

CHROM. 9778

## CAPILLARY GAS CHROMATOGRAPHY OF ALKYL BENZENES

### II. CORRELATIONS BETWEEN THE STRUCTURES AND METHYLENE GROUP INCREMENTS AND DIFFERENCES IN RETENTION INDICES OF ISOMERS

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(Received October 26th, 1976)

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#### SUMMARY

The contribution to gas chromatographic retention behaviour of methylene group increments and differences in the retention indices ( $\delta I$ ) of isomers of alkylbenzenes up to  $C_{16}$  on squalane and acetyltri-*n*-butyl citrate was studied. The methylene group increments appear to vary over a wide range (60–100 i.u.) and depend on the magnitude, positions and relative lengths of the alkyl chains and on the number of carbon atoms.

Anomalous retention behaviour of *n*-propylbenzene and its derivatives, except for molecules in which there are alkyl groups in both positions vicinal to the *n*-propyl group, was found. Hence, the correlations of  $I_{CH_2}$  in homologous series can serve as indicators of fine structural peculiarities of the molecules.

The applicability of regularities in methylene group increments and  $\delta I$  values, based on precise measurements of retention indices of low-molecular-weight alkylbenzenes, for confirmation of the identities of high-molecular-weight alkylbenzenes ( $>C_{10}$ ) is demonstrated.

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#### INTRODUCTION

A lack of standards, tabulated retention data and mass spectra for high-molecular-weight alkylbenzenes justifies correlating structure and retention as a means for identification. Because of the low precision of calculation methods for predicting retention data and the reproducibility of data reported in the literature, especially for polar phases, we have focused our attention on structure-retention correlations based on precise measurements for alkylbenzenes of lower molecular weight.

In an earlier paper<sup>1</sup>, we reported the effect and control of factors such as the measurement of retention time, nature and inlet pressure of the carrier gas, temperature and ageing of the column on the precision of retention data for all alkylbenzenes up to C<sub>10</sub> and some up to C<sub>15</sub>. In this paper we consider the retention indices of a further 29 isomers up to C<sub>16</sub>.

In this paper, fine structure-retention correlations, resulting from all of these data and based on the increment of a methylene group ( $I_{\text{CH}_2}$ ) as well as the differences between the retention indices of pairs of isomers on a single phase ( $\delta I$ ), are discussed in detail.

Structure-retention correlations according to temperature increments ( $dI/dT$ ) and the nature and inlet pressure of the carrier gas and differences in retention indices on two and/or three stationary phases, and the relationship between  $\Delta I$  and  $dI/dT$ , will be discussed in subsequent papers.

## EXPERIMENTAL

The experimental conditions were discussed in Part I<sup>1</sup>. In this work, we measured the retention indices of another 29 alkylbenzenes with a carbon number between 11 and 16, which were obtained as a mixture of the products of catalytic dehydrogenation<sup>2</sup> of C<sub>11</sub>-C<sub>16</sub> *n*-alkanes and the alkylation of benzene with *n*-octyl bromide<sup>3</sup>.

The measurements were carried out on shorter columns (about 20 m) with squalane and acetyltri-*n*-butyl citrate as the stationary phases. The precision of these measurements, effected either by stop-watch or by measurement of distances on the chromatogram, corresponds to a standard deviation of *ca.* 0.3 retention index unit (i.u.). The retention indices of these 29 alkylbenzenes are given in Table I.

## RESULTS AND DISCUSSION

### *Contribution of a methylene group to the retention index*

The methylene group increment is referred to the members of a homologous series analyzed on one liquid phase at a constant temperature. According to Ettre<sup>4</sup>, for low carbon numbers (<4 or 5), the value of this increment deviates from 100. The deviations for higher carbon numbers (>5) are ascribed mainly to experimental errors. Studying the correlation between structure and chromatographic behaviour, the methylene group increment is considered as the most simple correlation. Recently, Švob and Deur-Šiftar<sup>5</sup> reported a methylene group increment for alkylbenzenes of 89 i.u., this value being the difference in the retention indices of *n*-propylbenzene and ethylbenzene on SE-30 at 65°.

The methylene group increments on squalane at 95.4° ( $I_{\text{CH}_2}^{\text{SQ}}$ ) and on acetyltri-*n*-butyl citrate at 95.2° ( $I_{\text{CH}_2}^{\text{ATC}}$ ) for the homologous series of alkylbenzenes are given in Table II.

In Fig. 1, the methylene group increment is given as a function of the number of carbon atoms for the homologous series of *n*-alkyl- and *o*-dialkylbenzenes. The regularities and irregularities are similar for both stationary phases.

*n*-Alkylbenzenes. The  $I_{\text{CH}_2}$  values for *n*-alkylbenzenes vary between 88.5 and 99.9 i.u. on squalane and between 87.1 and 100.3 i.u. on acetyltri-*n*-butyl citrate.

TABLE I

RETENTION INDICES OF SOME C<sub>11</sub>-C<sub>16</sub> ALKYL BENZENES ON SQUALANE AT 95.4° AND ACETYLTRI-*n*-BUTYL CITRATE AT 95.2°Carrier gas and inlet pressure: for squalane, 4.0 atm H<sub>2</sub>; for acetyltri-*n*-butyl citrate, 1.0 atm N<sub>2</sub>.

