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CAPILLARY GAS CHROMATOGRAPHY OF ALKYL BENZENES

IV. CORRELATIONS BETWEEN RETENTION INDICES ON STATIONARY PHASES OF DIFFERENT POLARITY AND STRUCTURE

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SUMMARY

Correlations were studied between the structure and the retention indices of alkylbenzenes on three stationary phases with different polarities and ΔI values.

It is demonstrated that high-precision measurements of the retention indices of alkylbenzenes on these stationary phases yield sufficient structural details to permit some new correlations in this area.

The extent to which ΔI values can be used for identification purposes on the basis of comparisons between measured retention data and tabulated data and/or calculated data based on retention index increments corresponding to characteristic functional groups in the molecules is discussed.

It is shown that alkylbenzenes that have close ΔI values can be differentiated by virtue of their dI/dT values.

INTRODUCTION

In previous parts of this study of the gas chromatographic behaviour of alkylbenzenes, structure and retention behaviour were correlated on the basis of high-precision retention data¹ on individual stationary phases. Correlations between the structure and the retention index increment of a methylene group (I_{CH_2}) and the differences in the retention indices of two isomers on the same stationary phase² (δI), as well as the temperature- and pressure-variation coefficients (dI/dT and dI/dP) and the nature of the carrier gas³, were discussed.

In the present work, correlations were made of the retention indices of alkylbenzenes on different stationary phases (two or three) and ΔI values, where ΔI is the

difference between the retention indices of a given component on a polar and a non-polar stationary phase ($I^P - I^{NP}$)⁴.

The dependence of retention data on the polarity of the stationary phase is usually employed for the identification of compounds with different functional groups. For the identification of isomers, this approach is difficult⁵. A detailed study of this type of correlation was carried out by Walraven⁶. Recently, Döring *et al.*⁷ and Engewald and Wennrich⁸ correlated ΔI values with the structure of alkylbenzenes.

The difficulty in comparing measured with tabulated or calculated retention data is the insufficient precision of these data, especially on polar stationary phases. Another complication is the possibility of interactions between different functional groups in the molecules of a compound.

It is the aim of this paper to show that high-precision measurements of the retention indices of alkylbenzenes on three stationary phases of different polarity yield sufficient structural details to permit some new correlations in this area. The extent to which ΔI values can be used for the identification of alkylbenzenes on the basis of comparisons between measured retention data and tabulated data and/or data based on retention index increments corresponding to characteristic functional groups in the molecules is considered.

EXPERIMENTAL

The experimental conditions employed and the retention indices of 47 alkylbenzenes up to C₁₅ and benzene measured on squalane (SQ), acetyltributyl citrate (ATC) and 1,2,3-triscyanoethoxypropane (TCEP) were as given in Part I (ref. 1). The values of $\Delta I_1 = I_{80}^{ATC} - I_{80}^{SQ}$ and $\Delta I_2 = I_{80}^{TCEP} - I_{80}^{SQ}$ calculated from the measured retention indices of the alkylbenzenes are given in Table I (in order of retention indices as measured on squalane at 80°).

RESULTS AND DISCUSSION

The relationship between the retention indices of the alkylbenzenes on non-polar squalane and those on moderately polar acetyltributyl citrate (for benzene $\Delta I_{80} = 136.2$ i.u.) is illustrated in Fig. 1. It can be seen that the expansion of the points in the direction of the polar-phase coordinate, which occurs on increasing the polarity of the stationary phase, is relatively small; the maximum scatter of the points around the straight line amounts to about ± 7 i.u. However, a more detailed analysis of the dependence showed that it is possible to draw roughly straight and parallel lines for different homologous series of alkylbenzenes.

A finer resolution was obtained by correlating the retention indices of alkylbenzenes on squalane and on high-polarity 1,2,3-triscyanoethoxypropane (for benzene $\Delta I_{80} = 483.8$ i.u.). This relationship is shown in Fig. 2.

Certain regularities for homologous series and information on the number of carbon atoms and the magnitude and positions of the alkyl groups are apparent and are discussed below.

(1) Correlations for alkylbenzenes with different numbers of carbon atoms in the molecule showed that both parallel and divergent lines were obtained for the individual structural types. A CH₂ substitution in the alkyl chain gives almost parallel

TABLE I

VALUES OF $\Delta I_1 (I_{80}^{\Delta TC} - I_{80}^{SO})$ AND $\Delta I_2 (I_{80}^{TCEP} - I_{80}^{SO})$ OF ALKYL BENZENES

