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IDENTIFICATION OF ALKYL BENZENES UP TO C₁₂ BY CAPILLARY GAS CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

II. RETENTION INDICES ON OV-101 COLUMNS AND RETENTION–MOLECULAR STRUCTURE CORRELATIONS

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SUMMARY

Synthesized multicomponent mixtures of alkylbenzenes with carbon atom numbers greater than ten were analyzed by capillary gas chromatography on the poly(dimethyl silicone) stationary phase OV-101 and gas chromatography–mass spectrometry with electron impact ionization. From the mass spectra acquired, the molecular weights were determined and the alkyl substituents specified. The assignment of the positions of the alkyl substituents of C₁₁ and C₁₂ alkylbenzenes was based on correlations between the retention data and molecular structures of alkylbenzenes arranged into homologous series. Retention indices on OV-101 at 100°C and temperature coefficients, dI/dT , are given for 34 C₇–C₁₀, 34 C₁₁ and 42 C₁₂ alkylbenzenes. The regularities of the chromatographic retention behaviour of alkylbenzenes are summarized.

INTRODUCTION

High-resolution capillary gas chromatography (HRCGC) is the most generally useful method for the analysis of complex hydrocarbon mixtures when the ultimate aim is to separate and identify or at least classify all the components. Several GC methods are available for the detailed analysis of C₇–C₁₀ alkylbenzenes and of some alkylbenzenes up to C₁₅ in petroleum samples and distillates¹. In a recently published review article on alkylbenzenes² it was shown that the best interlaboratory reproducibility of isothermal retention data was achieved on the non-polar stationary phases

squalane and silicones. However, due to the low temperature stability of squalane and therefore the long analysis time for the analysis of alkylbenzenes with more than nine carbon atoms, the non-polar silicones OV-101 and SE-30 are much more preferable. There are published isothermal retention indices on OV-101³⁻⁵ and SE-30^{6,7} for alkylbenzenes with carbon atom numbers up to C₁₀. For higher alkylbenzenes, particularly isomers with several short alkyl chains in the aromatic ring, there are very few published retention data on non-polar silicones^{3,5,7}.

Chromatographic techniques are often insufficient for the positive identification of components in a multicomponent mixture. Obtaining both retention index and spectrometric data by capillary gas chromatography-mass spectrometry (CGC-MS) has greatly improved the identification of unknown individual components in complex hydrocarbon mixtures⁸. The most widely used technique, CGC-MS with electron-impact (EI) ionization, can unambiguously detect alkylbenzenes in hydrocarbon mixtures⁹⁻¹². However, because of some drawbacks with this technique in the differentiation of structural isomers, the lack of standard materials and the low precision of calculation methods for predicting retention data⁶, structure-retention correlations based on precise measurements for alkylbenzenes of lower molecular weight may be justified for the identification of alkylbenzenes of higher molecular weight¹³.

The GC retention parameters of hydrocarbons are usually determined in particular by intermolecular van der Waals forces, specifically by dispersion forces if the separation occurs in a column containing a non-polar liquid stationary phase. The retention index value is determined by the structural characteristics of the compounds analyzed, by the type and position of the functional groups, the position of the double bond and by steric effects¹⁴⁻²⁴. The dependence of the retention behaviour of alkylbenzenes on their molecular structure has been studied for various stationary phases: non-polar, squalane²⁴⁻³⁰, OV-101^{3,30,31}, SE-30⁶; slightly polar, UCON LB-550^{28,32}, UCON HP-250²⁸, Citroflex A-4²⁵⁻²⁷; polar, Carbowax 20M^{28,32}, 6000³³, 400^{33,34}, TCEP²⁵⁻²⁷. Physico-chemical properties and structural parameters were also utilized for the calculation and prediction of retention indices of alkylbenzenes³⁵⁻³⁸.

The aim of the present paper was to increase the number of published retention indices of alkylbenzenes with carbon atom numbers greater than ten on the non-polar silicone stationary phase OV-101 and to broaden the knowledge of retention behaviour of alkylbenzenes in connection with their molecular structure. Owing to the lack of standard higher alkylbenzenes, mixed samples were prepared by alkylation reactions of benzene or alkylbenzenes using alkyl halogenides described previously (Part I)³⁹. The characterization of the alkylbenzenes with carbon atom numbers > 10 and without published retention indices was performed on the basis of GC-MS results, correlation between retention data and molecular structure and by application of quantum chemistry methods for studying the stability of isomers formed during synthesis and for interpretation of retention data of alkylbenzenes.

