III

COMPARISON OF GROUP RETENTION INDICES FOR *n*-ALKYL AND *n*-ALKOXY GROUPS BONDED TO SILICON IN SYMMETRICAL TETRAALKYL- AND TETRAALKOXYSILANES

R	*Diff.* $[I^{ApL}_{160}(ROSi) - I^{ApL}_{160}(RSi)]$	*Diff.* $[I^{XE}_{160}(ROSi) - I^{XE}_{160}(RSi)]$
Me	+62	+118.0
Et	−17.7	+ 15.8
Pr	− 7.7	+ 22.7
Bu	− 0.6	+ 23.2
Pe	0	+ 23

being too low to be of any importance. For larger RO groups, the presence of the oxygen atom has only a minor influence on the retention of tetraalkoxysilanes on the non-polar stationary phase.

For the XE-60 phase, there is still a difference of about 20 index units between I(ROSi) and I(RSi) for R = butyl and pentyl. This difference can be considered as the contribution of the oxygen atom in the RO group to the retention on the polar phase.

The ΔI values are also markedly influenced by the charge of the terminal methyl groups. Thus, low ΔI values are connected with a negative charge: Me_4Si ($\Delta I = 17$), Pr_4Si ($\Delta I = 11.5$), Me_nSiPr_{4-n} ($\Delta I = 11$–15); and high ΔI values with a positive charge: Et_4Si ($\Delta I = 25.9$), Bu_4Si ($\Delta I = 23.1$), Et_nSiBu_{4-n} ($\Delta I = 23$–27).

Equation for the calculation of retention indices

Semlyen and Phillips[4] observed the non-additivity of group retentions in mixed tetraalkylsilanes and concluded that the more similar were the sizes of the alkyl groups in a mixed tetraalkylsilane, the smaller was the deviation from additivity. A rough correction method was based on this observation, but it does not permit accurate calculation of the retentions of mixed tetraalkylsilanes. In a previous paper[1], an equation was given for the calculation of retention indices of mixed tetraalkoxysilanes from those of the symmetrical counterparts. If this equation is applied to mixed tetraalkylsilanes, it will become

$$I(R_4Si) = \Sigma I(RSi) + \Sigma(n \cdot d \cdot k)_{R-R} \qquad (1)$$

where

R = *n*-alkyl;
I(RSi) = group retention index (see Table II);
n = combination number (cf. refs. 1 and 3);
d = carbon number difference between alkyl groups in a combination;
k = constant, dependent on the smallest alkyl group in a combination.

When eqn. 1 was applied to the calculation of retention indices of mixed tetraalkylsilanes, it appeared that there were certain limitations in its utilization. Thus, when the equation was applied to mixed tetraalkylsilanes containing methyl groups bonded to silicon, deviations between the experimental and calculated retention indices of up to 13 index units were obtained, which is considerably more than the experimental error. When applied to mixed tetraalkylsilanes with ethyl as the smallest group, eqn. 1 gave values in much better agreement with the experimental values (see Table I). In the material investigated, no mixed tetraalkylsilanes with a group larger than ethyl as the smallest group are present. However, it is believed that eqn. 1 may be used for the calculation of retention indices of all types of mixed tetraalkylsilanes with good accuracy except for those which contain methyl groups. The results for the latter compounds are, as shown by Table I, only approximate, the deviation amounting to 1–13 index units. Another method of calculating retention indices of mixed tetraalkylsilanes with methyl groups is given later in this paper.

The reason for the different behaviour of mixed tetraalkylsilanes with and without methyl groups is associated with the different structures of the two types of tetraalkylsilanes. It was previously shown[1] that the correction term in the equation for the calculation of retention indices of mixed tetraalkoxysilanes (identical with the correction term in eqn. 1) could be obtained by summing a number of interaction increments arising from an assumed interaction between certain CH_3 and CH_2 groups. From this group interaction point of view, the CH_3CH_2Si group is equivalent to the CH_3OSi group, the $CH_3CH_2CH_2Si$ group to the CH_3CH_2OSi group, etc., while the CH_3Si group has no counterpart among the ROSi groups. It is thus understandable that eqn. 1, which is identical with the equation used for calculating the retention indices of mixed tetraalkoxysilanes, is not suitable for accurate calculations on mixed tetraalkylsilanes that contain methyl groups.