Compound	$I_{95.4}^{SQ}$	$I_{95.2}^{ATC}$
1-Ethyl-2-propylbenzene	1114.7	1246.7
1-Methyl-2-butylbenzene	1140.3	1272.0
1,2-Dipropylbenzene	1187.5	1317.7
1-Ethyl-2-butylbenzene	1207.9	1340.2
<i>n</i> -Hexylbenzene	1228.0	1359.3
1-Methyl-2-pentylbenzene	1235.3	1367.9
1-Propyl-2-butylbenzene	1279.3	1409.3
1-Ethyl-2-pentylbenzene	1302.1	1434.7
4-Phenyloctane	1311.2	—
3-Phenyloctane	1321.5	—
<i>n</i> -Heptylbenzene	1327.7	1459.5
1-Methyl-2-hexylbenzene	1332.1	1465.0
2-Phenyloctane	1357.8	—
1,2-Dibutylbenzene	1370.0	1502.2
1-Propyl-2-pentylbenzene	1371.9	1502.2
1-Ethyl-2-hexylbenzene	1397.7	1530.4
<i>n</i> -Octylbenzene	1427.3	1559.7
1-Methyl-2-heptylbenzene	1431.3	1564.6
1-Butyl-2-pentylbenzene	1460.6	1591.9
1-Propyl-2-hexylbenzene	1466.8	1597.8
1-Ethyl-2-heptylbenzene	1496.4	1630.4
<i>n</i> -Nonylbenzene	1527.2	1660.0
1-Methyl-2-octylbenzene	1530.5	1664.7
1,2-Dipentylbenzene	1551.8	1683.5
1-Butyl-2-hexylbenzene	1555.1	1686.5
1-Propyl-2-heptylbenzene	1564.3	1695.7
1-Ethyl-2-octylbenzene	1595.0	1728.8
<i>n</i> -Decylbenzene	1626.8	1759.5
1-Methyl-2-nonylbenzene	1629.8	1763.9

They increase with increasing carbon number, and approach a constant value of 100 from *n*-hexylbenzene. For the second and third points of the plots, the regularity of the dependence of  $I_{CH_2}$  on carbon number is disturbed. For *n*-propylbenzene-ethylbenzene the  $I_{CH_2}$  increments are minimal.

*o*-Dialkylbenzenes. The  $I_{CH_2}$  values for *o*-dialkylbenzenes vary within wider limits (64–100 i.u.). The contribution of a methylene group to the retention index of *o*-dialkylbenzenes is smaller than that for corresponding *n*-alkylbenzenes; with increase in the alkyl chain from 1-methyl-2-alkyl- to 1-octyl-2-alkylbenzene they decrease regularly. The  $I_{CH_2}$  values, in a homologous series, increase with increasing carbon number. After about six carbon atoms in the alkyl chain (from the beginning of the new structural trait), they approach a value of 100 i.u. For the second and third points of these plots, the regularities are systematically disturbed. The deviations tend towards lower values for the second points and higher values for the third points of the plots. The methylene group increments tend to be larger on acetyltri-*n*-butyl citrate and the anomalies are also greater on this stationary phase.

TABLE II  
CONTRIBUTION OF ONE METHYLENE GROUP TO THE RETENTION INDICES OF  
HOMOLOGOUS SERIES OF ALKYL BENZENES ON SQUALANE AT 95.4° AND ACET-  
YLTRI-*n*-BUTYL CITRATE AT 95.2°

Series	No. of carbon atoms	Compound	$I_{CH_2}^{SQ}$	$I_{CH_2}^{ATC}$	
<i>n</i> -Alkylbenzenes	C <sub>7</sub>	Methylbenzene	90.1	91.5	
	C <sub>8</sub>	Ethylbenzene	88.5	87.1	
	C <sub>9</sub>	Propylbenzene	99.7	100.2	
	C <sub>10</sub>	Butylbenzene	96.6	97.3	
	C <sub>11</sub>	Pentylbenzene	97.6	97.9	
	C <sub>12</sub>	Hexylbenzene	99.7	100.2	
	C <sub>13</sub>	Heptylbenzene	99.6	100.2	
	C <sub>14</sub>	Octylbenzene	99.9	100.3	
	C <sub>15</sub>	Nonylbenzene	99.6	99.5	
	C <sub>16</sub>	Decylbenzene			
1-Methyl-2-alkylbenzenes	C <sub>8</sub>	1-Methyl-2-methylbenzene	81.0	81.3	
	C <sub>9</sub>	1-Methyl-2-ethylbenzene	81.4	79.7	
	C <sub>10</sub>	1-Methyl-2-propylbenzene	96.3	96.1	
	C <sub>11</sub>	1-Methyl-2-butylbenzene	95.0	95.9	
	C <sub>12</sub>	1-Methyl-2-pentylbenzene	96.8	97.1	
	C <sub>13</sub>	1-Methyl-2-hexylbenzene	99.2	99.6	
	C <sub>14</sub>	1-Methyl-2-heptylbenzene	99.2	100.1	
	C <sub>15</sub>	1-Methyl-2-octylbenzene	99.3	99.2	
	C <sub>16</sub>	1-Methyl-2-nonylbenzene			
	1-Ethyl-2-alkylbenzenes	C <sub>9</sub>	1-Ethyl-2-methylbenzene	74.8	75.0
C <sub>10</sub>		1-Ethyl-2-ethylbenzene	77.3	75.5	
C <sub>11</sub>		1-Ethyl-2-propylbenzene	93.2	93.5	
C <sub>12</sub>		1-Ethyl-2-butylbenzene	94.2	94.5	
C <sub>13</sub>		1-Ethyl-2-pentylbenzene	97.0	96.6	
C <sub>14</sub>		1-Ethyl-2-hexylbenzene	97.3	98.7	
C <sub>15</sub>		1-Ethyl-2-heptylbenzene	98.6	98.8	
C <sub>16</sub>		1-Ethyl-2-octylbenzene			
1-Propyl-2-alkylbenzenes		C <sub>10</sub>	1-Propyl-2-methylbenzene	70.7	70.8
		C <sub>11</sub>	1-Propyl-2-ethylbenzene	72.8	71.0
	C <sub>12</sub>	1-Propyl-2-propylbenzene	91.8	91.6	
	C <sub>13</sub>	1-Propyl-2-butylbenzene	92.6	92.5	
	C <sub>14</sub>	1-Propyl-2-pentylbenzene	94.9	96.0	
	C <sub>15</sub>	1-Propyl-2-hexylbenzene	97.5	97.9	
	C <sub>16</sub>	1-Propyl-2-heptylbenzene			
	1-Butyl-2-alkylbenzenes	C <sub>11</sub>	1-Butyl-2-methylbenzene	67.6	68.2
C <sub>12</sub>		1-Butyl-2-ethylbenzene	71.4	69.1	
C <sub>13</sub>		1-Butyl-2-propylbenzene	90.7	90.0	
C <sub>14</sub>		1-Butyl-2-butylbenzene	90.6	92.6	
C <sub>15</sub>		1-Butyl-2-pentylbenzene	94.5	94.6	
C <sub>16</sub>		1-Butyl-2-hexylbenzene			
1-Pentyl-2-alkylbenzenes		C <sub>12</sub>	1-Pentyl-2-methylbenzene	66.8	66.8
	C <sub>13</sub>	1-Pentyl-2-ethylbenzene	69.8	67.1	
	C <sub>14</sub>	1-Pentyl-2-propylbenzene	89.8	90.1	
	C <sub>15</sub>	1-Pentyl-2-butylbenzene	90.1	91.6	
	C <sub>16</sub>	1-Pentyl-2-pentylbenzene			
	1-Hexyl-2-alkylbenzenes	C <sub>13</sub>	1-Hexyl-2-methylbenzene	67.0	66.3
C <sub>14</sub>		1-Hexyl-2-ethylbenzene	67.7	66.5	
C <sub>15</sub>		1-Hexyl-2-propylbenzene	88.3	88.7	
C <sub>16</sub>		1-Hexyl-2-butylbenzene			
1-Heptyl-2-alkylbenzenes		C <sub>14</sub>	1-Heptyl-2-methylbenzene	65.1	65.4
	C <sub>15</sub>	1-Heptyl-2-ethylbenzene	67.9	65.7	
	C <sub>16</sub>	1-Heptyl-2-propylbenzene			
	1-Octyl-2-alkylbenzenes	C <sub>15</sub>	1-Octyl-2-methylbenzene	64.5	64.1
C <sub>16</sub>		1-Octyl-2-ethylbenzene			