<i>Alkylbenzene</i>	ΔI_1	ΔI_2
Benzene	136.2	483.8
Toluene	130.9	467.4
Ethylbenzene	132.0	448.2
<i>p</i> -Xylene	124.8	446.4
<i>m</i> -Xylene	126.2	448.3
<i>o</i> -Xylene	133.7	480.2
Isopropylbenzene	131.4	418.5
<i>n</i> -Propylbenzene	130.3	420.2
1-Methyl-3-ethylbenzene	127.5	427.3
1-Methyl-4-ethylbenzene	125.8	426.8
1-Methyl-2-ethylbenzene	133.8	457.2
1,3,5-Trimethylbenzene	121.8	425.2
<i>tert.</i> -Butylbenzene	132.2	405.6
1,2,4-Trimethylbenzene	127.7	455.8
Isobutylbenzene	126.4	380.8
<i>sec.</i> -Butylbenzene	129.0	388.6
1-Methyl-3-isopropylbenzene	127.4	399.0
1,2,3-Trimethylbenzene	136.3	488.8
1-Methyl-4-isopropylbenzene	125.2	398.8
1-Methyl-2-isopropylbenzene	134.7	429.0
1,3-Diethylbenzene	128.2	405.2
1-Methyl-3-propylbenzene	125.6	397.2
<i>n</i> -Butylbenzene	130.8	401.9
1,2-Diethylbenzene	134.4	432.5
1-Methyl-4-propylbenzene	124.0	397.3
1,4-Diethylbenzene	126.6	405.6
1-Methyl-2-propylbenzene	132.5	428.1
1,3-Dimethyl-5-ethylbenzene	123.4	404.3
1,4-Dimethyl-2-ethylbenzene	128.7	432.6
1-Methyl-3- <i>tert.</i> -butylbenzene	128.8	387.3
1,3-Dimethyl-4-ethylbenzene	128.1	432.3
2-Phenyl-2-methylbutane	130.5	384.8
1,2-Dimethyl-4-ethylbenzene	129.1	434.4
1,3-Dimethyl-2-ethylbenzene	136.8	462.0
1-Methyl-4- <i>tert.</i> -butylbenzene	126.3	386.3
2-Phenylpentane	129.0	365.4
1,2-Dimethyl-3-ethylbenzene	136.7	462.7
1,2,4,5-Tetramethylbenzene	129.5	458.8
1,2,3,5-Tetramethylbenzene	130.5	460.0
1,3-Diisopropylbenzene	126.3	343.7
<i>n</i> -Pentylbenzene	131.9	380.4
1,2,3,4-Tetramethylbenzene	137.6	490.0
1,3-Dimethyl-5- <i>tert.</i> -butylbenzene	125.6	366.1
1,4-Diisopropylbenzene	125.5	345.9
1,3,5-Triethylbenzene	126.0	358.7
Pentamethylbenzene	138.7	486.7
1,3,5-Triisopropylbenzene	123.4	273.2

lines with *n*-alkylbenzenes, while a CH₃ substitution in the benzene ring results in divergent lines. The latter is most pronounced with vicinally substituted alkylbenzenes (e.g., 1-, 1,2-, 1,2,3-, 1,2,3,4- and pentamethylbenzenes). With symmetrically sub-

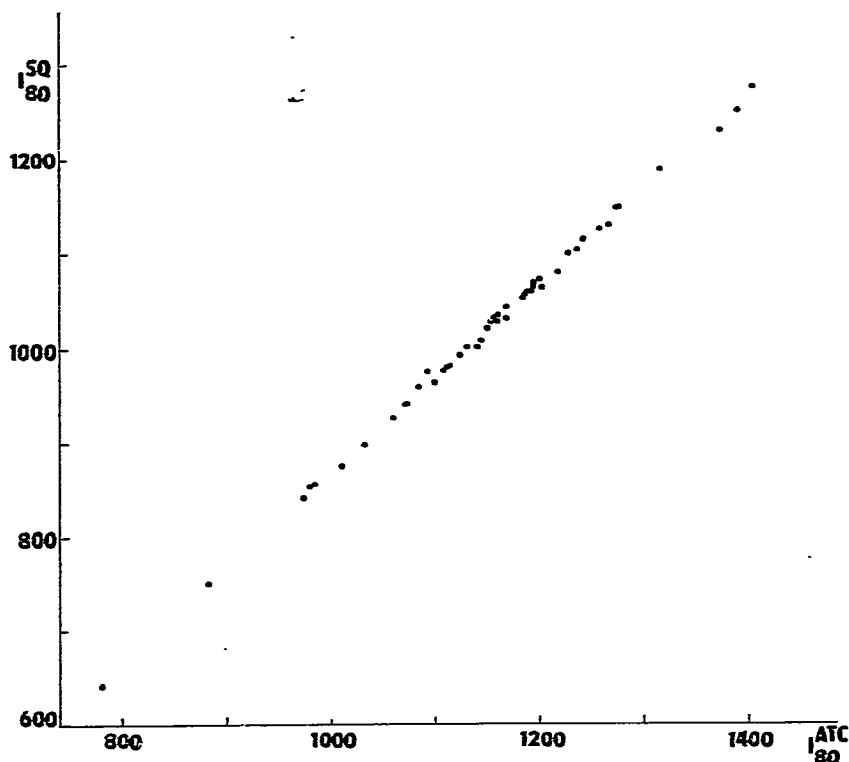


Fig. 1. Plot of the retention indices of alkylbenzenes on squalane *versus* those on acetyltributyl citrate at 80°.

stituted compounds (*e.g.*, 1-, 1,3- and 1,3,5-methylbenzenes) this effect is greatly reduced. Unfortunately, the homologous series are too short for the behaviour discussed above to be generalized. Moreover, *n*-propyl derivatives of alkylbenzenes, which display anomalous behaviour similar to that for structure-retention correlations in homologous series², are included in these correlations. The *n*-propyl derivatives of alkylbenzenes (*n*-propyl-, 1-methyl-4-, 1-methyl-3-, and 1-methyl-2-propylbenzene) lie above the line through the first two members of their homologous series. It appears that isobutylbenzene shows an anomalous behaviour similar to that found for *n*-propylbenzene. For *sec*-butylbenzene, this anomaly was not confirmed. After appropriate correction for the anomalous behaviour, the homologous series of alkylbenzenes (*i.e.*, *sec*-, *iso*-, *tert*-, *n*-, 1,4-, 1,3- and 1,2-dialkylbenzenes) show almost parallel lines.