Temperature dependence of retention indices

The measured change in retention index with temperature for symmetrical and mixed tetraalkylsilanes is given in Table IV. In the previous investigations of tetraalkoxysilanes[1,2], their change in retention index with temperature was found to be always negative and to increase with molecular size. For the tetraalkylsilanes, the temperature increments are considerably lower and alternate between positive and negative values in an apparently erratic manner. However, there is also a tendency towards increasing negative values for larger molecules.

With the tetraalkoxysilanes, it was shown that approximate values of $10\,\mathrm{d}I/\mathrm{d}T$ for mixed compounds could be obtained by addition of group values, derived from the symmetrical counterparts by division by four. When the same method was applied to mixed tetraalkylsilanes, the mean deviation between experimental and calculated values of $10\,\mathrm{d}I/\mathrm{d}T$ for Apiezon L was found to be 0.35. Better agreement resulted when ($I - 100 \cdot$ carbon number) was plotted against $10\,\mathrm{d}I/\mathrm{d}T$. It appeared that the points were collected along three straight lines, one for symmetrical tetraalkylsilanes, one for mixed compounds containing methyl groups and one for mixed compounds without methyl groups. The calculated values in Table IV were obtained from the equations of these three straight lines (see Table V). The mean deviation between experimental and calculated values by this method is 0.17 for both columns.

The above relationship means that the sign and magnitude of the retention index temperature increment for a tetraalkylsilane is dependent on the difference between its retention index and the retention index of the *n*-alkane with the same number of carbon atoms. Thus, when the former index is smaller than the latter, *i.e.* the difference is negative, the temperature increment is always negative. When the difference is positive, the temperature increment is always positive for tetraalkylsilanes

TABLE IV

COMPARISON OF EXPERIMENTAL AND CALCULATED TEMPERATURE INCREMENTS OF RETENTION INDICES FOR TETRAALKYLSILANES

Compound	*10dI/dT(ApL)*			*10dI/dT(XE-60)*		
	Temp. range (°C)	*Exptl.*	*Calcd.*	*Temp. range (°C)*	*Exptl.*	*Calcd.*
Me$_4$Si	80–120	0	0.1	80–120	(0)*	
Et$_4$Si	100–180	+1.9	+1.9	100–150	+2.6	+2.6
Pr$_4$Si	120–180	−0.4	−0.4	120–150	+0.7	+0.7
Bu$_4$Si	140–180	−2.0	−2.2	120–150	−0.6	−0.6
Pe$_4$Si	160–180	−3.5	−3.3	150–160	(−1.5)*	
Me$_3$SiEt	100–140	0	+0.2	100–120	+0.7	+0.7
Me$_2$SiEt$_2$	100–140	+0.8	+0.7	100–120	+0.9	+1.1
MeSiEt$_3$	100–140	+1.2	+1.0	100–120	+2.0	+1.6
Me$_3$SiPr	120–160	0	−0.1	120–140	0.0	+0.4
Me$_2$SiPr$_2$	120–160	+0.3	+0.1	120–150	+0.5	+0.5
MeSiPr$_3$	120–160	+0.3	−0.1	120–150	+0.4	+0.3
Me$_3$SiBu	140–180	−0.5	−0.2	120–150	0.0	+0.3
Me$_2$SiBu$_2$	140–180	−0.4	−0.4	120–150	0.0	+0.1
MeSiBu$_3$	140–180	−0.9	−1.0	120–150	−0.1	−0.5
Me$_2$SiPe$_2$	160–180	−0.3	−0.7			
MeSiPe$_3$	160–180	−1.6	−1.6			
Et$_3$SiPr	140–180	+1.4	+1.5	120–150	+2.5	+2.4
Et$_2$SiPr$_2$	140–180	+1.3	+1.0	120–150	+2.1	+1.8
EtSiPr$_3$	140–180	+0.8	+0.5	120–150	+1.2	+1.1
Et$_3$SiBu	160–180	+1.1	+1.2	120–150	+1.7	+2.1
Et$_2$SiBu$_2$	160–180	+0.7	+0.4	120–150	+0.8	+1.1
EtSiBu$_3$	160–180	−0.5	−0.5	120–150	0.0	0.0
Et$_3$SiPe	160–180	+1.0	+1.1			
Et$_2$SiPe$_2$	160–180	−0.5	—0.1			
EtSiPe$_3$	160–180	−1.2	−1.3			

* Approximate values.

