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## CAPILLARY GAS CHROMATOGRAPHY OF ALKYL BENZENES

### III. CORRELATIONS BETWEEN THE TEMPERATURE AND PRESSURE COEFFICIENTS OF THE RETENTION INDEX AND STRUCTURE

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#### SUMMARY

Correlations between the structures of alkylbenzenes and the temperature and pressure coefficients of their retention indices were studied, in addition to their dependence on the polarity of the stationary phase, the column inlet pressure and the nature of the carrier gas.

The temperature coefficients ( $dI/dT$ ) vary within relatively wide limits and reflect fine-structural differences in the alkylbenzenes. They are inversely proportional to the symmetry of the molecules and the size of their alkyl groups. The  $dI/dT$  values are about one order of magnitude larger on the highly polar 1,2,3-triscyanoethoxypropane (TCEP) than on squalane.

Although the data on the pressure coefficients on TCEP are limited, there are indications that correlations similar to the  $dI/dT$ -structure correlations also hold. Under the same experimental conditions, a change in the carrier gas from hydrogen to nitrogen at a constant inlet pressure (1 atm) has an effect on the retention index of alkylbenzenes of the same order as that resulting from an increase in the inlet pressure of nitrogen of 1 atm.

The possible application of  $dI/dP$  values for identification purposes in combination with gas chromatography at higher pressures is discussed.

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#### INTRODUCTION

The study of the temperature coefficient of the retention index ( $dI/dT$ ) is useful as it enables a rapid choice of the operating temperature for the analysis of complex mixtures to be made. In addition, it can be used to check on discrepancies in the oper-

ating temperatures cited for published retention data by means of test mixtures of alkanes with different degrees of branching and accurately known  $dI/dT$  values<sup>1</sup>. Further, it permits the calculation of retention indices at different temperatures, which greatly enhances table matching for identification purposes. Another interesting aspect of this parameter is its ability to confirm the identification of unknown compounds in complex mixtures. In this respect it can be considered as a valuable tool for fine structure-retention correlations. Obviously, the fine-structural differences will be the more apparent the more precise are the measurements. The application of these possibilities has been discussed elsewhere for *cis-trans* isomers of *n*-alkenes<sup>2</sup>. For very precise measurements, the absolute value of  $dI/dT$  can be used directly for the identification of alkylbenzenes in some instances, as will be shown in this paper. Correlation between  $dI/dT$  values and the structures of alkylbenzenes make it possible to predict the temperature coefficients of some alkylbenzenes that have not previously been measured.

The relationship between the temperature coefficient of the retention index and structure for hydrocarbons was studied by Hively and Hinton<sup>3</sup> on squalane. They found that the magnitude of  $dI/dT$  is a function of the size of the molecule and that  $dI/dT$  increased as the number, size and position of the substituents increased. They postulated that, on squalane, the temperature coefficient increases with an increase in the minimum cross-sectional area of the molecule.

Soják and Hrivňák<sup>4</sup> reported on the temperature dependence of the retention indices of C<sub>6</sub>-C<sub>10</sub> aromatic hydrocarbons on the highly polar liquid phase PEG 400. They indicated that the  $dI/dT$  values on this stationary phase are a function of the gas chromatographic polarity, and showed that it was possible to discriminate between indanes and alkylbenzenes. However, the precision of the measurements (about 1 index unit (i.u.)) was not sufficient for fine structure-retention correlations to be proposed for alkylbenzene isomers.

Döring *et al.*<sup>5</sup> reported a large number of  $dI/dT$  values for alkylbenzenes up to C<sub>12</sub>. The repeatability of their measurements was high (0.2 i.u.) but they concluded that no unambiguous conclusions could be drawn about their relationship with the structures of alkylbenzenes.

Mitra and Saha<sup>6</sup> summarized the  $dI/dT$  values of aromatic hydrocarbons reported in the literature. They concluded that although the  $dI/dT$  values of aromatics are larger than those of other types of hydrocarbons, the differences between individual aromatics are very small, irrespective of the nature of the stationary phase. They were able to point out only some influence of the *ortho*-effect on the magnitude of  $dI/dT$ .

Contrary to the conclusions drawn by other workers, in this paper it is shown that fine structure-retention correlations based on  $dI/dT$  values exist and can be used for the identification of alkylbenzenes.

The dependence of retention on the nature of the carrier gas and the inlet pressure in capillary gas chromatography has been reported by Goldup and co-workers<sup>7,8</sup>. The effect of higher pressures on the thermodynamics of chromatographic sorption was studied by Ezrets and Vigdergauz<sup>9</sup>, who found that the pressure can be used for the regulation of column selectivity for the resolution of mixtures of compounds of different chemical nature.

In this work, we examined the resolution not only of structurally different

groups of hydrocarbons (alkylbenzenes/*n*-alkanes), but also the fine-structure correlations of alkylbenzene isomers as function of pressure and nature of the carrier gas.

## EXPERIMENTAL

The experimental conditions and the temperature coefficients of the retention indices of alkylbenzenes based on precise measurements of retention indices in the temperature range 80–95° on an apolar (squalane), a medium polar (acetyltributyl citrate) and a highly polar stationary phase (1,2,3-triscyanoethoxypropane, TCEP), were given in Part I<sup>10</sup>.