Alkylbenzenes were identified in 25 synthesized mixed samples prepared by various Friedel-Crafts alkylation reactions described in our previous paper³⁹ using glass capillary columns (50 m × 0.25 mm I.D.) statically coated with the stationary phase OV-101.

EXPERIMENTAL

GC measurements were performed on a Carlo Erba gas chromatograph (Model 2350, Milan, Italy) equipped with a flame ionization detector and a stream splitter, using nitrogen as the carrier gas at a linear velocity of about 10 cm/s under isothermal conditions at 100 and 120°C. Methane was used for the determination of the gas hold-up time. The elution time was measured with a digital stop-watch Time calculator RM 4111 (Tesla Rožnov, Czechoslovakia).

GC-MS measurements with EI ionization were performed using an HP 5995 instrument under temperature-programmed conditions (initial temperature 80°C, increased at 1°C/min, final temperature 190°C with the isothermal experiment) in an HP column Ultra 2 (50 m × 0.2 mm I.D.) with the chemically bonded phase SE-54. Helium was used as the carrier gas.

RESULTS AND DISCUSSION

Samples of alkylbenzenes obtained by Friedel-Crafts alkylation reactions with the aim of preparing C₁₂ alkylbenzenes with two or more small alkyl substituents in the benzene ring comprised multicomponent mixtures due to the formation of C₁₄ and C₁₅ alkylbenzenes and as the result of isomerization, disproportionation and transalkylation reactions³⁹. All the components of 25 samples were characterized by their retention indices at 100°C and their temperature coefficients, dI/dT , measured on OV-101 capillary columns with a film thickness of 0.35 μm which should be sufficient for the measurement of reproducible retention data⁴⁰. The efficiency of the columns used was $N_e = 127\,866$ for $k = 5$. The separation of several isomers did not improve significantly when using a more efficient system ($N_e = 395\,720$, $k = 4.4$).

After GC-MS analysis in EI ionization mode, from collected mass spectra it was possible to determine the molecular weights of individual alkylbenzenes (from the molecular ions), the type and number of alkyl groups². In several cases, however, when the concentration of the solute analyzed was small and therefore the quality of the spectra acquired was low, it was not possible to determine the type and number of alkyls in the ring, only the number of carbon atoms. For alkylbenzenes with carbon numbers > 10, for which there are no literature retention and mass spectral data, the most probable structures were proposed by interpretation of the mass spectra acquired (according to the characteristic fragment ions), however without determination of the positions of the alkyl substituents.

The assignment of the final structure (position of substituents) of alkylbenzenes was based mainly on structure-retention correlations. First we used the dependences of the retention indices, I , selective indices, I^* (ref. 41) and homeomorph factors, H (refs. 15-17) on the number of carbon atoms (nC) of the alkylbenzenes arranged in homologous series⁴². The dependences of I on nC were linear for series with narrow (straight) alkyl substituents (see Fig. 1), and for in all other series studied the correlation coefficients of the dependences were very close to 1 as the scale on the y axis (700-1500 i.u.) was significantly different compared to the scale on the x axis ($nC = 7-15$). The precision of these dependences for the assignment of structure to the given alkylbenzenes is not sufficient. The largest differences between the measured retention indices and those calculated by linear regression were found for n -propyl-