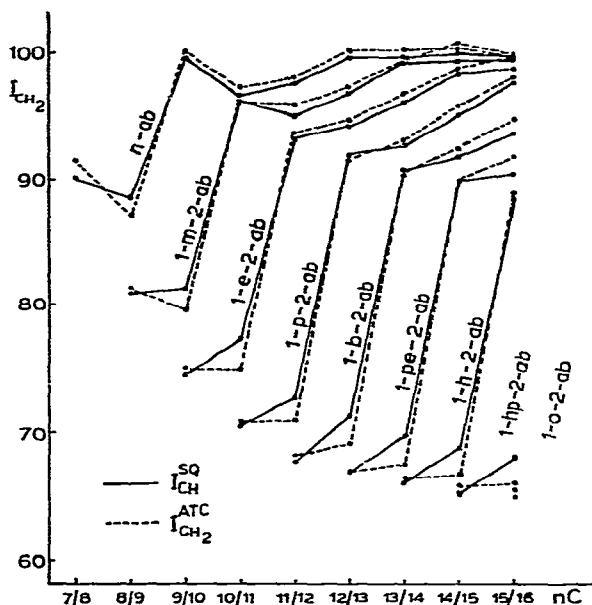
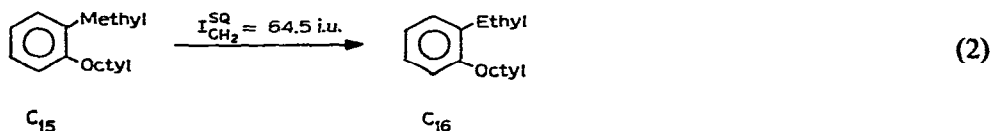
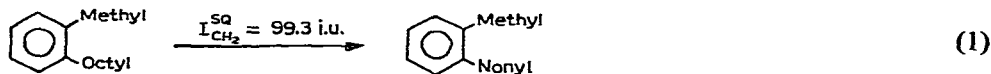


Fig. 1. Dependence of  $I_{CH_2}^{SQ}$  and  $I_{CH_2}^{ATC}$  on number of carbon atoms for homologous series of alkylbenzenes. *n*-ab = *n*-alkylbenzenes; 1-*m*-2-ab = 1-methyl-2-alkylbenzenes; 1-*e*-2-ab = 1-ethyl-2-alkylbenzenes; 1-*p*-2-ab = 1-propyl-2-alkylbenzenes; 1-*b*-2-ab = 1-butyl-2-alkylbenzenes; 1-*pe*-2-ab = 1-pentyl-2-alkylbenzenes; 1-*h*-2-ab = 1-hexyl-2-alkylbenzenes; 1-*hp*-2-ab = 1-heptyl-2-alkylbenzenes; 1-*o*-2-ab = 1-octyl-2-alkylbenzenes.

(In all of these instances of anomalies, the derivatives of *n*-propylbenzene are concerned.)

In Table III, methylene group increments on squalane at 95.4° are presented for series of *o*-dialkylbenzenes, arranged in a way that enables one to compare the effects of the lengths of the two alkyl chains on the value of  $I_{CH_2}$ . The regularities are again apparent. Irregularities in these correlations are also observed only for *n*-propyl derivatives.