## RESULTS AND DISCUSSION

### *Effect of temperature on structure-retention correlations*

The standard deviation of the measurements of retention indices increased slightly with increasing polarity of the stationary phase: 0.03 i.u. for squalane (SQ), 0.07 i.u. for acetyltributyl citrate (ATC) and 0.17 i.u. for TCEP. The  $dI/dT$  values were about one order of magnitude higher on TCEP compared with SQ, while the values on ATC were lower than those on SQ. Obviously the  $dI/dT$  values do not increase regularly with increase in the polarity of the stationary phase.

The  $dI/dT$  values on these stationary phases differ within wide limits: 0.015–0.452 i.u./°C for SQ, –0.074–0.432 i.u./°C for ATC and 1.28–3.60 i.u./°C for TCEP. Obviously this wide range reflects fine-structural differences of the individual alkylbenzenes. This is shown in Fig. 1, where the  $dI/dT$  values of 47 C<sub>7</sub>–C<sub>15</sub> alkylbenzenes and benzene are plotted against their retention indices on squalane. A similar plot for 22 possible C<sub>10</sub> alkylbenzene isomers on all three stationary phases is shown in Fig. 2.

Fine structure-retention correlations based on the  $dI/dT$  values of alkylbenzenes of different structural types are discussed below. As the most precise retention data were obtained on squalane, the discussion relates mainly to  $dI/dT$  values for this stationary phase.

*Monoalkylbenzenes.* It is shown in Table I that the  $dI/dT$  values of the first members of this series of *n*-alkylbenzenes increase slightly with increasing number of carbon atoms and then become virtually constant.

The effect of the configuration of the monoalkylbenzenes on their  $dI/dT$  values is also shown in Table I. The  $dI/dT$  values increase slightly in the order *n*- < *tert*- < *iso*- < *sec*-butylbenzene. However, for the propylbenzenes the  $dI/dT$  values increase in the order *iso*- < *n*- and for the pentylbenzenes 2-phenylpentane < 2-phenyl-2-methylbutane; a surprisingly high value is observed for 2-phenyl-2-methylbutane. The differentiation of mono- (except *n*-) from polyalkylbenzenes for the C<sub>10</sub> isomers on the basis of their  $dI/dT$  values is demonstrated in Fig. 2.

*Dialkylbenzenes.* For identical structural types of dialkylbenzenes, but differing in the positions of the alkyl groups, the  $dI/dT$  values (Table II) increase in the order 1,3- < 1,4- < 1,2-dialkylbenzenes. For the corresponding positional isomers of C<sub>10</sub> dialkylbenzenes, the  $dI/dT$  values increase in the order: methylisopropyl- < diethyl- < methyl-*n*-propylbenzene. With increasing number of carbon atoms, the  $dI/dT$  values change slightly, with systematically higher values for *n*-propyl- than for isopropyl-