TABLE V

CONSTANTS IN AND CORRELATION COEFFICIENTS FOR THE LINEAR RELATIONSHIP 10dI/dT=$k\cdot(I-100\times$CARBON NUMBER$)+l$ FOR TETRAALKYLSILANES COLLECTED IN THREE GROUPS

Group	*Apiezon L*			*XE-60*		
	k	*l*	*r*	*k*	*l*	*r*
R$_4$Si	0.017	−0.25	0.997	0.013	+0.63	1.00
Me$_n$SiR$_{4-n}$	0.015	−0.50	0.95	0.015	−0.28	0.90
Et$_n$SiR$_{4-n}$	0.015	−0.10	0.96	0.017	+0.27	0.96

without methyl groups, but positive or negative for tetraalkylsilanes that contain methyl groups. In the latter instance, the negative increment values are associated with smaller index differences up to about 30 index units. It can be concluded that the possibility of predicting reasonably accurate retention index temperature increments for tetraalkylsilanes not included in this study, on the basis of the equations given in Table V, seems to be rather good.

Relationship between retention indices and carbon numbers

Although available data are limited, it seems justifiable to state that for homologous series of tetraalkylsilanes there will exist an approximately linear relation between retention index and carbon number counted from the third or fourth member in a series.

Pollard *et al.*[6] reported a linear relationship between the logarithm of the retention volume and the carbon number for tetraalkylsilanes belonging to the series R_4Si–R_3SiR'–$R_2SiR'_2$–$RSiR'_3$–SiR'_4. However, this is true only for certain series. Thus, for the seven series Me_nSiR_{4-n} (R = ethyl to pentyl) and Et_nSiR_{4-n} (R = propyl to pentyl) studied in this work, the above statement is approximately correct only for the two series Me_nSiEt_{4-n} and Et_nSiPr_{4-n}. For the other five series, there will be an increased deviation from linearity with increase in the difference in size between the two alkyl groups in the tetraalkylsilane, as a consequence of the increased departure from additivity of the group retention indices as expressed by the correction term in eqn. 1. Similar relationships were previously found to exist for the corresponding series of tetraalkoxysilanes.

Retention indices of homologous series of mixed tetraalkylsilanes versus retention indices of the symmetrical counterparts

When the retention indices of homologous series of mixed tetraalkylsilanes were plotted against retention indices of the symmetrical counterparts, the points for the majority of the series were found to lie on very nearly straight lines. The largest deviation existed for the series Me_3SiR on Apiezon L (see Table VI). The reported correlation coefficient ($r = 0.9995$) means that when the retention indices for the members in the series are calculated from the equation

$$I(R_xSiR'_{4-x}) = p_x I(R'_4Si) + q_x \tag{2}$$

TABLE VI

VALUES OF p_x AND q_x IN EQN. 2 AND OF THE CORRESPONDING CORRELATION COEFFICIENT r

R	*x*	*Apiezon L*			*XE-60*		
		p_x	q_x	r	p_x	q_x	r
Me	3	0.2945	281.1	0.9995	0.2992	287.2	0.9998
	2	0.5702	155.4	0.9997	0.5721	159.0	0.9998
	1	0.8115	55.2	0.99993	0.8055	64.6	0.99993
Et	3	0.2704	672.7	0.99991	0.2723	691.1	0.99993
	2	0.5330	429.9	0.99999	0.5281	448.7	0.99997
	1	0.7757	206.0	1.00000	0.7706	217.7	0.99999

(R = Me, $x = 3$), taking the values of p_x and q_x from Table VI and the values of $I^{\mathrm{ApL}}_{160}(\mathrm{R'_4Si})$ from Table I, the standard deviation between calculated and experimental values will become 2.9 index units. This value is greater than the error in the index measurement. However, for the majority of the series in Table VI, the standard deviation will be comparable with the error in the index measurement.