From the relationship for the homologous series of *n*-alkylbenzenes (five members of the series) on squalane and TCEP, it follows that the slope increases slightly with increasing carbon number. The divergent lines for both symmetrically and asymmetrically (vicinally) substituted methylbenzenes show a similar effect. The tie-lines for the corresponding pairs of 1,3- and 1,2-, 1,4- and 1,2-, and 1,3- and 1,4-isomers are not exactly parallel when members with higher carbon numbers are included in the correlation.

(2) Alkylbenzenes with the same number of carbon atoms can be distinguished

by characteristic half-ellipses with flat bases. Although all possible isomers of alkylbenzenes only up to C_{10} had been included in the correlation, also eleven C_{11} - C_{15} alkylbenzenes appear to behave similarly. It can be expected that the situation will be more complicated for the higher alkylbenzenes because of an increasing number of possible isomers.

For isomeric alkylbenzenes that have the same number of carbon atoms, a dependence on the size and position of the alkyl groups can be seen, as demonstrated by the schematic representation for C_{10} alkylbenzenes in Fig. 2. In the direction of

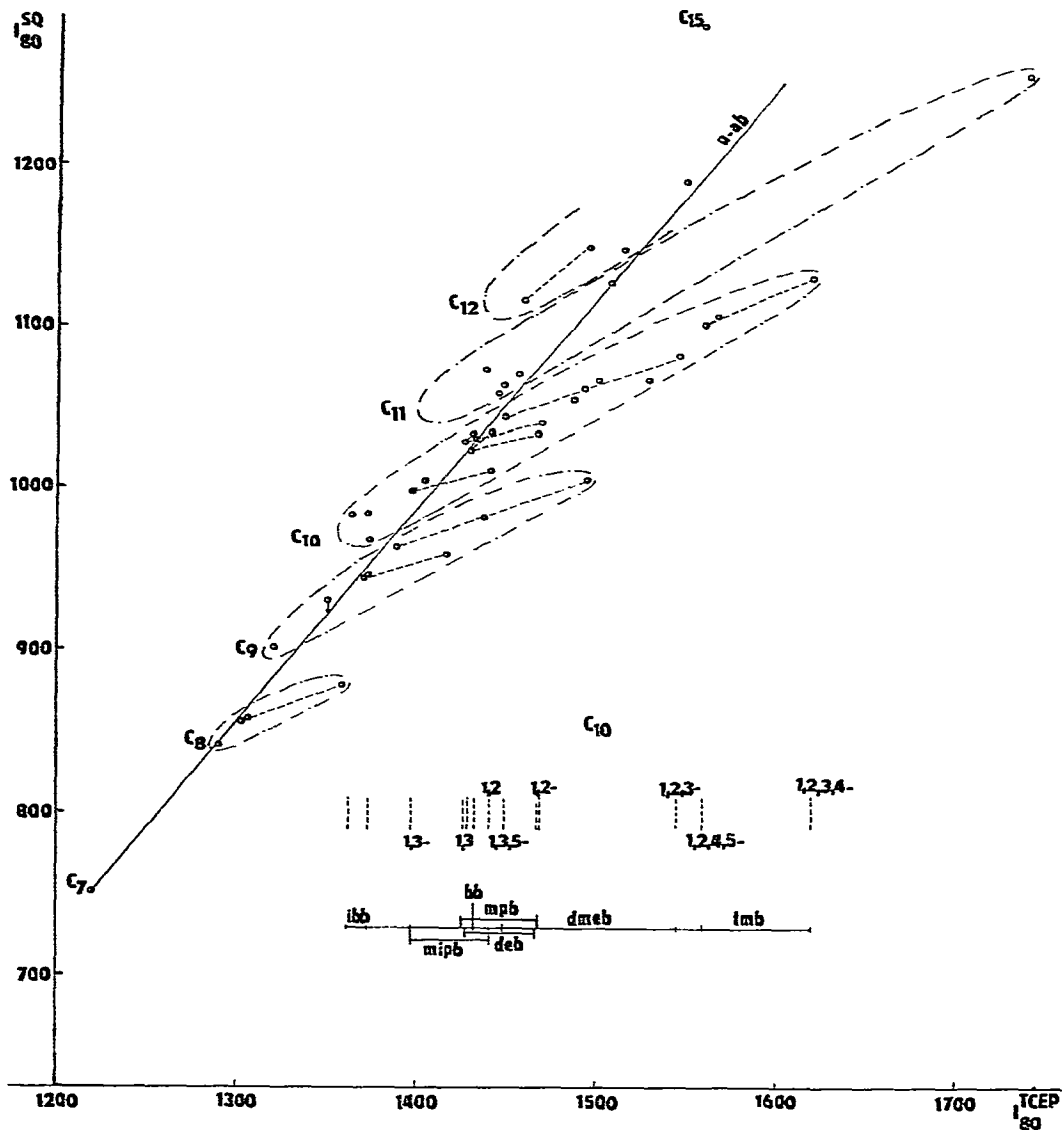


Fig. 2. Plot of the retention indices of alkylbenzenes on squalane versus those on 1,2,3-triscyanoethoxypropane at 80° . In the schematic representation for C_{10} alkylbenzenes the following abbreviations are used: b = benzene, butyl, d = di, e = ethyl, i = iso, m = methyl, p = propyl, and t = tetra.

the polar phase coordinate the retention is shifted according to shortening of the alkyl chain length from butyl- to methylbenzenes. The retention of the isoalkylbenzenes is lower than that of the corresponding *n*-alkylbenzenes. Multiple alkyl groups manifest themselves in the sense mentioned above, so that the order of retention is methylpropyl- < dimethylethyl- < tetramethylbenzene. Further, a resolution is also apparent for the individual structural types (positional isomers): the retention is shifted from the more symmetrical 1,3-, 1,3,5- and 1,2,4,5-alkylbenzenes to the more asymmetrical vicinally substituted 1,2-, 1,2,3- and 1,2,3,4-alkylbenzenes.

The fine-structure retention correlations based on ΔI values of alkylbenzenes of different structural types are discussed below.

Monoalkylbenzenes