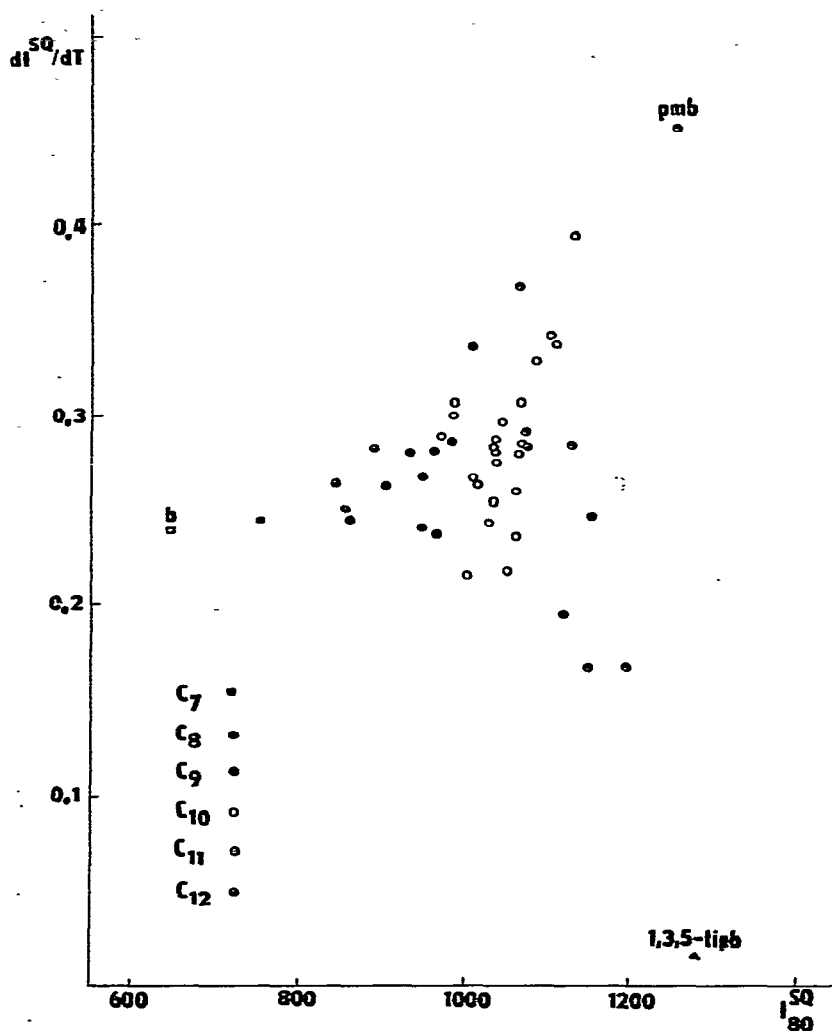


Fig. 1. Temperature increments of retention indices of 47 alkylbenzenes up to  $C_{15}$  as a function of retention index on squalane at  $80^\circ$ . b = Benzene; pmb = pentamethylbenzene; 1,3,5-tipb = triisopropylbenzene.

alkylbenzenes. With an increase in the length of the alkyl chain in methylalkylbenzenes, the  $dI/dT$  values for the 1,4-isomers approach those of the 1,2-isomers. For methylisopropylbenzenes, the  $dI/dT$  value for the 1,4-isomer is already slightly higher than that for the 1,2-isomer (the *ortho*-effect is compensated for), while the difference between the 1,4- and 1,3-isomers increases and that between the 1,3- and 1,2-isomers is virtually constant.

**Trialkylbenzenes.** For trialkylbenzenes, the effect of structure on  $dI/dT$  (Table III) is more apparent. The effect of the position of the alkyl chain on the magnitude of  $dI/dT$  increases in the order 1,3,5- < 1,2,4- < 1,2,3-trialkylbenzenes. In addition to the position of the alkyl groups, the size of these groups also plays an important

TABLE I

TEMPERATURE COEFFICIENTS OF RETENTION INDICES OF MONOALKYL BENZENES ON SQUALANE ( $dI^{SQ}/dT$ ), ACETYLTRIBUTYL CITRATE ( $dI^{ATC}/dT$ ) AND 1,2,3-TRIS-CYANOETHOXYPROPANE ( $dI^{TCEP}/dT$ ) (IN i.u./°C)

<i>Monoalkylbenzene</i>	$dI^{SQ}/dT$	$dI^{ATC}/dT$	$dI^{TCEP}/dT$
Benzene	0.240	0.192	1.96
Toluene	0.245	0.213	2.03
Ethylbenzene	0.265	0.225	2.14
Propylbenzene	0.282	0.245	2.22
Butylbenzene	0.284	0.251	2.29
Pentylbenzene	0.286	0.234	2.37
Isopropylbenzene	0.264	0.214	2.11
Propylbenzene	0.282	0.245	2.22
Butylbenzene	0.284	0.251	2.29
<i>tert.</i> -Butylbenzene	0.290	0.255	2.21
Isobutylbenzene	0.301	0.263	2.21
<i>sec.</i> -Butylbenzene	0.308	0.263	2.21
Pentylbenzene	0.286	0.233	2.37
2-Phenylpentane	0.286	0.260	2.32
2-Phenyl-2-methylbutane	0.369	0.330	2.34

role. The combination of both of these effects, which is clearly demonstrated in Table III, is discussed below.

<sup>1</sup> The introduction of a methyl group into a monoalkylbenzene results in only a slight change in the  $dI/dT$  values for 1,3- and 1,4-isomers but a larger change for

TABLE II

TEMPERATURE COEFFICIENTS OF RETENTION INDICES OF DIALKYL BENZENES ON SQUALANE ( $dI^{SQ}/dT$ ), ACETYLTRIBUTYL CITRATE ( $dI^{ATC}/dT$ ) AND 1,2,3-TRIS-CYANOETHOXYPROPANE ( $dI^{TCEP}/dT$ ) (IN i.u./°C)

<i>Dialkylbenzene</i>	$dI^{SQ}/dT$	$dI^{ATC}/dT$	$dI^{TCEP}/dT$
1,3-Dimethylbenzene	0.245	0.213	2.07
1,4-Dimethylbenzene	0.251	0.214	2.14
1,2-Dimethylbenzene	0.284	0.253	2.42
1,3-Diethylbenzene	0.244	0.201	2.19
1,4-Diethylbenzene	0.277	0.244	2.23
1,2-Diethylbenzene	0.289	0.253	2.36
1,3-Diisopropylbenzene	0.195	0.137	1.94
1,4-Diisopropylbenzene	0.247	0.197	2.02
1-Methyl-3-ethylbenzene	0.242	0.213	2.07
1-Methyl-4-ethylbenzene	0.269	0.207	2.24
1-Methyl-2-ethylbenzene	0.282	0.268	2.37
1-Methyl-3-propylbenzene	0.255	0.217	2.21
1-Methyl-4-propylbenzene	0.282	0.246	2.25
1-Methyl-2-propylbenzene	0.298	0.265	2.37
1-Methyl-3-isopropylbenzene	0.216	0.180	2.07
1-Methyl-2-isopropylbenzene	0.264	0.224	2.26
1-Methyl-4-isopropylbenzene	0.267	0.228	2.13