It can be concluded that for *o*-dialkylbenzenes (up to  $C_{16}$ ) the  $I_{CH_2}^{SQ}$  value depends on the lengths of the two alkyl chains and varies between 64.5 and 99.9 i.u. This is shown by comparing the methylene group increments resulting from substitution of a methylene group into a longer (octyl) chain and a shorter (methyl) chain of 1-methyl-2-octylbenzene:



1-Methyl-2-octylbenzene is the eighth member of the homologous series of 1-methyl-2-alkylbenzenes and, obviously, it is also the first member of the series of 1-octyl-2-

TABLE III

 $I_{CH_2}^{SO}$  VALUES FOR VARIOUS ALKYL CHAINS OF *o*-DIALKYLBENZENES AT 95.4°



















No. of carbon atoms									
									
7 → 8	90.2								
8 → 9	81.0	88.4							
9 → 10	74.8	81.4	99.7						
10 → 11	70.7	77.3	96.3	96.6					
11 → 12	67.6	72.8	93.2	95.0	97.6				
12 → 13	66.8	71.4	91.8	94.2	96.8	99.7			
13 → 14	67.0	69.8	90.7	92.6	97.0	99.2	99.6		
14 → 15	65.1	67.7	88.7	90.6	94.9	97.3	99.2	99.9	
15 → 16	64.5	67.9	88.3	90.1	93.4	97.5	98.6	99.3	99.6

TABLE IV

 $I_{CH_2}^{SO}$  VALUES FOR POSITIONAL 1,2-, 1,3-, 1,4-DIALKYLBENZENES AT 80°

No. of carbon atoms	1-Methyl-2-alkylbenzene		1-Methyl-3-alkylbenzene		1-Methyl-4-alkylbenzene	
	$I_{80}^{SO}$	$I_{CH_2}^{SO}$	$I_{80}^{SO}$	$I_{CH_2}^{SO}$	$I_{80}^{SO}$	$I_{CH_2}^{SO}$
C <sub>8</sub>	881.6	81.0	861.5	85.3	859.6	89.8
C <sub>9</sub>	962.6	81.4	946.8	84.9	949.4	88.0
C <sub>10</sub>	1044.0		1031.7		1037.4	

alkylbenzenes. A methylene substitution in the longer chain (eqn. 1) gives an increment of almost 100 i.u. in this example. It must be mentioned, however, that if the length of the short chain is increased, this increment will decrease. A methylene substitution in the short chain (eqn. 2) results in a considerably lower  $I_{CH_2}$  value. In this instance, a decrease in the length of the longer chain will result in an increased  $I_{CH_2}$  value. Therefore, the  $I_{CH_2}$  increment values for all other *o*-dialkylbenzenes (up to C<sub>16</sub>) are between 64.5 and 100 i.u.

The  $I_{CH_2}$  values depend not only on the lengths of the two alkyl chains but also on their mutual positions. In Table IV are presented the methylene group increments of positional *ortho*-, *meta*- and *para*-isomers of dialkylbenzenes. The increments increase in the order *o*- < *m*- < *p*-dialkylbenzene (the values for *m*- and *p*-dialkylbenzenes were measured only up to C<sub>10</sub>). Considering these data for *o*-dialkylbenzenes up to C<sub>16</sub>, it can be expected that the increments for *m*- and *p*-dialkylbenzenes will depend on the number of carbon atoms in a similar way. The systematic deviations for *n*-propyl derivatives of *m*- and *p*-dialkylbenzenes are also observed in this instance.

**Trialkylbenzenes.** Methylene group increments for trialkylbenzenes, particularly for trimethyl-, dimethylethylbenzenes, on squalane and acetyltri-*n*-butyl citrate at 80° are presented in Table V.

A methylene substitution in the last alkyl group results in an increase in the increment in the order 1,2,3- < 1,3,5- < 1,2,4-trialkylbenzene. For a substitution in the middle alkyl group, this increase follows the order 1,2,3- < 1,2,4- ≤ 1,3,5-tri-

TABLE V

 $I_{CH_2}^{SO}$  AND  $I_{CH_2}^{ATC}$  VALUES OF TRIALKYLBENZENES AT 80°

Compounds	$I_{CH_2}^{SO}$	$I_{CH_2}^{ATC}$
1,2,3-Trimethylbenzene-1,2-dimethyl-3-ethylbenzene	76.5	77.0
1,3,5-Trimethylbenzene-1,3-dimethyl-5-ethylbenzene	80.8	82.4
1,2,4-Trimethylbenzene-1,2-dimethyl-4-ethylbenzene	85.3	86.6
1,2,3-Trimethylbenzene-1,3-dimethyl-2-ethylbenzene	60.7	61.2
1,2,4-Trimethylbenzene-1,3-dimethyl-4-ethylbenzene	80.7	81.1
1,3,5-Trimethylbenzene-1,3-dimethyl-5-ethylbenzene	80.8	82.4

alkylbenzene. In the substitution 1,2,3-trimethylbenzene-1,3-dimethyl-2-ethylbenzene, the  $I_{CH_2}$  increment has the smallest value of all of the alkylbenzenes studied ( $I_{CH_2}^{SO} = 60.7$  i.u.).

*Anomalies.* Considering the anomalous retention behaviour of *n*-propylbenzene and its dialkyl derivatives, it can be concluded that they all have a lower retention index than that derived from the regular dependence of retention index on the number of carbon atoms. This effect with *n*-propylbenzene and 1-methyl-2-propylbenzene on squalane has been briefly pointed out in an earlier paper<sup>6</sup>. Similar effects are observed for homologous series of *n*-alkenes<sup>7</sup> and *n*-alkynes<sup>8</sup> and have recently been confirmed by Rang *et al.*<sup>9,10</sup>. The explanation of these effects is a subject of quantum chemical and NMR structural studies<sup>11,12</sup>.