From Table II, it can be seen that the ΔI_2 values, as expected^{4,6,7}, decrease with increasing number of carbon atoms in *n*-alkylbenzenes. The ΔI_1 values, however, are virtually independent of the number of carbon atoms. The latter result is in disagreement with the literature^{4,6,7}, where the introduction of an alkyl group led to a decrease in the ΔI values. Consistent with the ΔI_2 values, a decrease in ΔI_1 values on substitution in the alkyl chain of monoalkylbenzenes occurs in separation systems that have higher ΔI values. In these systems the shielding effect of the alkyl group influences both the specific and dispersion interactions more strongly.

TABLE II

ΔI_1 AND ΔI_2 VALUES OF MONOALKYLBENZENES

<i>Monoalkylbenzene</i>	ΔI_1	ΔI_2
Benzene	136.2	483.8
Toluene	130.9	467.4
Ethylbenzene	132.0	448.2
<i>n</i> -Propylbenzene	130.3	420.2
<i>n</i> -Butylbenzene	130.8	401.9
<i>n</i> -Pentylbenzene	131.9	380.4
<i>n</i> -Propylbenzene	130.3	420.2
Isopropylbenzene	131.4	418.5
Isobutylbenzene	126.4	380.8
<i>sec.</i> -Butylbenzene	129.0	388.6
<i>n</i> -Butylbenzene	130.8	401.9
<i>tert.</i> -Butylbenzene	132.2	405.6
2-Phenylpentane	129.0	365.4
<i>n</i> -Pentylbenzene	129.3	377.8
2-Phenyl-2-methylbutane	130.5	384.8

Also in Table II, ΔI values of C₃-, C₄- and C₅-alkyl-substituted benzenes are compared. With butylbenzenes, both the ΔI_1 and ΔI_2 values increase in the order *iso*- < *sec.*- < *n*- < *tert.*-butylbenzene. In comparison with the results of other workers^{7,8}, there is a reversal of the order of *n*- and *tert.*-butylbenzene. For propylbenzenes, the retention is characterized by *n*-propyl- < isopropylbenzene for ΔI_1 but by *iso*- < *n*-propylbenzene for ΔI_2 . Thus, in the case of ΔI_1 values an increase in the dipole moment, associated with branching (isopropylbenzene), manifests itself,

whereas with ΔI_2 values the steric hindrance resulting from specific interactions due to the more bulky isopropyl group compared with the *n*-propyl group predominates.

Dialkylbenzenes

It can be seen from Table III that for dialkylbenzenes that differ only in the positions of the alkyl groups, the ΔI_1 values increase in the order 1,4- < 1,3- < 1,2-dialkylbenzenes. For the corresponding ΔI_2 values of 1,3- and 1,4-isomers, the differences decrease with increasing length of the alkyl chain. For diisopropylbenzenes, the order of the ΔI_2 values is reversed (1,3- < 1,4-diisopropylbenzene).