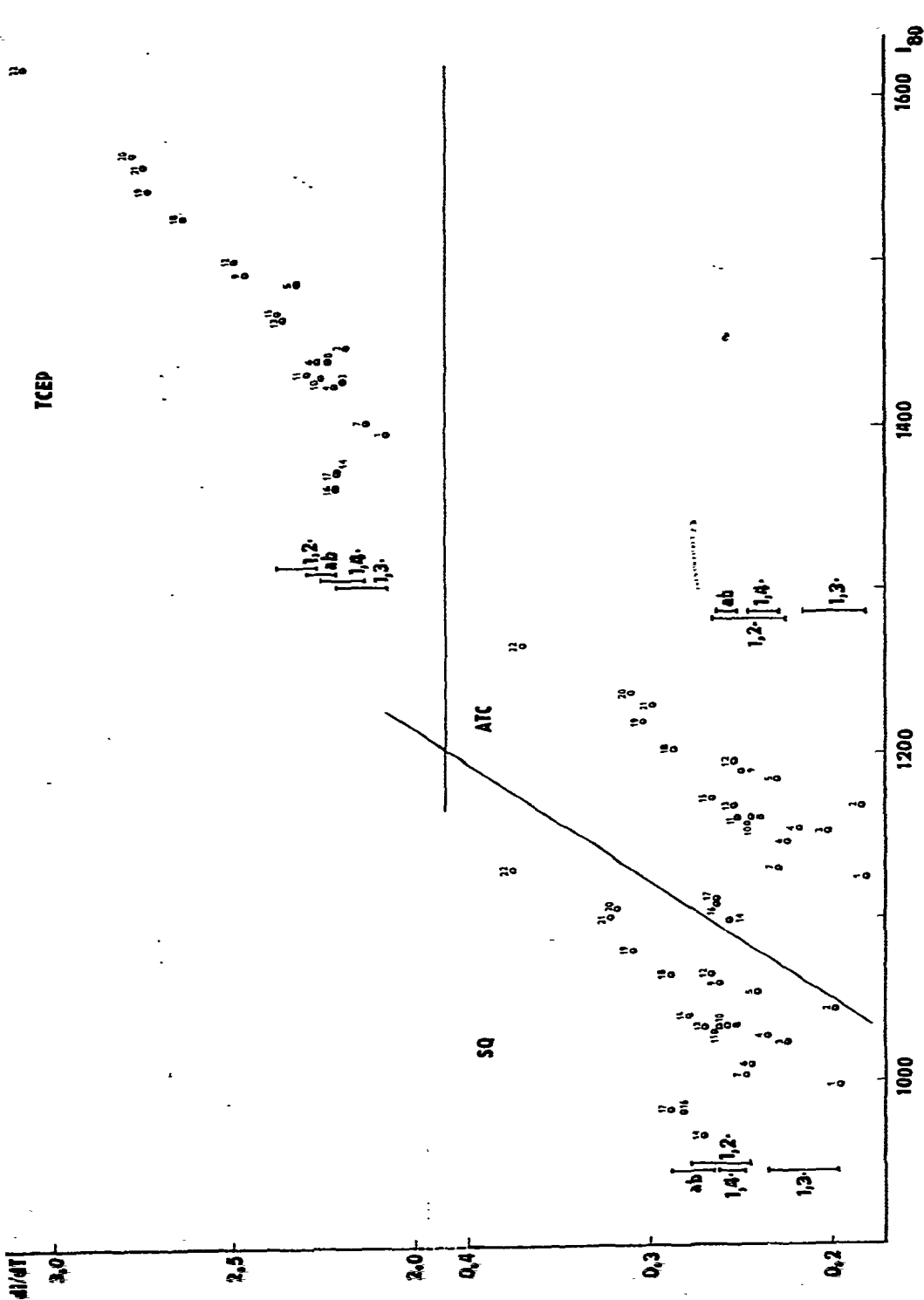


Fig. 2. Temperature increments of retention indices of all  $C_{10}$  alkylbenzene isomers as a function of retention index at  $80^\circ$  on squalane, acetyltributyl citrate and 1,2,3-triscyanoethoxypropane. ab = Alkylbenzenes; 1,2, 1,3, 1,4 = 1,2-, 1,3-, 1,4-dialkylbenzenes, respectively. 1 = 1-Methyl-3-isopropylbenzene; 2 = 1,3-dimethyl-5-ethylbenzene; 3 = 1,3-diethylbenzene; 4 = 1-methyl-3-propylbenzene; 5 = 1,4-dimethyl-2-ethylbenzene; 6 = 1-methyl-2-isopropylbenzene; 7 = 1-methyl-4-isopropylbenzene; 8 = 1,4-diethylbenzene; 9 = 1,3-dimethyl-4-ethylbenzene; 10 = 1-methyl-4-propylbenzene; 11 = butylbenzene; 12 = 1,2-dimethyl-4-ethylbenzene; 13 = 1,2-diethylbenzene; 14 = *tert.*-butylbenzene; 15 = 1-methyl-2-propylbenzene; 16 = isobutylbenzene; 17 = *sec.*-butylbenzene; 18 = 1,3-dimethyl-2-ethylbenzene; 19 = 1,2-dimethyl-3-ethylbenzene; 20 = 1,2,3,5-tetramethylbenzene; 21 = 1,2,4,5-tetramethylbenzene; 22 = 1,2,3,4-tetramethylbenzene.