A relationship identical with that in eqn. 2 was recently reported for tetraalkoxysilanes[2]. In this case, an improved method for calculating retention indices for mixed tetraalkoxysilanes from the retention indices of the symmetrical counterparts could be developed from eqn. 2. However, in the present instance no further simplification of eqn. 2 is possible. Consequently, no simple relationship exists among either the p_x or the q_x values for the three series $\mathrm{R}_x\mathrm{SiR'}_{4-x}$ ($x = 1$–3), which was found to be the case for the corresponding tetraalkoxysilanes (see ref. 2).

Retention indices for homologous series of mixed tetraalkylsilanes versus retention indices for tetraalkoxysilanes

Several linear relationships exist between retention indices for homologous series of mixed tetraalkylsilanes on the one hand and retention indices for tetraalkoxysilanes on the other. Thus, the following relationship holds for mixed tetraalkylsilanes and the corresponding mixed tetraalkoxysilanes:

$$I(\mathrm{R}_x\mathrm{SiR'}_{4-x}) = k_1 I(\mathrm{RO})_x\mathrm{Si(OR')}_{4-x} + l_1 \qquad (3)$$

In this expression, R and x are the same throughout a series, while the R′ groups form a "homologous" suite (see full lines in Fig. 1). The good linearity of this relationship, especially for R = Me, is shown by the correlation coefficients in Table VII. The broken lines in Fig. 1 demonstrate that in addition to the above linear relationship there exists another, which concerns mixed tetraalkylsilanes, $\mathrm{R}_x\mathrm{SiR'}_{4-x}$ ($x = 0$–4), and the corresponding mixed tetraalkoxysilanes, where one group is exchanged for another in a regular manner. However, the linearity of the correlations for these series is not as good as for the former.

It was previously shown[1,2] that a linear relationship exists between the retention indices for homologous series of mixed tetraalkoxysilanes, $(\mathrm{RO})_x\mathrm{Si(OR')}_{4-x}$, and the retention indices for their symmetrical counterparts, $(\mathrm{R'O})_4\mathrm{Si}$. Accordingly, it follows from eqn. 3 that the following relationship will be valid:

$$I(\mathrm{R}_x\mathrm{SiR'}_{4-x}) = k_2 I(\mathrm{R'O})_4\mathrm{Si} + l_2 \qquad (4)$$

The values of k_2 and l_2 and of the correlation coefficient r for six series on two stationary phases are given in Table VIII.

The significance of a linear relationship between retention indices for two homologous series of compounds is as follows. There will exist a constant ratio between the increase in retention for corresponding compounds in the two series, as expressed by the change in retention index or its equivalent, the logarithm of the retention volume, when a $\mathrm{CH_2}$ group is added to the compounds in question. This is partly a consequence of the linear relationship between retention index and carbon number for homologous series. However, the linear relationship between retention indices of homologous series, discussed in this section, is also valid for the first part of the series where the retention index is non-linear with the carbon number. For