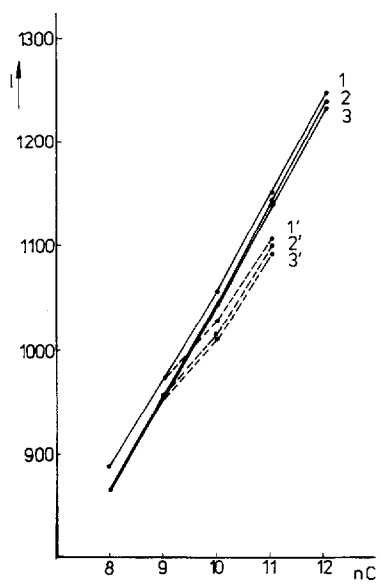


Fig. 1. The dependence of Kováts indices, I , on the number of carbon atoms (nC) for homologous series 1–3 and 1'–3'. Series: (1) 1,2-DiMeB, 1-Me-2-EtB, 1-Me-2-*n*-PrB, 1-Me-2-*n*-BuB, 1-Me-2-*n*-PeB; (2) 1,4-DiMeB, 1-Me-4-EtB, 1-Me-4-*n*-PrB, 1-Me-4-*n*-BuB, 1-Me-4-*n*-PeB; (3) 1,3-DiMeB, 1-Me-3-EtB, 1-Me-3-*n*-PrB, 1-Me-3-*n*-BuB, 1-Me-3-*n*-PeB; (1') 1,2-DiMeB, 1-Me-2-EtB, 1-Me-2-*iso*-PrB, 1-Me-2-*sec.*-BuB; (2') 1,4-DiMeB, 1-Me-4-EtB, 1-Me-4-*iso*-PrB, 1-Me-4-*sec.*-BuB; (3') 1,3-DiMeB, 1-Me-3-EtB, 1-Me-3-*iso*-PrB, 1-Me-3-*sec.*-BuB. See Table I for abbreviations.

benzene (about 5 i.u.) which is connected with the so-called propyl effect^{25–27}. The measured and calculated retention indices for some homologous series are given in Table I.

For a particular solute the retention behaviour is determined by the magnitude of the intermolecular forces involved in its interaction with the stationary phase. With *n*-alkanes these forces are exclusively dispersion forces which are additive and increase with molecular weight. As heteroatoms and multiple bonds are introduced into a molecule, polar forces contribute increasingly to the overall retention. The retention behaviour of any solute is dependent upon its size, shape and functionality. The homeomorph factors, H , and selective indices, I^* , reflect the combined effects of molecular shape and functionality the values of which are closely related to molecular structure^{15–17,28,41}. According to definition, they are calculated from

$$H = I - I_n(\text{alkane}) \quad (1)$$

where I = measured retention index of an analyte and $I_n(\text{alkane})$ = index of *n*-alkane having the same carbon skeleton as that of the analyte, and

$$I^* = I - I_M \quad (2)$$

where I_M = the retention index of an hypothetical *n*-alkane having the same molecular weight as that of the analyte and defined by the expression $I_M = (M - 2.016)/$

TABLE I

MEASURED, y , AND LINEAR REGRESSION CALCULATED, Y , RETENTION INDICES FOR THREE HOMOLOGOUS SERIES FROM THE EQUATION

$y = a + bx$, where $x = nC$. $L_{1,2}$ = Confidence intervals. B = Benzene; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl.

Homologous series	Substance	x	y	Y	L_1	L_2
1	1,2-DiMeB	8	888.8	884.2	870.3	898.1
	1-Me-2-EtB	9	973.2	974.2	964.4	984.0
	1-Me-2- <i>n</i> -PrB	10	1057.0	1064.2	1056.2	1072.2
	1-Me-2- <i>n</i> -BuB	11	1153.3	1154.2	1144.4	1164.0
	1-Me-2- <i>n</i> -PeB	12	1248.7	1244.2	1230.3	1258.1
$y = 164.3 + 89.99x; r = 0.99941; s_{y,x} = 5.63$						
2	1,4-DiMeB	8	865.8	863.1	853.7	872.5
	1-Me-4-EtB	9	957.1	957.1	950.5	963.7
	1-Me-4- <i>n</i> -PrB	10	1045.6	1051.1	1045.7	1056.5
	1-Me-4- <i>n</i> -BuB	11	1145.5	1145.1	1138.6	1151.7
	1-Me-4- <i>n</i> -PeB	12	1241.5	1239.1	1229.7	1248.5
$y = 111.3 + 93.98x; r = 0.99975; s_{y,x} = 3.81$						
3	1,3-DiMeB	8	865.8	862.8	852.9	872.7
	1-Me-3-EtB	9	954.8	955.2	948.2	962.2
	1-Me-3- <i>n</i> -PrB	10	1041.9	1047.5	1041.8	1053.2
	1-Me-3- <i>n</i> -BuB	11	1140.1	1139.9	1132.9	1146.9
	1-Me-3- <i>n</i> -PeB	12	1235.1	1232.4	1222.5	1242.3
$y = 123.64 + 92.39x; r = 0.9997; s_{y,x} = 4.03$						

0.14026. With alkylbenzenes, extension of the π -electron system increases selectivity on an apolar phase. In the case of alkyl substitution, the values of H and I^* appear to be dependent upon the nature and position of the substituent groups. For the individual homologous series of alkylbenzenes (1–3) studied, characteristic dependences were obtained for both these parameters. The courses of the dependences were similar (Figs. 2 and 3).