In this paper, we point out the general features of this anomaly for mono- and dialkylbenzenes on stationary phases of different polarity, and *n*-propyl anomalies also occur with trialkylbenzenes. An exception has been found when there are alkyl groups in both positions vicinal to an *n*-propyl group, as can be seen in Table VI, according to measurements by Döring *et al.*<sup>3</sup> on 1,2-dimethyl-4-alkyl-, 1,3-dimethyl-5-alkyl- and 1,3-dimethyl-2-alkylbenzenes on Ucon LB 550X and Carbowax 20M. This exception indicates that the cause of the anomalies is a stereospecific arrangement of the *n*-propyl group that provides for an interaction with the  $\pi$ -electron structure of the aromatic ring, analogously to the effects found with *n*-alkenes<sup>6</sup> and *n*-alkynes<sup>7</sup>.

The magnitude of these anomalies, expressed in retention index units, was obtained by graphical interpolation starting from the systematic dependence of  $I_{CH_2}$  on the number of carbon atoms for the individual homologous series of alkylbenzenes.

TABLE VI

 $I_{CH_2}$  VALUES OF 1,2,3-, 1,2,4- AND 1,3,5-TRIALKYLBENZENES ON UCON LB 550X AND CARBOWAX 20M AT 90°<sup>3</sup>

Alkyl group	1,2-Dimethyl-4-alkylbenzene		1,3-Dimethyl-5-alkylbenzene		1,3-Dimethyl-2-alkylbenzene	
	$I_{CH_2}^{UC}$	$I_{CH_2}^{CW}$	$I_{CH_2}^{UC}$	$I_{CH_2}^{CW}$	$I_{CH_2}^{UC}$	$I_{CH_2}^{CW}$
Methyl	84.5	79.2	79.5	76.7	54.1	45.7
Ethyl	81.7	73.5	78.5	66.4	74.7	62.6
Propyl			98.9	96.6	94.6	90.6
Butyl						

TABLE VII

DIFFERENCES BETWEEN RETENTION INDICES CALCULATED BY INTERPOLATION AND MEASURED DATA FOR *n*-PROPYL DERIVATIVES OF BENZENE ON SQUALANE AND ACETYLTRI-*n*-BUTYL CITRATE (IN i.u.)

No. of carbon atoms	Compound	SQ	ATC	$\Delta$
C <sub>9</sub>	Propylbenzene	4.8	5.6	0.7
C <sub>10</sub>	1-Methyl-2-propylbenzene	5.2	5.8	0.6
C <sub>11</sub>	1-Ethyl-2-propylbenzene	5.0	5.7	0.7
C <sub>12</sub>	1,2-Dipropylbenzene	5.9	6.6	0.7
C <sub>13</sub>	1-Butyl-2-propylbenzene	5.9	6.6	0.7
C <sub>14</sub>	1-Pentyl-2-propylbenzene	6.1	7.2	1.1

The results show that the retention indices of *n*-propylbenzenes on squalane and acetyltri-*n*-butyl citrate are lower, on average, by 5.5 and 6.3 i.u., respectively, than would be expected by interpolation (Table VII). For 1,2-di-*n*-propylbenzene a double anomaly is observed. An increase in the polarity of the stationary phase enhances the anomalous effect of structure on the retention index. A similar dependence was also found with anomalous structures of *n*-alkenes.

According to the relationship<sup>13</sup>  $\delta I \approx 5\delta T_b$ , where  $T_b$  is the boiling point, the anomalous value of the difference in the retention index for *n*-propylbenzene, amounting to 5.5 i.u., corresponds to a difference in boiling points of about 1.1°. This value is in good agreement with the value of 1.2° obtained by a similar correlation of methylene group increments, derived from tabulated boiling points of alkylbenzenes<sup>14</sup>. From Table VIII, it can be seen that incremental differences in the boiling points of *n*-alkylbenzenes decrease irregularly with increasing carbon number, as the boiling points of *n*-alkylbenzenes with an odd number of carbon atoms are higher than those

TABLE VIII

COMPARISON OF DIFFERENCES OF INCREMENTS  $\delta I_{CH_2}^{SQ}$  AND  $\delta I_{CH_2}^{ATC}$  AND DIFFERENCES OF BOILING POINTS,  $\delta T_b$

$\delta T_{b1}$  = difference of boiling points;  $\delta T_{b2}$  = difference of  $\delta T_{b1}$  values;  $\delta I_{CH_2}$  = difference of methylene group increments.

<i>n</i> -Alkylbenzene	Boiling point (°C) <sup>14</sup>	$\delta T_{b1}$	$\delta T_{b2}$	$\delta I_{CH_2}^{SQ}$	$\delta I_{CH_2}^{ATC}$	<i>n</i> -Alkane	$\delta T_{b2}$
Methylbenzene	110.6	25.6					
Ethylbenzene	136.2	23.0	2.6	-1.6	-4.4	<i>n</i> -Octane	2.11
Propylbenzene	159.2	24.1	-1.1	11.2	13.1	<i>n</i> -Nonane	1.81
Butylbenzene	183.3	22.2	1.9	-3.1	-2.9	<i>n</i> -Decane	1.55
Pentylbenzene	205.5	20.6	1.6	1.0	0.6	<i>n</i> -Undecane	1.38
Hexylbenzene	226.1	19.9	0.7	2.1	2.3	<i>n</i> -Dodecane	1.23
Heptylbenzene	246.0	18.4	1.5	-0.1	0.0	<i>n</i> -Tridecane	1.03
Octylbenzene	264.4	17.6	0.8	0.3	0.1	<i>n</i> -Tetradecane	1.07
Nonylbenzene	282.0	15.9	1.7	-0.3	-0.8	<i>n</i> -Pentadecane	0.90
Decylbenzene	297.9	15.3	0.6			<i>n</i> -Hexadecane	1.13
Undecylbenzene	313.2					<i>n</i> -Heptadecane	0.73



for the *n*-alkylbenzenes with an even number of carbon atoms. This effect is in agreement with the retention behaviour of *n*-alkylbenzenes (see Fig. 1). For *n*-alkanes, these irregularities in boiling points are considerably lower (Table VIII).