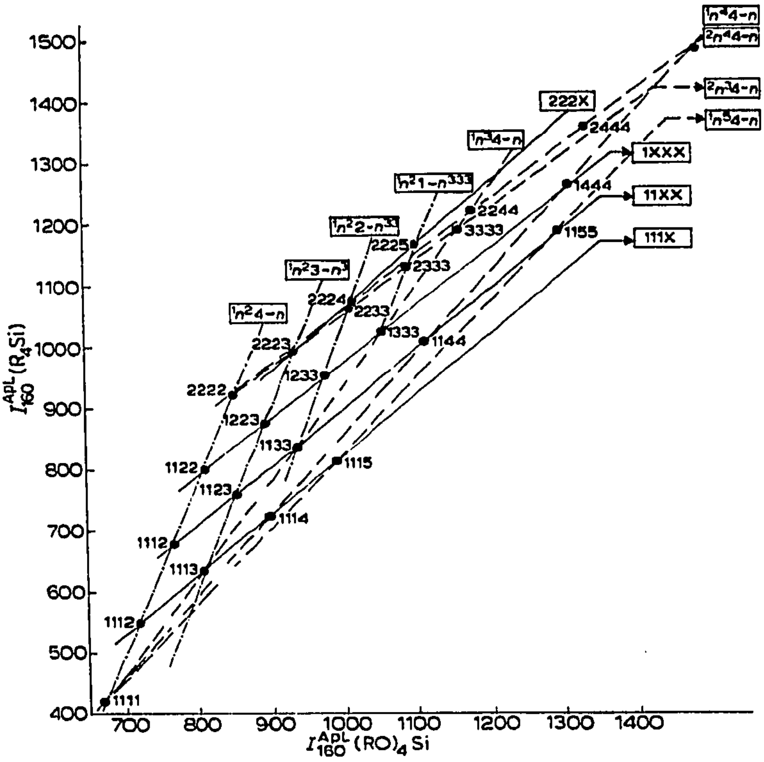


Fig. 1. I_{160}^{ApL} (R$_4$Si) *versus* I_{160}^{ApL} ((RO)$_4$Si). ———, "homologous" lines; – – – –, exchange of methyl (1) for propyl (3), butyl (4) and pentyl (5) or ethyl (2) for propyl (3) and butyl (4); —·—·—, exchange of methyl (1) for ethyl (2).

TABLE VII

VALUES OF k_1 AND l_1 IN EQN. 3 AND OF THE CORRESPONDING CORRELATION COEFFICIENT r

The retention indices for the tetraalkoxysilanes used in the calculation were taken from ref. 2.

R	*x*	*Apiezon L*			*XE-60*		
		k_1	l_1	r	k_1	l_1	r
Me	3	0.9605	−142.4	1.0000	1.0205	−395.0	0.99996
	2	0.9631	− 64.4	1.0000	1.0185	−294.0	0.99996
	1	0.9361	39.0	0.99998	0.9880	−159.7	0.9997
Et	3	0.9816	79.0	0.99998	1.0336	−100.9	0.9998
	2	0.9890	62.4	0.9997	1.0001	− 69.6	0.99999
	1	0.977	70.4	0.9997	1.0091	− 93.2	0.99999

compounds on this part of the curve, the linearity depends on the fact that the retention indices of the two compounds, *e.g.* Me$_2$SiEt$_2$ and (MeO)$_2$Si(OEt)$_2$, deviate equally from linearity in their respective retention index–carbon number plots.

TABLE VIII

VALUES OF k_2 AND l_2 IN EQN. 4 AND OF THE CORRESPONDING CORRELATION COEFFICIENT r

The retention indices for the tetraalkoxysilanes used in the calculation were taken from ref. 2.

R	*x*	*Apiezon L*			*XE-60*		
		k_2	l_2	r	k_2	l_2	r
Me	3	0.2730	317.3	0.99999	0.2906	274.4	0.99994
	2	0.5284	225.8	0.99998	0.5564	132.9	0.99994
	1	0.7517	115.6	0.9998	0.7825	29.5	0.99990
Et	3	0.2583	693.6	0.99999	0.2623	682.0	0.9998
	2	0.5106	468.9	0.9998	0.5225	409.5	1.00000
	1	0.7422	264.1	0.9998	0.7675	151.6	0.99999

TABLE IX

COMPARISON OF EXPERIMENTAL AND CALCULATED RETENTION INDICES FOR TRIFUNCTIONAL TETRAALKYLSILANES

Compound	*Exptl.*	*Calcd. (eqn. 1)*	*Diff.*	*Calcd. (eqn. 3)*	*Diff.*
$Me_2SiEtPr$	759	766	+7	758	−1
$MeSiEt_2Pr$	877	886	+9	876	−1
$MeSiEtPr_2$	953	957	+4	951	−2

Calculation of retention indices for mixed tetraalkylsilanes containing methyl groups

It was mentioned that eqn. 1 was less adequate for calculating retention indices for mixed tetraalkylsilanes containing methyl groups. On this account, we have investigated the usefulness of the linear relationships discussed in the previous section for making such calculations. It appeared that eqn. 3 was best suited for this purpose. In order to test the validity of eqn. 3, some trifunctional tetraalkylsilanes were prepared and their retention indices on Apiezon L determined. In Table IX, the experimental values are compared with those obtained using eqn. 1 and eqn. 3, respectively. Eqn. 3 is seen to be superior, and the agreement between experimental and calculated values is good. This proves that all mixed tetraalkylsilanes that contain one methyl group lie on the 1XXX line in Fig. 1, and all mixed tetraalkylsilanes that contain two methyl groups on the 11XX line.