For the identification of individual alkylbenzenes with $nC > 10$, homeomorph factors were utilized. Alkylbenzenes with narrow or branched substituents were arranged into homologous series, and from the measured retention data the homeomorph factors were calculated. The characteristic dependences of H on nC were used for assignment of the positions of the alkyl substituents in isomers of all C_{11} and many C_{12} alkylbenzenes studied and of some higher alkylbenzenes. Examples of the dependences of H on nC for several homologous series are given in Figs. 3–5. In series of alkylbenzenes with increasing numbers of methyl groups in the benzene ring the homeomorph factors increase with increasing number of carbon atoms, Fig. 4 (homologous series 4–8). In alkylbenzenes with increasing alkyl chain length, in homologous series the homeomorph factor decreases and is approximately constant (Figs. 3 and 5). When the homologous series starts with a relatively high number of carbon atoms (10) it was not possible to propose a structure for C_{11} , C_{12} or higher alkylben-

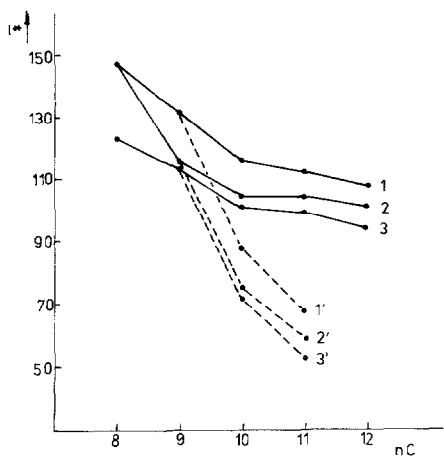


Fig. 2. The dependence of selectivity indices, I^* , on nC for homologous series 1–3 and 1'–3' (the same as in Fig. 1).

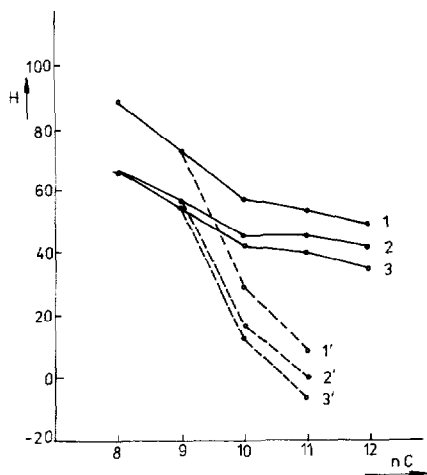


Fig. 3. The dependence of homeomorph factors, H , on nC for homologous series 1–3 and 1'–3' (the same as in Fig. 1).

zenes. Instead the structures of some isomers of C_{11} , C_{12} alkylbenzenes were assigned by application of a quantum chemistry method for compound identification by studying the stability of the isomers and the probability of their formation during synthesis⁴³. Quantum chemistry was further used for the interpretation of retention data of alkylbenzenes with the aim of finding and interpreting relationships between reten-

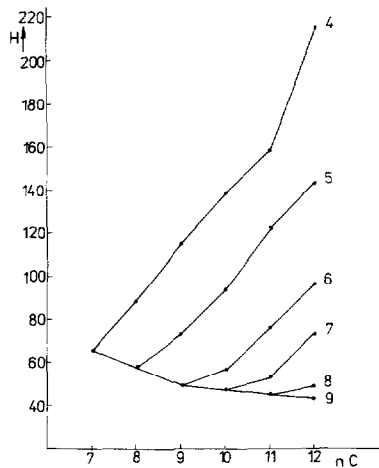


Fig. 4. The dependence of homeomorph factors, H , on nC for homologous series 4–9. Series: (4) MeB, 1,2-DiMeB, 1,2,3-TriMeB, 1,2,3,4-TetraMeB, 1,2,3,4,5-PeMeB, 1,2,3,4,5,6-HeMeB; (5) EtB, 1-Me-2-EtB, 1,2-DiMe-3-EtB, 1,2,3-TriMe-4-EtB, 1,2,3,4-TetraMe-5-EtB; (6) *n*-PrB, 1-Me-2-*n*-PrB, 1,2-DiMe-3-*n*-PrB, 1,2,3-TriMe-4-*n*-PrB; (7) *n*-BuB, 1-Me-2-*n*-BuB, 1,2-DiMe-3-*n*-BuB; (8) *n*-PeB, 1-Me-2-*n*-PeB; (9) MeB, EtB, *n*-PrB, *n*-BuB, *n*-PeB, *n*-HeB.