Hence, the correlations of  $I_{CH_2}$  in homologous series can serve as indicators of fine structural peculiarities of the molecules.

#### Differences between the retention indices of two isomers

The  $I_{CH_2}$  values show a dependence on the number of carbon atoms not only in a homologous series, but also between the individual homologous series of alkylbenzenes. It can be seen in Fig. 1 that it is possible to draw fairly regular curves through the points of the first, second, third, etc., points of the plots. They can be extrapolated to higher members of the series and/or members of new homologous series, e.g., 1-nonyl-2-alkylbenzenes (net extrapolation).

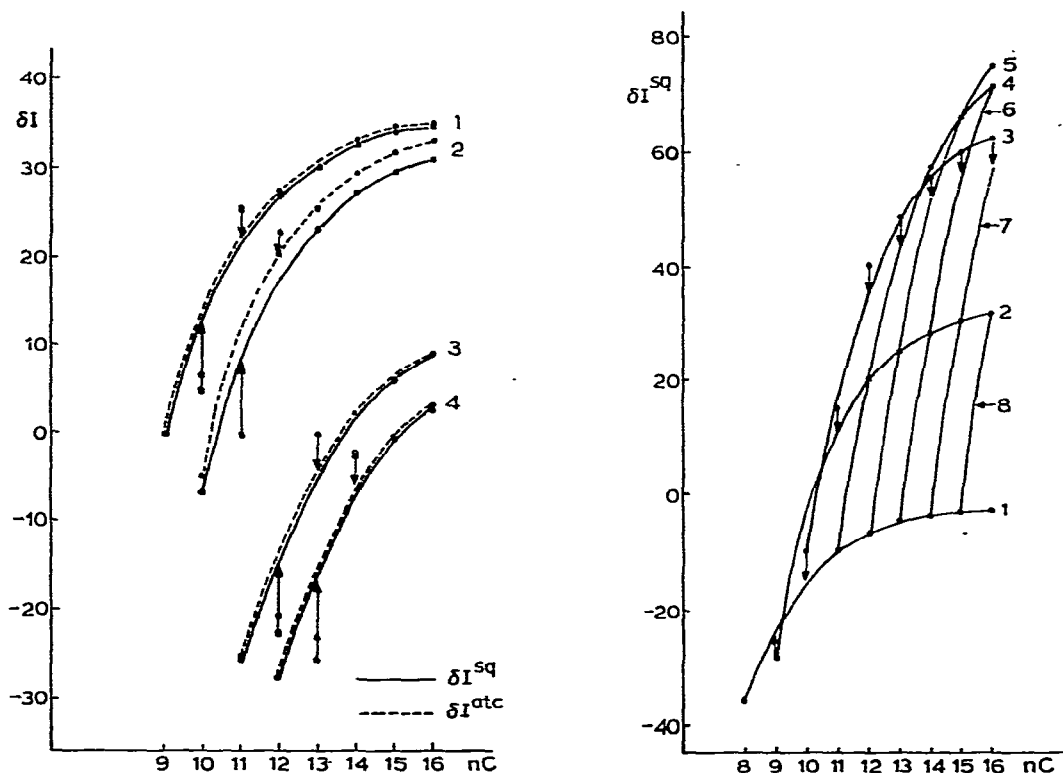


Fig. 2. Dependence of  $\delta I^{sq}$  and  $\delta I^{atc}$  on number of carbon atoms for pairs of isomers differing by one carbon atom at the beginning of homologous series. 1 = 1-Methyl-2-alkyl-1-ethyl-2-alkylbenzenes; 2 = 1-ethyl-2-alkyl-1-propyl-2-alkylbenzenes; 3 = 1-propyl-2-alkyl-1-butyl-2-alkylbenzenes; 4 = 1-butyl-2-alkyl-1-pentyl-2-alkylbenzenes.

Fig. 3. Dependence of  $\delta I^{sq}$  on number of carbon atoms for pairs of isomers differing by 1-8 carbon atoms at the beginning of homologous series. 1 = *n*-Alkyl-1-methyl-2-alkylbenzenes; 2 = *n*-alkyl-1-ethyl-2-alkylbenzenes; 3 = *n*-alkyl-1-propyl-2-alkylbenzenes; 4 = *n*-alkyl-1-butyl-2-alkylbenzenes; 5 = *n*-alkyl-1-pentyl-2-alkylbenzenes; 6 = *n*-alkyl-1-hexyl-2-alkylbenzenes; 7 = *n*-alkyl-1-heptyl-2-alkylbenzenes; 8 = *n*-alkyl-1-octyl-2-alkylbenzenes.

TABLE IX  
DIFFERENCES IN RETENTION INDICES OF CHARACTERISTIC PAIRS OF ALKYL BENZENE ISOMERS ON SQUALANE,  $\delta I_{SQ}^{SQ}$ , AND ACETYLTRI-*n*-BUTYL CITRATE,  $\delta I_{ATC}^{ATC}$