TABLE III

TEMPERATURE COEFFICIENTS OF RETENTION INDICES OF TRIALKYLBENZENES ON SQUALANE ( $dI^{SQ}/dT$ ), ACETYLTRIBUTYL CITRATE ( $dI^{ATC}/dT$ ) AND 1,2,3-TRISCY-ANOETHOXYPROPANE ( $dI^{TCEP}/dT$ ) (IN i.u./°C)

Trialkylbenzene	$dI^{SQ}/dT$	$dI^{ATC}/dT$	$dI^{TCEP}/dT$
1,3,5-Trimethylbenzene	0.239	0.206	2.20
1,2,4-Trimethylbenzene	0.288	0.264	2.38
1,2,3-Trimethylbenzene	0.337	0.312	2.65
1,3-Dimethyl-5-ethylbenzene	0.218	0.182	2.18
1,4-Dimethyl-2-ethylbenzene	0.260	0.229	2.32
1,3-Dimethyl-4-ethylbenzene	0.281	0.249	2.46
1,2-Dimethyl-4-ethylbenzene	0.286	0.253	2.49
1,3-Dimethyl-2-ethylbenzene	0.309	0.287	2.63
1,2-Dimethyl-3-ethylbenzene	0.329	0.303	2.73
1,3,5-Triisopropylbenzene	0.015	-0.074	1.28
1,3,5-Triethylbenzene	0.167	0.117	2.20
1,3,5-Trimethylbenzene	0.239	0.206	2.20
1,3,5-Triethylbenzene	0.239	0.206	2.20
1,3-Dimethylbenzene	0.245	0.213	2.07
Methylbenzene	0.245	0.213	2.03
1,3,5-Triethylbenzene	0.167	0.117	2.20
1,3-Diethylbenzene	0.244	0.201	2.19
Ethylbenzene	0.265	0.225	2.14
1,3,5-Triisopropylbenzene	0.015	-0.074	1.28
1,3-Diisopropylbenzene	0.195	0.137	1.94
Isopropylbenzene	0.264	0.214	2.11

1,2-isomers. Substitution of an alkyl group into a dialkylbenzene causes a considerable change in the magnitude of  $dI/dT$ . This is illustrated below by a few examples.

Substitution of a methyl group into a dialkylbenzene in the *meta*-position, which results in a 1,3,5-configuration of the trialkylbenzene (a larger and more symmetrical molecule than the original), leads to a decrease in the  $dI/dT$  values. For instance, for 1-methyl-3-*tert*-butylbenzene  $dI/dT = 0.236$  i.u./°C, while for 1,3-dimethyl-5-*tert*-butylbenzene this  $dI/dT = 0.167$  i.u./°C, the difference being 0.069 i.u./°C. On the other hand, a similar substitution in the *ortho*-position, which results in a 1,2,3-configuration of the trialkylbenzene (a larger and less symmetrical molecule than the original), the  $dI/dT$  value increases. For instance, for 1-methyl-3-ethylbenzene ( $dI/dT = 0.242$  i.u./°C) and 1,2-dimethyl-3-ethylbenzene ( $dI/dT = 0.329$  i.u./°C) the increase is 0.087 i.u./°C.

For trialkylbenzenes, the replacement of a smaller alkyl group with a larger one will result in a decrease in the  $dI/dT$  value, and this effect is more significant with symmetrical molecules. For instance, for 1,3,5-trimethylbenzene and 1,3-dimethyl-5-ethylbenzene the  $dI/dT$  values are 0.239 and 0.218 i.u./°C, respectively, the decrease being 0.021 i.u./°C, while for 1,2,3-trimethylbenzene ( $dI/dT = 0.337$  i.u./°C) and 1,2-dimethyl-3-ethylbenzene ( $dI/dT = 0.329$  i.u./°C) the decrease is only 0.008 i.u./°C. The  $dI/dT$  values decrease very markedly as the size of the alkyl group increases in 1,3,5-trialkylbenzenes.

The effect of the symmetry of molecules on  $dI/dT$  increases significantly with

TABLE IV

TEMPERATURE COEFFICIENTS OF RETENTION INDICES OF ALKYL BENZENES HAVING A LOWER  $dI/dT$  VALUE THAN THAT OF BENZENE ON SQUALANE (IN i.u./°C)

Alkylbenzene	$dI^{SO}/dT$	$dI^{ATC}/dT$	$dI^{TCEP}/dT$
Benzene	0.240	0.192	1.96
1,3,5-Trimethylbenzene	0.239	0.206	2.20
1,3-Dimethyl-5-ethylbenzene	0.218	0.182	2.18
1-Methyl-3-isopropylbenzene	0.216	0.180	2.07
1,3-Diisopropylbenzene	0.195	0.137	1.94
1,3-Dimethyl-5- <i>tert.</i> -butylbenzene	0.167	0.119	2.05
1,3,5-Triethylbenzene	0.167	0.117	2.20
1,3,5-Triisopropylbenzene	0.015	-0.074	1.28

increase in the size of the alkyl chain and results in a lower temperature increment. It is therefore understandable why 1,3,5-triisopropylbenzene has a  $dI/dT$  value similar to that of an *n*-alkane. These results are contrary to the hypothesis of Hively and Hinton<sup>3</sup>. Table IV gives values for the alkylbenzenes that have a lower  $dI^{SO}/dT$  than that of benzene. Obviously in all of these instances 1,3-dialkyl- and 1,3,5-trialkylbenzenes are concerned.