TABLE III
 ΔI_1 AND ΔI_2 VALUES OF DIALKYL BENZENES

Dialkylbenzene	ΔI_1	ΔI_2
1,4-Dimethylbenzene	124.8	446.4
1,3-Dimethylbenzene	126.2	448.3
1,2-Dimethylbenzene	133.7	480.2
1,4-Diethylbenzene	126.6	405.6
1,3-Diethylbenzene	128.2	405.2
1,2-Diethylbenzene	134.4	432.5
1,4-Diisopropylbenzene	125.5	345.9
1,3-Diisopropylbenzene	126.3	343.7
1-Methyl-4-ethylbenzene	125.8	426.8
1-Methyl-3-ethylbenzene	127.5	427.3
1-Methyl-2-ethylbenzene	133.8	457.2
1-Methyl-4-propylbenzene	124.0	397.3
1-Methyl-3-propylbenzene	125.6	397.2
1-Methyl-2-propylbenzene	132.5	428.1
1-Methyl-4-isopropylbenzene	125.2	398.8
1-Methyl-3-isopropylbenzene	127.4	399.0
1-Methyl-2-isopropylbenzene	134.7	429.0

Such effects, as will also be shown below, can again be explained in terms of changes in the electron distribution and steric effects caused by the increasing length of the alkyl chains in separation systems with different ΔI values.

On comparing ΔI values of mono- and dialkylbenzenes, it can be seen that on substitution in the aromatic ring, the ΔI values can either increase or decrease. For instance, the substitution methylbenzene \rightarrow 1,4- or 1,3-dimethylbenzene results in decreases in ΔI_1 of 6.1 and 4.7 i.u., respectively. For substitution into the 1,2-position, the ΔI_1 value increases by 2.8 i.u.

Trialkylbenzenes

For the positional isomers of trimethylbenzenes, according to Table IV, the ΔI values increase in the order 1,3,5- < 1,2,4- < 1,2,3-trimethylbenzene. The ΔI values of dimethylethylbenzenes (DM-EB) increase in the order 1,3-DM-5-EB < 1,3-DM-4-EB < 1,4-DM-2-EB < 1,2-DM-4-EB < 1,2-DM-3-EB < 1,3-DM-2-EB. For ΔI_2 the order of the last two is reversed, i.e., 1,3-DM-2-EB < 1,2-DM-3-EB.

TABLE IV
 ΔI_1 AND ΔI_2 VALUES OF TRIALKYLBENZENES

<i>Trialkylbenzene</i>	ΔI_1	ΔI_2
1,3,5-Trimethylbenzene	121.8	425.2
1,2,4-Trimethylbenzene	127.7	455.8
1,2,3-Trimethylbenzene	136.3	488.8
1,3-Dimethyl-5-ethylbenzene	123.4	404.3
1,3-Dimethyl-4-ethylbenzene	128.1	432.3
1,4-Dimethyl-2-ethylbenzene	128.7	432.6
1,2-Dimethyl-4-ethylbenzene	129.1	434.4
1,2-Dimethyl-3-ethylbenzene	136.7	462.7
1,3-Dimethyl-2-ethylbenzene	136.8	462.0
1,3,5-Trimethylbenzene	121.8	425.2
1,3,5-Triisopropylbenzene	123.4	273.2
1,3,5-Triethylbenzene	126.0	358.7
1,3,5-Trimethylbenzene	121.8	425.2
1,3-Dimethylbenzene	126.2	448.3
Methylbenzene	130.9	467.4
1,3,5-Triethylbenzene	126.0	358.7
1,3-Diethylbenzene	128.2	405.2
Ethylbenzene	132.0	448.2
1,3,5-Triisopropylbenzene	123.4	273.2
1,3-Diisopropylbenzene	126.3	343.7
Isopropylbenzene	131.4	418.5

Considering the effect of the size of the alkyl group in 1,3,5-trialkylbenzenes the ΔI_1 values obviously increase in the order 1,3,5-trimethyl- < 1,3,5-triisopropyl- < 1,3,5-triethylbenzene, whereas the ΔI_2 values increase in the order 1,3,5-triisopropyl- < 1,3,5-triethyl- < 1,3,5-trimethylbenzene.

On the replacement of methyl with ethyl groups the ΔI_2 values decrease and the ΔI_1 values increase for both the symmetrical 1,3,5- and the asymmetrical 1,2,3-trimethylbenzenes (but ΔI_1 for 1,3,5-triisopropyl- < 1,3,5-triethylbenzene).

On introducing a methyl group into a dialkylbenzene, the ΔI value of the resulting trialkylbenzene can again either decrease or increase. For instance, on introducing a methyl group into 1-methyl-3-*tert.*-butylbenzene to give 1,3-dimethyl-5-*tert.*-butylbenzene, the ΔI_1 and ΔI_2 values decrease by 3.2 and 21.2 i.u., respectively, but with the corresponding reaction with 1-methyl-3-ethylbenzene to give 1,2-dimethyl-3-ethylbenzene the ΔI_1 and ΔI_2 values increase by 9.3 and 35.4 i.u., respectively. Hence, with both the $\delta(dI/dT)$ and the $\delta(\Delta I)$ values the effect of substitution in relation to the symmetry of the molecule is evident³. Upon symmetrical alkyl substitution in the benzene ring, *i.e.* 1- \rightarrow 1,3- \rightarrow 1,3,5-, the value of $\delta(\Delta I)$ decreases with increase in the number of alkyl groups introduced. With methylbenzenes, the decrease is 3.8 i.u. for methyl- \rightarrow 1,3-dimethylbenzene and 4.4 i.u. for 1,3-dimethyl- \rightarrow 1,3,5-trimethylbenzene. With ethylbenzenes, the decreases for ethyl- \rightarrow 1,3-diethylbenzene and 1,3-diethyl- \rightarrow 1,3,5-triethylbenzene are 3.8 and 2.2 i.u., respectively. With isopropylbenzenes, for isopropyl- \rightarrow 1,3-diisopropyl- \rightarrow 1,3,5-triisopropylbenzene the decreases are 5.1 and 2.9 i.u., respectively. The introduction of the third alkyl group