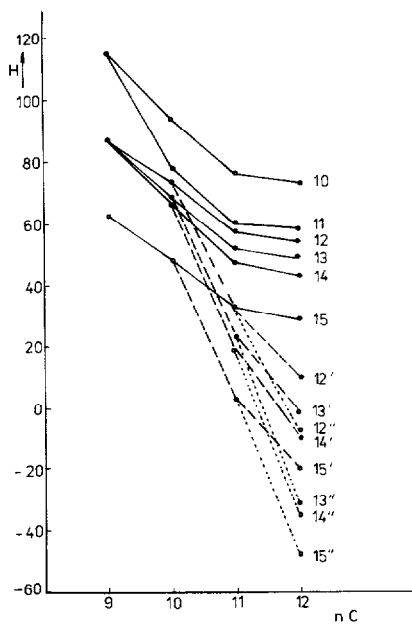


Fig. 5. The dependence of homeomorph factors, H , on nC for homologous series 10–15, 12'–15' and 12''–15''. Series: (10) 1,2,3-TriMeB, 1,2-DiMe-3-EtB, 1,2-DiMe-3-*n*-PrB, 1,2-DiMe-3-*n*-BuB; (11) 1,2,3-TriMeB, 1,3-DiMe-2-EtB, 1,3-DiMe-2-*n*-PrB, 1,3-DiMe-2-*n*-BuB; (12) 1,2,4-TriMeB, 1,2-DiMe-4-EtB, 1,2-DiMe-4-*n*-PrB, 1,2-DiMe-4-*n*-BuB; (13) 1,3,4-TriMeB, 1,3-DiMe-4-EtB, 1,3-DiMe-4-*n*-PrB, 1,3-DiMe-4-*n*-BuB; (14) 1,2,4-TriMeB, 1,4-DiMe-2-EtB, 1,4-DiMe-2-*n*-PrB, 1,4-DiMe-2-*n*-BuB; (15) 1,3,5-TriMeB, 1,3-DiMe-5-EtB, 1,3-DiMe-5-*n*-PrB, 1,3-DiMe-5-*n*-BuB; (12') 1,2,4-TriMeB, 1,2-DiMe-4-EtB, 1,2-DiMe-4-*iso*-PrB, 1,2-DiMe-4-*sec*-BuB; (13') 1,3,4-TriMeB, 1,3-DiMe-4-EtB, 1,3-DiMe-4-*iso*-PrB, 1,3-DiMe-4-*sec*-BuB; (14') 1,2,4-TriMeB, 1,4-DiMe-2-EtB, 1,4-DiMe-2-*iso*-PrB, 1,4-DiMe-2-*sec*-BuB; (15') 1,3,5-TriMeB, 1,3-DiMe-5-EtB, 1,3-DiMe-5-*iso*-PrB, 1,3-DiMe-5-*sec*-BuB; (12'') 1,2,4-TriMeB, 1,2-DiMe-4-EtB, 1,2-DiMe-4-*iso*-PrB, 1,2-DiMe-4-*tert*-BuB; (13'') 1,3,4-TriMeB, 1,3-DiMe-4-EtB, 1,3-DiMe-4-*iso*-PrB, 1,3-DiMe-4-*tert*-BuB; (14'') 1,2,4-TriMeB, 1,4-DiMe-2-EtB, 1,4-DiMe-2-*iso*-PrB, 1,4-DiMe-2-*tert*-BuB; (15'') 1,3,5-TriMeB, 1,3-DiMe-5-EtB, 1,3-DiMe-5-*iso*-PrB, 1,3-DiMe-5-*tert*-BuB.

tion indices and calculated interaction energies (between partitioned substances and the stationary phase) and to use the obtained correlation equations for the prediction of retention data. Alkylbenzenes (C_{11} , C_{12}) with defined structure, their retention indices, I , and temperature coefficients, dI/dT , on OV-101 are given in Table II. Also included are data for alkylbenzenes with $nC \leq 10$ for interlaboratory comparison of retention data of alkylbenzenes of lower molecular weight.