For the mixed tetraalkylsilanes in Table I, a similar comparison between experimental and calculated retention indices shows that for compounds without methyl groups, eqns. 1 and 3 give comparable values, while for compounds that contain methyl groups, eqn. 3 is superior and should be used.

I_{160}^{ApL} *versus* I_{160}^{XE}

When I_{160}^{ApL} values for tetraalkylsilanes are plotted against the corresponding I_{160}^{XE} values, it appears that the points fall satisfactorily on a straight line of equation

$$I_{160}^{XE}(R_4Si) = 1.011 \cdot I_{160}^{ApL}(R_4Si) + 8.3 \qquad (5)$$

The correlation coefficient is 0.9997 when all available data are utilized, giving a standard deviation of ±4.2 index units. The fact that the relationship between polar and non-polar retention indices for all of the tetraalkylsilanes investigated can be approximately expressed by the equation of a single straight line is in sharp contrast to the case for tetraalkoxysilanes, in which the retention indices for each homologous series of compounds fell on their own straight line (see Fig. 4 in ref. 1). The reason for this difference is the low polarity of the tetraalkylsilanes, as previously discussed in connection with the ΔI values.

In the case of the two-phase plot for tetraalkoxysilanes, two linear relationships existed. One was that mentioned above for homologous series and the other was for compounds belonging to the same structure group. A structure group is formed from compounds with the same number of $CH_3(a)$, $CH_2(b)$, $CH(d)$ and $C(e)$ groups and the code is written *a–b–d–e*. As only compounds with normal alkyl or alkoxy groups bonded to silicon are considered here the code will become *a–b*–0–0.

It was found that tetraalkyl- and tetraalkoxysilanes differ in the two-phase plot also for compounds that belong to the same structure group. In the latter case, there is a very good linear relationship between I^{ApL}_{160} and I^{XE}_{160} for all compounds within a structure group, while for the tetraalkylsilanes there is a considerable scatter in the points representing a structure group. However, closer inspection reveals that, in fact, linear relationships exist between the retention indices for certain compounds within a structure group.

This is demonstrated in Fig. 2 for the structure group 4–6–0–0. There are two parallel diagonal lines and three additional lines intersecting them, and the compounds 1117–1126–1225–2224* and 1135–1234–2233 are collected along the two diagonal lines. The tetraalkylsilanes in these two series are obtained from the first compound by the systematic transfer of a CH_2 group from an alkyl group larger than propyl to a methyl group. The compounds 1144–1135–1126, 1333–1234–1225 and 2233–2224 are gathered along the three intersecting lines. These series are formed from the first compound by transfer of a CH_2 group from a propyl group to another propyl or another, larger, alkyl group, or between alkyl groups larger than propyl. The significance of these linear relationships is that there exists a constant relationship between the change in I^{XE}_{160} and I^{ApL}_{160} for a CH_2 transfer in each of the series mentioned. The generality of these linear relationships between tetraalkylsilanes within a structure group cannot be decided on the basis of the available material, and more data are necessary in order to answer this question.

From a comparison between Fig. 2 in this paper and Fig. 4 in ref. 1, another difference between tetraalkyl- and tetraalkoxysilanes is apparent. In the structure group 4–6–0–0 for tetraalkoxysilanes, and all other structure groups investigated, the compounds are eluted according to decreasing formula code. In the structure group 4–6–0–0 for tetraalkylsilanes, the elution of compounds along the diagonal lines takes place according to increasing formula code and along the intersecting lines according to decreasing formula code. This means that in both of the latter cases the elution takes place according to symmetry with the important difference that along the diagonal lines the least symmetrical compounds are eluted first and along the intersecting lines the most symmetrical are eluted first.

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[*] The figures in the formula code denote the *n*-alkyl groups bonded to the central silicon atom: 1 = methyl, 2 = ethyl, 3 = propyl, etc.