No. of carbon atoms	<i>1-Methyl-2-n-ab</i> *		<i>1-Ethyl-2-1-ethyl-2-ab</i> *		<i>1-Ethyl-2-1-propyl-2-ab</i> *		<i>1-Propyl-2-1-butyl-2-ab</i> *		<i>1-Butyl-2-1-pentyl-2-ab</i> *	
	$\delta I_{SQ}^{SQ}$	$\delta I_{ATC}^{ATC}$	$\delta I_{SQ}^{SQ}$	$\delta I_{ATC}^{ATC}$	$\delta I_{SQ}^{SQ}$	$\delta I_{ATC}^{ATC}$	$\delta I_{SQ}^{SQ}$	$\delta I_{ATC}^{ATC}$	$\delta I_{SQ}^{SQ}$	$\delta I_{ATC}^{ATC}$
C <sub>8</sub>	36.0	38.1								
C <sub>9</sub>	28.5	32.3	0.0	0.0						
C <sub>10</sub>	10.2	11.8	6.6	4.7	-6.6	-4.7				
C <sub>11</sub>	9.9	10.6	25.6	25.3	0.0	0.0	-25.6	-25.3		
C <sub>12</sub>	7.3	8.6	27.4	27.7	20.4	22.5	-20.4	-22.5		
C <sub>13</sub>	4.4	5.5	30.0	30.3	22.8	25.4	0.0	0.0	-27.4	-27.7
C <sub>14</sub>	4.0	4.9	32.2	33.3	27.2	28.2	1.9	2.5	-22.8	-25.4
C <sub>15</sub>	3.3	4.7	34.1	34.5	29.6	32.6	6.2	5.9	-1.9	-2.5
C <sub>16</sub>	3.0	4.4	34.8	35.1	30.7	33.1	9.2	9.2	0.0	0.0
Difference between first and last value	33.0	33.7	34.8	35.1	37.3	37.8	34.8	34.5	30.7	30.7
Number of carbon atom considered	9	9	8	8	7	7	6	6	5	5

\* ab = Alkylbenzene.

The dependence of  $\delta I$  on the number of carbon atoms, based on the differences between the retention indices of two alkylbenzene isomers on squalane and acetyltri-*n*-butyl citrate, is shown in Fig. 2. They display a relatively regular increase up to about constant values, and irregularities are again apparent with *n*-propyl derivatives. Comparison of the  $\delta I$  values of the pairs of isomers whose first members of the series differ by one carbon atom in the molecule (1-methyl-2-alkyl- -1-ethyl-2-alkylbenzene; 1-ethyl-2-alkyl- -1-propyl-2-alkyl benzene; 1-propyl-2-alkyl- -1-butyl-2-alkyl benzene; and 1-butyl-2-alkyl- -1-pentyl-2-alkylbenzene) results in a difference of about 35 i.u. in the upper part of the curve (Table IX).

On comparison in the same way of the pairs *n*-alkylbenzenes-1-ethyl-2-alkylbenzenes, *i.e.*, the series of which the first members differ by two carbon atoms, it is found that the corresponding  $\delta I$  value is increased to about 60 i.u. This change in  $\delta I$  value increases regularly but not linearly with the difference in carbon number of the first members of the series, as is shown in Fig. 3 and Table X for pairs of *n*-alkylbenzenes and *o*-dialkylbenzenes.

The applicability of this effect is demonstrated by the following example for branched-chain alkylbenzenes. A shift of the phenyl group in some series of phenylalkanes towards the centre of the alkyl chain results in a decrease in the difference in retention indices between two neighbouring positional isomers on squalane. For 1--2-, 2--3- and 3--4-phenyloctanes these differences are 69.7, 36.3 and 10.3 i.u., respectively. With an increase in the number of carbon atoms, the  $\delta I$  values for the pairs of isomers increase. For instance, with 1-phenyl- -2-phenylalkanes, the values of  $\delta I^{\text{SQ}}$  for the C<sub>9</sub>, C<sub>10</sub>, C<sub>11</sub> and C<sub>14</sub> compounds are 28.7, 46.3, 54.4 and 69.7 i.u., respectively.

From these results (Tables IX and X), it is possible to derive rules for the elution order and the distance of pairs of isomers in a chromatogram on squalane and acetyltri-*n*-butyl citrate. It can also be seen from these tables that the differences in the  $\delta I$  values of pairs of isomers depend on the number of carbon atoms. There are three possibilities, all of which are demonstrated in Fig. 4 as an example:

- the  $\delta I$  values may decrease to about a constant difference;
- the elution order of the isomers may be reversed;
- the  $\delta I$  values may increase to about a constant difference.

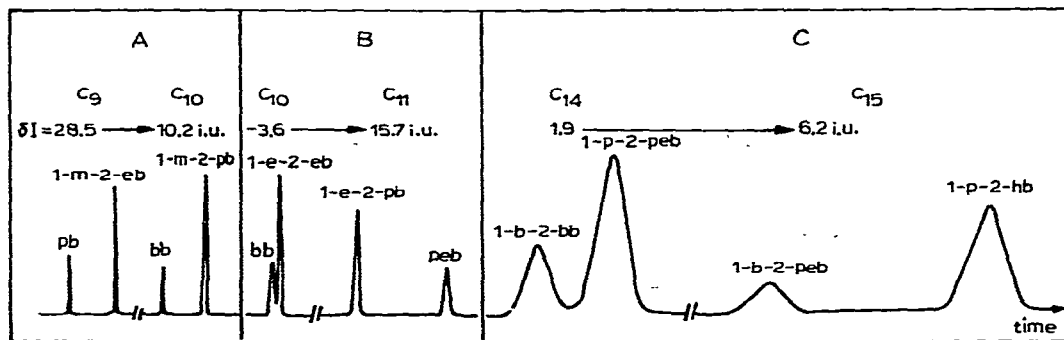


Fig. 4. Changes in separation of pairs of isomers of alkylbenzenes with number of carbon atoms on squalane. pb = propylbenzene; 1-m-2-eb = 1-methyl-2-ethylbenzene; bb = butylbenzene; 1-m-2-pb = 1-methyl-2-propylbenzene; 1-e-2-eb = 1-ethyl-2-ethylbenzene; 1-e-2-pb = 1-ethyl-2-propylbenzene; peb = pentylbenzene; 1-b-2-bb = 1-butyl-2-butylbenzene; 1-p-2-peb = 1-propyl-2-pentylbenzene; 1-b-2-peb = 1-butyl-2-pentylbenzene; 1-p-2-hb = 1-propyl-2-hexylbenzene.