compared with that of the second group results in a smaller decrease in the ΔI value. On the other hand, upon a substitution that results in asymmetry of the alkylbenzene molecule the ΔI value increases, for instance for 1,3-dimethyl- \rightarrow 1,2,3-trimethylbenzene the ΔI_1 and ΔI_2 values increase by 10.1 and 40.5 i.u., respectively.

Tetra- and pentamethylbenzenes

With tetramethylbenzenes the ΔI values increase in the order 1,2,4,5- < 1,2,3,5- < 1,2,3,4-tetramethylbenzene (Table V).

TABLE V

ΔI_1 AND ΔI_2 VALUES OF TETRA- AND PENTAALKYL BENZENES

Alkylbenzene	ΔI_1	ΔI_2
1,2,4,5-Tetramethylbenzene	129.5	458.8
1,2,3,5-Tetramethylbenzene	130.5	460.0
1,2,3,4-Tetramethylbenzene	137.6	490.0
Methylbenzene	130.9	467.4
1,2-Dimethylbenzene	133.7	480.2
1,2,3-Trimethylbenzene	136.3	488.8
1,2,3,4-Tetramethylbenzene	137.6	490.0
Pentamethylbenzene	138.7	486.7

The ΔI_1 values vary in a manner similar to that for the ΔI values on Ucon LB 550X and squalane found by other workers⁸, and increase with increasing number of vicinal substituents up to hexamethylbenzene. The ΔI_2 values, however, vary in the same way as the ΔI values for Carbowax 20M and Ucon LB 550X described elsewhere⁷. Here a decrease in the ΔI values from 1,2,3,4-tetramethylbenzene up to hexamethylbenzene was found. As both polarity and steric effects determine the retention behaviour, this controversial behaviour is only virtual.

On introducing methyl groups into benzene the following values of $\delta(\Delta I_1)$ and $\delta(\Delta I_2)$ are obtained, respectively: benzene \rightarrow methylbenzene, -5.3 and -16.4 i.u.; methyl- \rightarrow 1,2-dimethylbenzene, 2.8 and 12.8 i.u.; 1,2-dimethyl- \rightarrow 1,2,3-trimethylbenzene, 2.6 and 8.6 i.u.; 1,2,3-trimethyl- \rightarrow 1,2,3,4-tetramethylbenzene, 1.3 and 1.2 i.u.; and 1,2,3,4-tetramethyl- \rightarrow pentamethylbenzene, 1.1 and -3.3 i.u. A plot of these values as a function of the number of substituted methyl groups in vicinally substituted methylbenzenes is shown in Fig. 3.

The similarity and regularity of this relationship in both instances can be considered as an indication that it is the result of the mutual influence of polarity and steric effects. These effects are the result of changes in the number of vicinally substituted methyl groups in the benzene ring, and are demonstrated most markedly with the ΔI_2 values.

Upon substitution in a non-vicinal position, the ΔI_1 and ΔI_2 values again either decrease or increase, depending on the symmetry of the resulting alkylbenzene molecule. For instance, for 1,2,3-trimethyl- \rightarrow 1,2,3,5-tetramethylbenzene the ΔI_1 and ΔI_2 values decrease by 5.8 and 28.8 i.u., respectively, while for the substitution 1,3,5-trimethyl- \rightarrow 1,2,3,5-tetramethylbenzene these values increase by 8.7 and 34.8 i.u., respectively.

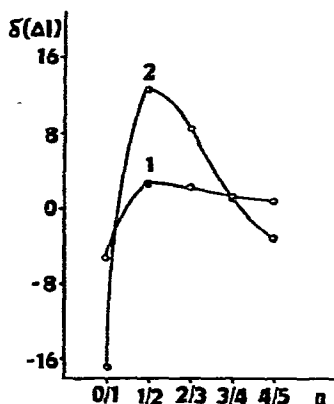


Fig. 3. $\delta(\Delta I_1)$ and $\delta(\Delta I_2)$ values as a function of the number of substituted methyl groups in vicinally substituted methylbenzenes.

With the alkylbenzenes studied, the ΔI_1 values vary between 121.8 i.u. (1,3,5-trimethylbenzene) and 138.7 i.u. (pentamethylbenzene), while for benzene $\Delta I_1 = 136.2$ i.u. The ΔI_2 values range from 273.2 i.u. for 1,3,5-triisopropylbenzene to 490.0 i.u. for 1,2,3,4-tetramethylbenzene. The ΔI_2 value for benzene is 483.8 i.u.