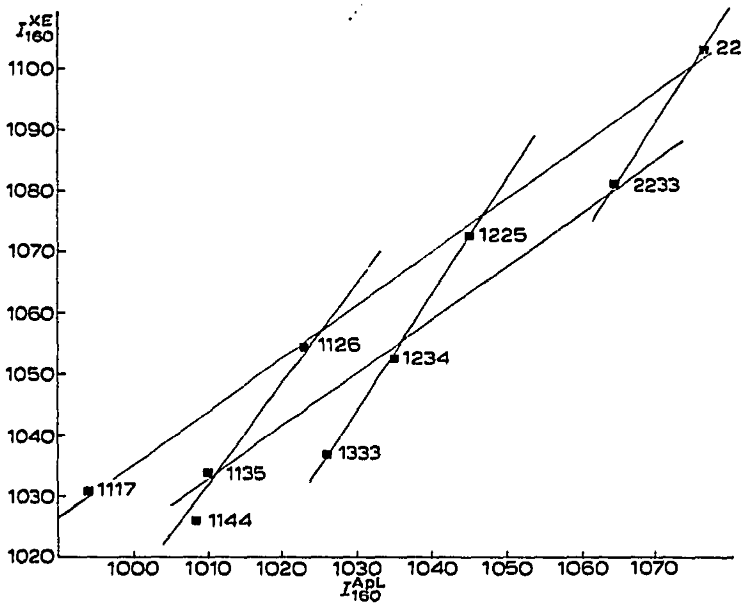

Fig. 2. Two-phase plot of I_{160}^{XE} *versus* I_{160}^{ApL} for tetraalkylsilanes belonging to the structure group 4–6–0–0.

The difference in elution behaviour of tetraalkyl- and tetraalkoxysilanes is perhaps best shown by comparing the elution order of the series of tetraalkylsilanes along the upper diagonal lines in Fig. 2 with that of the corresponding tetraalkoxysilanes along the 4–6–0–0 structure line in Fig. 4 in ref. 1. The two series of compounds, in order of elution on both Apiezon L and XE-60, are 1117–1126–1225–2224 and 2224–1225–1126–1117, *i.e.* the elution order is reversed for the tetraalkoxysilanes. Regarding the 4–6–0–0 tetraalkylsilane structure group as a whole, the elution picture is less clear. Thus, while the tetraalkoxysilanes within a structure group are eluted strictly according to decreasing formula code, the elution order of the tetraalkylsilanes is 1117–1144–1135–1126–1333–1234–1225–2233–2224 on the Apiezon L stationary phase and 1144–1117–1135–1333–1234–1126–1225–2233–2224 on the XE-60 stationary phase. This is a consequence of the variation of the $\delta I(\mathrm{CH_2})$ values (see Table II).

Boiling point versus retention index

Fig. 3 demonstrates the relationship between I_{160}^{ApL} and the boiling point for tetraalkylsilanes in the index range 400–1200. It appears that the curve in this range can be approximated by two linear relationships, one valid for tetraalkylsilanes containing two or three methyl groups bonded to silicon and the other for the remainder of the tetraalkylsilanes. The equation is

$$t(^\circ\mathrm{C}) = k \cdot I_{160}^{ApL} + l \qquad (6)$$

In this expression, $k = 0.2792$, $l = -90.2$ for the first group of tetraalkylsilanes and $k = 0.2319$, $l = -58.9$ for the second group. It is possible to calculate the boiling point from eqn. 6 to about 1°, *i.e.* with the same accuracy as that in the experimental boiling point determination[13].

For comparison, retention indices and boiling points for *n*-alkanes have also been plotted in Fig. 3. The curve for *n*-alkanes is seen to coincide with that for the second group of tetraalkylsilanes but not with that for the first group. This is another example of the divergent behaviour of tetraalkylsilanes that contain several methyl groups. The last tetraalkylsilane in Fig. 3, tetrabutylsilane ($I^{\mathrm{ApL}}_{160} = 1486$), lies far outside the *n*-alkane curve. Either the reported boiling point[13] for this compound is about 30° too low or the tetraalkylsilane curve makes a sharp turn for higher retention index values. The question of the appearance of the tetraalkylsilane curve outside of $I^{\mathrm{ApL}}_{160} = 1200$ cannot be decided on the basis of existing data, and a decision has to await the availability of further experimental results.