*Tetra- and pentamethylbenzenes.* For tetramethylbenzenes the  $dI/dT$  values (Table V) increase in the order 1,2,3,5-  $\leq$  1,2,4,5-  $<$  1,2,3,4-tetramethylbenzene. A comparison of the  $dI/dT$  values of vicinal methylbenzenes shows that these values increase with increasing number of methyl groups. This increase is almost linear (*ca.* 0.05 i.u. per methyl group). Compared with alkylbenzenes with the same number of carbon atoms, these types of alkylbenzenes have substantially higher  $dI/dT$  values.

The largest  $dI/dT$  values were observed for alkylbenzenes that have alkyl groups in the vicinal position (asymmetric) and the symmetrical isomers have the lowest  $dI/dT$  values. For other isomers that were not investigated (up to C<sub>15</sub>) the  $dI/dT$  values will fall between these limits. A similar relationship between symmetry and  $dI/dT$  was also observed for *cis-trans* isomers of *n*-alkenes<sup>2</sup>, and is in agreement with the fact that when the structure of the hydrocarbon is asymmetrical, the changes in the vapour pressure upon variation in temperature are greater.

TABLE V

TEMPERATURE COEFFICIENTS OF RETENTION INDICES OF TETRA- AND PENTAMETHYLBENZENES ON SQUALANE ( $dI^{SO}/dT$ ), ACETYLTRIBUTYL CITRATE ( $dI^{ATC}/dT$ ) AND 1,2,3-TRICYANOETHOXYPROPANE ( $dI^{TCEP}/dT$ ) (IN i.u./°C)

Alkylbenzene	$dI^{SO}/dT$	$dI^{ATC}/dT$	$dI^{TCEP}/dT$
1,2,3,5-Tetramethylbenzene	0.338	0.309	2.77
1,2,4,5-Tetramethylbenzene	0.341	0.298	2.74
1,2,3,4-Tetramethylbenzene	0.395	0.370	3.07
Methylbenzene	0.245	0.213	2.03
1,2-Dimethylbenzene	0.284	0.253	2.42
1,2,3-Trimethylbenzene	0.337	0.312	2.65
1,2,3,4-Tetramethylbenzene	0.395	0.370	3.07
Pentamethylbenzene	0.452	0.432	3.60



The temperature increments on polar stationary phases illustrate the effect of polarity. The changes in the  $dI/dT$  values for  $C_{10}$  mono- and 1,2-, 1,3- and 1,4-dialkylbenzenes with polarity of the stationary phase are demonstrated in Fig. 2. In general, for SQ and ATC the structure-retention correlations are similar, the  $dI/dT$  values on SQ being about 0.04 i.u./°C greater than those on ATC. This difference,  $\Delta(dI/dT)$ , is smaller for asymmetrical (e.g., for pentamethylbenzene, 0.020) and larger for symmetrical alkylbenzenes. The last effect increases with increasing size of alkyl group and a maximal difference of 0.089 i.u./°C was found for 1,3,5-triisopropylbenzene. Similarly, on comparing the  $\Delta(dI/dT)$  values for TCEP and SQ, a maximal difference of 3.15 i.u./°C for pentamethylbenzene and a minimal difference of 1.26 i.u./°C for 1,3,5-triisopropylbenzene were observed; this result is opposite to that for the  $dI/dT$  values for SQ, which are greater than those for ATC. Hence the greater is the asymmetry for the alkylbenzene, the greater is the  $\Delta(dI/dT)$  value. For homologous series on TCEP, the  $dI/dT$  values increase with increasing carbon number. For isomers, in comparison with  $dI/dT$  on squalane, some differences can be observed. For instance, of the butylbenzene isomers the temperature increment of *n*-butylbenzene is greatest on TCEP, while on SQ this value is the lowest. A reversed order of  $dI/dT$  values is observed for methyl-, 1,3-dimethyl- and 1,3,5-trimethylbenzenes and also for ethylbenzenes substituted in a similar way. For longer alkyl chains substituted correspondingly (e.g., isopropylbenzenes) the order of the  $dI/dT$  values is the same for TCEP and SQ.

The relationship between the symmetry of alkylbenzenes and the  $dI/dT$  values is in agreement with the results of Korol and Sakharov<sup>11</sup>. They found that the higher the symmetry of the molecule, the greater was the effect of shielding on its interaction with the surroundings; the effect of shielding the centre of the molecule is the most important factor in determining the heat of solution. In a highly polar stationary phase (TCEP) the effect of symmetry on retention, as a result of the hindering effect of the stationary phase, is relatively lower.