In connection with the problem of reproducibility¹, the variation of ΔI values over a wide range indicates that there are difficulties in making identifications on the basis of comparisons of measured with tabulated retention indices and/or retention indices calculated from increments due to substituted functional groups. A simple elimination of systematic differences between tabulated or calculated and measured retention indices, considering the difference for only one compound (e.g. benzene or another alkylbenzene), is insufficient. The correlations between the ΔI values and the structures of alkylbenzenes can be used to solve these problems.

It can be seen from Table VI, in which ΔI and dI/dT values for C_{10} alkylbenzenes are summarized, that alkylbenzenes with close ΔI_1 values can be differentiated either by virtue of the ΔI_2 values or the dI/dT values, or both.

The sequences of the dI/dT values on squalane, ATC and TCEP are similar, but there are some exceptions on TCEP. Recently, Engewald and Wennrich⁸ showed that the orders of the ΔI and dI/dT values for positional polymethylbenzenes run parallel. According to our results, this correlation does not hold for positional mono- and polyalkyl isomers that have relatively close ΔI values, for instance for monoalkylbenzenes (isomeric butylbenzenes), dialkylbenzenes (1,3- and 1,4-isomers), trialkylbenzenes (1,3-dimethyl-4-ethyl- and 1,4-dimethyl-2-ethylbenzene), tetraalkylbenzenes (1,2,3,5- and 1,2,4,5-tetramethylbenzene). Comparing the ΔI and dI/dT values of C_{10} alkylbenzenes, it can be seen that this relationship is even more complicated. With an increase in the length of the alkyl substituents the orders of the ΔI_2 and dI/dT values become more parallel (e.g., for 1,3- and 1,4-isomers of diethyl-, methylpropyl- and diisopropylbenzenes).

In Fig. 4, ΔI_1 values are plotted against the dI^{SQ}/dT values of all possible C_{10} alkylbenzenes. A regularity in the characteristic arrangement of the points for the positional (1,4-, 1,3- and 1,2-) as well as the configurational (*iso*-, *sec*-, *tert*- and *n*-)

TABLE VI
COMPARISON OF ΔI AND dI/dT VALUES FOR C_{10} ALKYL BENZENES

Alkylbenzene	ΔI_1	ΔI_2	dI^{SQ}/dT	dI^{ATC}/dT	dI^{TCEP}/dT
1,3-Dimethyl-5-ethylbenzene	123.4	404.3	0.218	0.182	2.18
1-Methyl-4-propylbenzene	124.0	397.3	0.282	0.246	2.25
1-Methyl-4-isopropylbenzene	125.2	398.8	0.267	0.228	2.13
1-Methyl-3-propylbenzene	125.6	397.2	0.255	0.217	2.21
Isobutylbenzene	126.4	380.8	0.301	0.263	2.21
1,4-Diethylbenzene	126.6	405.6	0.277	0.244	2.23
1-Methyl-3-isopropylbenzene	127.4	399.0	0.216	0.180	2.07
1,3-Dimethyl-4-ethylbenzene	128.1	432.3	0.281	0.249	2.46
1,3-Diethylbenzene	128.2	405.2	0.244	0.201	2.19
1,4-Dimethyl-2-ethylbenzene	128.7	432.6	0.260	0.229	2.32
sec.-Butylbenzene	129.0	388.6	0.308	0.263	2.21
1,2-Dimethyl-4-ethylbenzene	129.1	434.4	0.286	0.253	2.49
1,2,4,5-Tetramethylbenzene	129.5	458.8	0.341	0.298	2.74
1,2,3,5-Tetramethylbenzene	130.5	460.0	0.338	0.309	2.77
n-Butylbenzene	130.8	401.9	0.284	0.251	2.29
tert.-Butylbenzene	132.2	405.6	0.290	0.255	2.21
1-Methyl-2-propylbenzene	132.5	428.1	0.298	0.265	2.37
1,2-Diethylbenzene	134.4	432.5	0.289	0.253	2.36
1-Methyl-2-isopropylbenzene	134.7	429.0	0.264	0.224	2.26
1,2-Dimethyl-3-ethylbenzene	136.7	462.7	0.329	0.303	2.73
1,3-Dimethyl-2-ethylbenzene	136.8	462.0	0.309	0.287	2.63
1,2,3,4-Tetramethylbenzene	137.6	480.0	0.395	0.370	3.07

isomers of alkylbenzenes can be observed. On plotting ΔI_2 values against dI^{SQ}/dT , certain mutual shifts of the above groups of isomers are achieved. Similar relationships were found also with C_8 and C_9 alkylbenzenes. The relationship between ΔI and dI/dT values thus provides further information for the identification of alkylbenzenes with closely related properties.

CONCLUSIONS

Relationships between the structures of alkylbenzenes and their gas chromatographic behaviour on squalane, acetyltributyl citrate and 1,2,3-triscyanoethoxypropane with respect to the problems associated with the identification of isomeric components are discussed. The graph of the retention indices of alkylbenzenes on a non-polar stationary phase (squalane) against those on a moderately polar stationary phase (acetyltributyl citrate) shows only a slight shift in the direction of the polar-phase coordinate. In the correlation with a highly polar stationary phase (1,2,3-triscyanoethoxypropane) this shift is substantially increased. It is possible in this way to obtain information about the number of carbon atoms and the sizes and positions of the alkyl groups in the alkylbenzenes studied.