TABLE X  
DIFFERENCES IN RETENTION INDICES OF *n*-ALKYLBENZENES AND *o*-DIALKYL BENZENES ON SQUALANE,  $\delta_{IS}^{SO}$

No. of carbon atoms	<i>n</i> -1-methyl- -2-ab*	<i>n</i> -1-ethyl- -2-ab*	<i>n</i> -1-propyl- -2-ab*	<i>n</i> -1-butyl- -2-ab*	<i>n</i> -1-pentyl- -2-ab*	<i>n</i> -1-hexyl- -2-ab*	<i>n</i> -1-heptyl- -2-ab*	<i>n</i> -1-octyl- -2-ab*	<i>n</i> -1-nonyl- -2-ab*
C <sub>8</sub>	-36.0								
C <sub>9</sub>	-28.5	-28.5							
C <sub>10</sub>	-10.2	-3.6	-10.2						
C <sub>11</sub>	-9.9	15.7							
C <sub>12</sub>	-7.3	20.1	40.5	20.1	-7.3				
C <sub>13</sub>	-4.4	25.6	48.4	48.4	25.6	-4.4			
C <sub>14</sub>	-4.0	28.2	55.4	57.3	55.4	28.2	-4.0		
C <sub>15</sub>	-3.3	30.8	60.4	66.6	66.6	60.4	30.8	-3.3	
C <sub>16</sub>	-3.0	31.8	62.5	71.7	75.0	71.7	62.5	31.8	-3.0
Difference between first and last value	33.0	60.3	72.7	81.6	82.3	76.1	66.5	35.1	3.0
Number of carbon atom considered	9	8	7	6	5	4	3	2	1

\* ab = Alkylbenzene.

(a) The first peak (*n*-propylbenzene) in Fig. 4a is the third member of the homologous series of *n*-alkylbenzenes and the second peak (1-methyl-2-ethylbenzene) is the second member of the homologous series of 1-methyl-2-alkylbenzenes. Therefore, the change in retention index for the next members of both of these series, which depends on the number of carbon atoms, will be different. In this instance, the relative change will decrease to a larger extent than for the next member of the series of the second peak. According to Tables IX and X, on increasing the carbon number, this effect will result in a decrease in  $\delta I$ , which will finally become constant.

(b) The reversed elution order shown in Fig. 4b can be explained in a similar manner. The reasons for this peak inversion are (1) a relatively small difference in the retention index and (2) the difference in carbon number of the first members of the homologous series considered. According to Tables IX and X, the elution orders of the pairs *n*-propylbenzene-1-ethyl-2-methylbenzene and *n*-butylbenzene-1-ethyl-2-ethylbenzene are the same. The elution order of all higher pairs of members of these series will be reversed.

(c) In Fig. 4c, an example is shown where the value  $\delta I$  increases with increasing carbon number. Here, the first peak (1-butyl-2-butylbenzene) is the fourth member of the series of 1-butyl-2-alkylbenzenes while the second peak (1-propyl-2-pentylbenzene) is the fifth member of the series 1-propyl-2-alkylbenzenes. Contrary to the example in Fig. 4a, the first peak is a member of a homologous series starting with a higher carbon number as the second peak. Therefore, the relative change in the retention index for the higher members of the first peak will increase to a larger extent than for those of the second series. Thus, in this instance, the difference in  $\delta I$  values increases with increasing carbon number.

The changes in the  $\delta I$  values of alkylbenzene isomers will be the larger the more the isomers differ in the number of carbon atoms in the first members of the homologous series. Similar dependences were also found with *n*-alkenes<sup>7</sup>, so that they can probably be generalized.

In a similar manner, the correlations discussed above were used for confirmation of the identities of the alkylbenzenes obtained from the catalytic dehydrogenation of *n*-alkanes given in Table I. No standards were available for any of these compounds.

## CONCLUSION

Correlations were carried out of retention indices of alkylbenzenes up to C<sub>16</sub> on squalane and acetyltri-*n*-butyl citrate as stationary phases, considering the contribution of a methylene group to the retention index and the difference between the retention indices of two isomers of alkylbenzenes on a single stationary phase.

The  $I_{\text{CH}_2}$  values depend on the mutual positions and lengths of the alkyl chains. The longer the alkyl chain, the smaller is the  $I_{\text{CH}_2}$  increment on the introduction of a methylene group into the shorter chain and, *vice versa*, substitution into the longer chain increases the increment. In homologous series of alkylbenzenes, the  $I_{\text{CH}_2}$  values vary over a wide range (60–100 i.u.), they increase with increasing number of carbon atoms and, after about six carbon atoms from beginning of the given homologous series, they approach a value of 100. The regularity of the dependences is disturbed with *n*-propylbenzene and its alkyl derivatives, except for the alkylbenzenes in which both positions vicinal to the *n*-propyl are substituted by other alkyl groups. On the

other hand, 1,2-dipropylbenzene shows a double anomaly. The retention indices of the *n*-propylbenzenes that show anomalous behaviour are lower, on average, by 5.5 and 6.3 i.u. on squalane and acetyltri-*n*-butyl citrate, respectively, than the values calculated from the regularities of these dependences. The correlations show that *n*-propylbenzene also has a boiling point lower by about 1°. Hence, the correlations of  $I_{CH_2}$  in homologous series can serve as indicators of fine structural differences in molecules.

The  $I_{CH_2}$  values show dependences on the number of carbon atoms not only within a given homologous series, but also among different homologous series of alkylbenzenes, so that extrapolations to higher-molecular-weight alkylbenzenes are possible. The separation of pairs of isomers from different homologous series, *i.e.*, the  $\delta I$  values, can either decrease or increase on increasing the number of carbon atoms, or a reversal of the order of retention of both isomers may occur, depending on the retention and on the difference in the number of carbon atoms of the first members of the corresponding homologous series of alkylbenzenes.

#### ACKNOWLEDGEMENT

This work was supported by the Scientific Exchange Agreement (SEA).

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