Considering the  $dI/dT$  values of members of homologous series of alkylbenzenes on squalane, it seems that *n*-propyl derivatives deviate from the regularity of the relationship between  $dI/dT$  and the size of the alkyl group. This is also indicated by the reversed order of the  $dI/dT$  values on squalane of isopropylbenzene ( $dI/dT = 0.264$  i.u./°C) and *n*-propylbenzene (0.282 i.u./°C) and of isobutylbenzene (0.301 i.u./°C) and *n*-butylbenzene (0.284 i.u./°C). Similarly, the  $dI/dT$  values of methylpropylbenzenes are slightly higher than those of the other methylalkylbenzenes. Hence, it appears that the anomalous correlation between structure and methylene group increments<sup>12</sup> for alkylbenzenes containing one or more *n*-propyl groups also holds for the correlation between temperature increments and the size of the alkyl group. Compared with the expected  $dI/dT$  values, on the basis of the regular dependence of  $dI/dT$  on carbon number, they display slightly higher values.

#### *Effect of inlet pressure and nature of the carrier gas on structure-retention correlations*

From results reported elsewhere<sup>10,13</sup>, it can be concluded that an increase in the inlet pressure and/or replacement of hydrogen with nitrogen as the carrier gas improves the selectivity of the separation of alkylbenzenes and alkanes. The magnitude of this effect increases with increasing polarity of the stationary phase (from SQ to TCEP). Variations in the retention index on TCEP up to 3 i.u. were observed when

hydrogen (inlet pressure 1 atm) was replaced with nitrogen (inlet pressure 2 atm) as the carrier gas.

A comparison of the changes in retention indices of some alkylbenzenes on TCEP with a change in temperature (per 1 °C), pressure (from 1 to 2 atm of nitrogen) and nature of the carrier gas (from 1 atm of hydrogen to 1 atm of nitrogen) is given in Table VI. It can be seen that the  $dI/dP$  values (pressure coefficient of the retention index) are approximately half the  $dI/dT$  values and that the ratio of  $dI/dT$  to  $dI/dP$  values is smaller for asymmetrical alkylbenzenes (e.g., 1,2,3-trimethylbenzene) than for symmetrical alkylbenzenes (e.g., 1,3-dimethyl-5-ethylbenzene). The most interesting result is that the  $dI/dP$  values indicate fine-structural differences of the alkylbenzenes. Unfortunately, only a few retention indices were measured at inlet pressures of both 1 and 2 atm of nitrogen. Although the data are inadequate for a full discussion of fine structure-retention correlation based on variations in the inlet pressure, these results are briefly discussed below.

It can be seen from Table VII that for the members of homologous series of *n*-alkylbenzenes the pressure coefficients are virtually constant, but for *n*-pentylbenzene a higher value is observed. For isomers, the pressure coefficient of the retention index is smaller for *iso*- than for *n*-alkylbenzenes; they are larger for *ortho*-compounds than for *meta*- and *para*-isomers; and they are smaller for symmetrical 1,3,5-compounds than for the 1,2,3-isomers. The  $dI/dP$  values obtained on PEG 400 for argon and carbon dioxide as carrier gases up to 30 atm, reported by Vigdergauz and Semkin<sup>13</sup>, are in agreement with our results.

This type of structure-retention correlation may be useful for the identification of alkylbenzenes by table matching, and should permit the correction of published

TABLE VI

CHANGES IN RETENTION INDICES OF ALKYL BENZENES ON TCEP WITH CHANGES IN TEMPERATURE, PRESSURE AND CARRIER GAS

Alkylbenzene*	$dI/dT$	$dI/dP$ (1-2 atm, N <sub>2</sub> )	$dI$ (H <sub>2</sub> -N <sub>2</sub> , 1 atm)
Toluene	2.0	1.0	1.7
1,4-Xylene	2.1	0.7	1.3
Isopropylbenzene	2.1	0.9	1.2
<i>n</i> -Propylbenzene	2.2	1.0	1.1
1,2-Xylene	2.4	1.2	1.2
1-Methyl-4-ethylbenzene	2.4	1.0	1.1
1-Methyl-3-isopropylbenzene	2.1	0.9	0.7
1-Methyl-4-isopropylbenzene	2.1	0.9	1.3
1-Methyl-2-ethylbenzene	2.4	1.2	1.2
1,3-Diethylbenzene	2.2	1.1	1.1
1-Methyl-2-isopropylbenzene	2.3	1.1	1.3
1,3-Dimethyl-5-ethylbenzene	2.2	0.9	1.2
1-Methyl-4- <i>tert.</i> -butylbenzene	2.1	1.2	1.2
1,2-Diethylbenzene	2.3	1.2	1.5
1,2,3-Trimethylbenzene	2.7	1.5	1.3
<i>n</i> -Pentylbenzene	2.4	1.4	1.1
1,3-Dimethyl-2-ethylbenzene	2.6	1.3	1.2
1,2-Dimethyl-3-ethylbenzene	2.7	1.3	1.3
1,2,4,5-Tetramethylbenzene	2.7	1.3	1.1
1,2,3,5-Tetramethylbenzene	2.8	1.3	1.1

\* In the order of retention indices on TCEP at 80°.