Regularities were found between the ΔI values ($\Delta I_1 = I^{ATC} - I^{SQ}$ and $\Delta I_2 = I^{TCEP} - I^{SQ}$) and the structures of mono-, di-, tri-, tetra- and pentaalkylbenzenes. The regularities are summarized in Table VII. On introducing an alkyl group into alkylbenzene molecules the ΔI values may either decrease or increase, depending on the

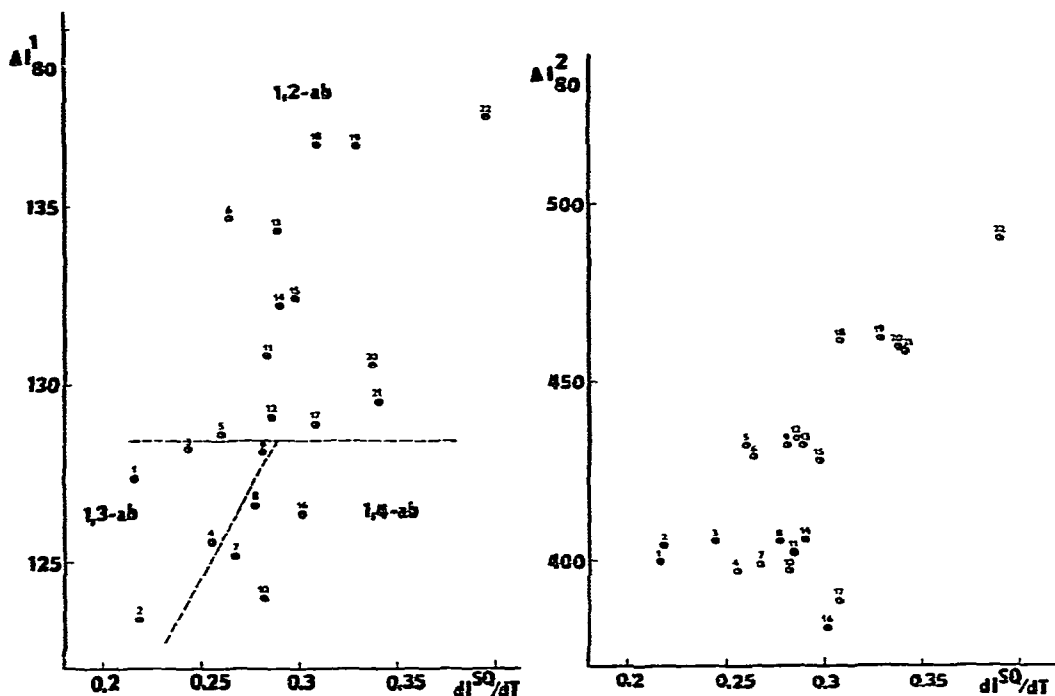


Fig. 4. Values of temperature increments of retention indices of all C_{10} alkylbenzenes isomers as a function of retention index at 80° on squalane, acetyltributyl citrate and 1,2,3-triscyanoethoxypropane. 1,2-, 1,3- and 1,4-ab = 1,2-, 1,3- and 1,4-dialkylbenzenes, respectively. 1 = 1-Methyl-3-isopropylbenzene; 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 = *n*-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 VII

ORDER OF ΔI VALUES DEPENDING ON THE STRUCTURES OF ALKYL BENZENES

The order of ΔI_1 and ΔI_2 values is identical except for 1,2,3,4- and pentamethylbenzenes, for which a reversed order of ΔI_2 values was found.

Alkylbenzene	Structure
Mono-	<i>iso</i> - < <i>sec</i> - < <i>n</i> - < <i>tert</i> -
Di-	1,4- < 1,3- < 1,2-
Tri-	1,3,5- < 1,2,4- < 1,2,3-
Tetra-	1,2,4,5- < 1,2,3,5- < 1,2,3,4-
Penta-	Methyl- < 1,2- < 1,2,3- < 1,2,3,4- < pentamethylbenzene

symmetry of the resultant molecule compared with that of the initial molecule. On substitution that leads to a more symmetrical molecule the ΔI values decrease and *vice versa* (Table VIII). The different behaviours of some alkylbenzenes relating to

TABLE VIII

EFFECT OF THE SYMMETRY OF ALKYL BENZENE MOLECULES ON THE ΔI VALUES

<i>Change in structure</i>	$\delta (\Delta I_1)$ (i.u.)	$\delta (\Delta I_2)$ (i.u.)
1,3-Dimethyl- \rightarrow 1,3,5-trimethylbenzene	-4.4	-23.1
1,3-Dimethyl- \rightarrow 1,2,3-trimethylbenzene	10.1	39.5
1,2,3-Trimethyl- \rightarrow 1,2,3,5-tetramethylbenzene	-5.8	-28.8
1,3,5-Trimethyl- \rightarrow 1,2,3,5-tetramethylbenzene	8.7	34.8

their ΔI_1 and ΔI_2 values as a result of changes in the mutual action of steric and charge effects have been discussed.

The differentiation of alkylbenzenes with close ΔI values can be achieved by correlating the ΔI values with their temperature increments.

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