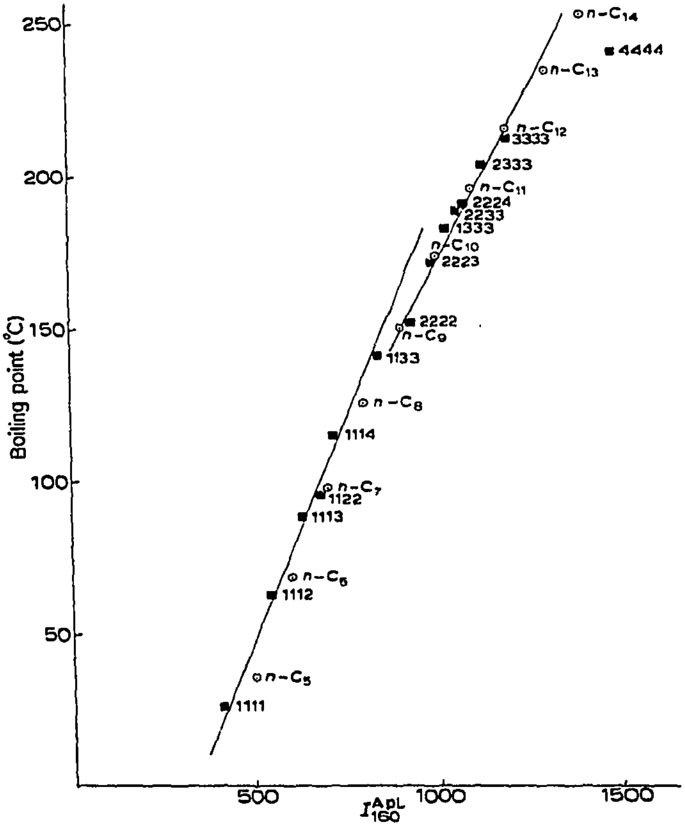

Fig. 3. Boiling point *versus* I^{ApL}_{160}: ■, tetraalkylsilanes; ⊙, *n*-alkanes.

Identification of tetraalkylsilanes

Tetraalkylsilanes can be recognized as a group and distinguished from most other types of organosilicon compounds by their small ΔI-values. However, the identification of a specific tetraalkylsilane by gas chromatography alone is by no means easy. As pointed out previously, the two-phase plot is less regular than for tetraalkoxysilanes and there is considerable crowding of points for the various compounds, which makes the interpretation more difficult. If, however, the linear relationships found to exist within the structure groups investigated are found to be of general validity, it opens possibilities for a more reliable identification on the basis of the two-phase plot.

It was previously shown[1] that in the case of tetraalkoxysilanes, the ΔI values were useful for the distinction of different types of compounds belonging to this group. For tetraalkylsilanes, some use may also be derived from this physical quantity. Thus, a low ΔI value (<20) is an indication of the presence of only methyl and/or propyl groups in the molecule or at least three of these groups together with ethyl or butyl. On the other hand, high ΔI values (>25) indicate the absence of methyl and propyl in the molecule. However, certain exceptions to these rules exist. Earlier in this paper, some rules were given for the estimation of the temperature increments for the retention indices for tetraalkylsilanes. These data may also be of value in identification work.

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REFERENCES

1 O. Ellrén, I.-B. Peetre and B. E. F. Smith, *J. Chromatogr.*, 88 (1974) 295.
2 I.-B. Peetre, *J. Chromatogr.*, 88 (1974) 311.
3 I.-B. Peetre, *J. Chromatogr.*, 90 (1974) 35.
4 J. A. Semlyen and C. S. G. Phillips, *J. Chromatogr.*, 18 (1965) 1.
5 J. A. Semlyen, G. R. Walker, R. E. Blofeld and C. S. G. Phillips, *J. Chem. Soc.*, (1964) 4948.
6 F. H. Pollard, G. Nickless and P. C. Uden, *J. Chromatogr.*, 19 (1965) 28.
7 A. D. M. Hailey and G. Nickless, *J. Chromatogr.*, 49 (1970) 187.
8 G. Garzó, J. Fekete and M. Blazsó, *Acta Chim. Acad. Sci. Hung.*, 51 (1967) 359.
9 M. Wurst and J. Churáček, *Collect. Czech. Chem. Commun.*, 36 (1971) 3497.
10 I.-B. Peetre, *Chromatographia*, 6 (1973) 257.
11 K. Fajans, *Chem. Eng. News*, 27 (1949) 900.
12 B. E. F. Smith, *Dissertation*, Gothenburg, 1951.
13 H. C. Kaufman, *Handbook of Organometallic Compounds*, Van Nostrand, Princeton, N.J., London, 1961.