TABLE VII

PRESSURE COEFFICIENTS OF RETENTION INDICES ( $dI/dP$ ) AND STRUCTURES OF ALKYL BENZENES ON TCEP AT 95.4° (BETWEEN 1 AND 2 atm OF NITROGEN)

Type of alkylbenzenes	Alkylbenzene	$dI/dP$
<i>n</i> -Alkylbenzenes	Toluene	1.0
	Propylbenzene	1.0
	Pentylbenzene	1.4
<i>Iso</i> -/ <i>n</i> -alkylbenzenes	Isopropylbenzene	0.9
	Propylbenzene	1.0
1,4-/1,2-Dialkylbenzenes	1,4-Dimethylbenzene	0.7
	1,2-Dimethylbenzene	1.2
	1-Methyl-4-ethylbenzene	1.0
	1-Methyl-2-ethylbenzene	1.2
	1-Methyl-4-isopropylbenzene	0.9
	1-Methyl-2-isopropylbenzene	1.1
1,3-/1,2-Dialkylbenzenes	1,3-Diethylbenzene	1.1
	1,2-Diethylbenzene	1.2
	1-Methyl-3-isopropylbenzene	0.9
	1-Methyl-2-isopropylbenzene	1.1
1,3,5-/1,2,3-Trialkylbenzenes	1,3-Dimethyl-5-ethylbenzene	0.9
	1,3-Dimethyl-2-ethylbenzene	1.3

retention data for systematic differences, including fine-structural differences, which result from the use of different experimental conditions.

Considering the results in Table VI, it can be concluded that the effect of changing the carrier gas from hydrogen to nitrogen on the retention index of alkylbenzenes is of the same order as for that resulting from an increase in the inlet pressure of nitrogen from 1 to 2 atm. In both instances the mean difference is about 1 i.u. Because of the few data available, a discussion of the effect of the nature of carrier gas on the structure-retention correlations of alkylbenzenes is not possible, as for  $dI/dP$  values.

$dI/dP$ , a useful parameter for the identification of isomers. There are sufficient indications to expect that the relationship that exists between fine-structural differences of alkylbenzenes and  $dI/dT$  is similar to that for  $dI/dP$ . It is therefore to be expected that a study of the pressure coefficient of the retention index will prove to be a valuable additional means for the identification of alkylbenzene isomers (and other compounds) by gas chromatography at higher pressures. In this connection, we refer to the work of Huber *et al.*<sup>14</sup>, who studied gas chromatography at higher pressures in order to increase the resolving power of the column. Considering the linear relationship between the inlet pressure and the retention index<sup>13</sup>, the magnitude of this effect can be expected to be comparable to the differences on stationary phases of different polarity ( $\Delta I$ ) in high-pressure gas chromatography. An additional advantage of the parameter  $dI/dP$  is that it can be used at only one (relatively low) temperature, so that the adverse influence of column ageing will be decreased considerably.

## CONCLUSIONS

The temperature coefficients of the retention indices of alkylbenzenes vary

within wide limits and reflect fine-structural differences. Numerous relationships between structure and temperature coefficients were observed, and they can be utilized to predict  $dI/dT$  values for alkylbenzenes of higher molecular weight and to discriminate between isomers. The temperature increment of the retention index of alkylbenzenes has a close relationship with the symmetry of the molecule. The largest  $dI/dT$  values were observed for asymmetrically vicinally substituted alkylbenzenes and the lowest values for symmetrically substituted 1,3,5-alkylbenzenes. The  $dI/dT$  value of 1,3,5-triisopropylbenzene on SQ (and ATC) approaches that of an  $n$ -alkane, which is contrary to the hypothesis of Hively and Hinton<sup>3</sup>. The  $dI/dT$  values on SQ and ATC differ by about 0.04 i.u./°C, higher values being found for SQ. A marked increase (about one order of magnitude) in  $dI/dT$  was observed for TCEP, which is a highly polar stationary phase.

The effect of the inlet pressure of the carrier gas (nitrogen) on the retention index of alkylbenzenes on highly polar TCEP as stationary phase compared with that on SQ is greater by about one order of magnitude. Changing the carrier gas from hydrogen to nitrogen and/or increasing the inlet pressure results in an improved selectivity of the separation of alkylbenzenes and alkanes. The correlation between the structures of alkylbenzenes and their pressure coefficients on TCEP shows that for a homologous series of alkylbenzenes  $dI/dP$  remains constant (for pentylbenzene a higher  $dI/dP$  value is observed). For some pairs of isomers, characteristic differences in the  $dI/dP$  values were found, e.g., *iso*- < *n*-, *para*- < *ortho*-, *meta*- < *ortho*-, 1,3,5- < 1,2,3-alkylbenzenes. The effect of changing the carrier gas from hydrogen to nitrogen at 1 atm is, from the point of view of structure-retention correlations, uncharacteristic and is the same order as the effect produced by changing the inlet pressure of nitrogen by 1 atm, under the same experimental conditions.

Possibly the study of the effect of pressure on retention in gas chromatography at higher pressures will prove to be a valuable means for the identification of alkylbenzenes and other compounds.

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