The regularities in the chromatographic retention of alkylbenzenes on the poly-(dimethyl silicone) stationary phase OV-101 were studied and explained by Gerasimenko and Nabivach³. The differences in retention indices of aromatic hydrocarbons between OV-101 and squalane are 10–12 i.u. and higher. The order of elution of alkylbenzenes corresponds to their boiling points; the dependence of the Kováts retention indices of lower alkylbenzenes on their boiling points is given in Fig. 6. Aromatic compounds possess systems of delocalized π -electrons which are capable of electron pair donor-acceptor interactions. Alkyl substituents as strong σ -donors evoke deformation of the electronic state of the benzene ring and therefore influence

TABLE II

RETENTION INDICES, I , OF ALKYL BENZENES ON OV-101 STATIONARY PHASE AT 100°C AND THEIR TEMPERATURE COEFFICIENTS, dI/dT

<i>Compound</i>	I	dI/dT	<i>Compound</i>	I	dI/dT
C_{7-10}					
MeB	765.5	0.260	1-Me-2- <i>iso</i> -PrB	1029.1	0.292
EtB	857.7	0.245	1-Me-3- <i>n</i> -PrB	1041.9	0.272
1,3-DiMeB	865.8	0.245	1,3-DiEtB	1039.5	0.244
1,4-DiMeB	865.8	0.250	1-Me-4- <i>n</i> -PrB	1045.6	0.280
1,2-DiMeB	888.8	0.290	<i>n</i> -BuB	1047.4	0.270
<i>iso</i> -PrB	919.5	0.275	1,4-DiEtB	1046.0	0.265
<i>n</i> -PrB	949.3	0.265	1,3-DiMe-5-EtB	1048.4	0.240
1-Me-3-EtB	954.8	0.246	1,2-DiEtB	1051.4	0.310
1-Me-4-EtB	957.1	0.254	1-Me-2- <i>n</i> -PrB	1057.0	0.334
1,3,5-TriMeB	963.0	0.240	1,4-DiMe-2-EtB	1067.2	0.300
1-Me-2-EtB	973.2	0.305	1,3-DiMe-4-EtB	1069.0	0.310
1,2,4-TriMeB	987.3	0.310	1,2-DiMe-4-EtB	1074.3	0.318
<i>tert.</i> -BuB	986.8	0.310	1,3-DiMe-2-EtB	1078.5	0.330
<i>sec.</i> -BuB	1005.2	0.310	1,2-DiMe-3-EtB	1094.1	0.360
1-Me-3- <i>iso</i> -PrB	1012.7	0.235	1,2,4,5-TetraMeB	1106.0	0.347
1,2,3-TriMeB	1015.5	0.370	1,2,3,5-TetraMeB	1109.3	0.375
1-Me-4- <i>iso</i> -PrB	1016.5	0.263	1,2,3,4-TetraMeB	1139.0	0.440
C_{11}					
1-Et-3- <i>iso</i> -PrB	1092.5	0.230	1,4-DiMe-2- <i>n</i> -PrB	1147.5	0.297
1-Me-3- <i>sec.</i> -BuB	1093.5	0.281	1,3-DiEt-4-MeB	1149.1	0.305
1-Et-2- <i>iso</i> -PrB	1098.2	0.314	1,3-DiMe-4- <i>n</i> -PrB	1152.1	0.302
1-Me-4- <i>sec.</i> -BuB	1100.0	0.282	1-Me-2- <i>n</i> -BuB	1153.3	0.328
1-Et-4- <i>iso</i> -PrB	1103.5	0.260	1,2-DiEt-4-MeB	1154.2	0.315
1,3-DiMe-5- <i>iso</i> -PrB	1102.8	0.214	1,3-DiEt-2-MeB	1156.9	0.370
1-Me-2- <i>sec.</i> -BuB	1108.7	0.341	1,2-DiMe-4- <i>n</i> -PrB	1157.9	—
1,4-DiMe-2- <i>iso</i> -PrB	1118.7	0.252	1,3-DiMe-2- <i>n</i> -PrB	1160.5	0.303
1,3-DiMe-4- <i>iso</i> -PrB	1123.4	0.276	1,2-DiEt-3-MeB	1170.3	—
1-Et-3- <i>n</i> -PrB	1124.1	0.258	1,2,4-TriMe-5-EtB	1173.0	0.315
1,3-DiEt-5-MeB	1129.8	0.240	1,2-DiMe-3- <i>n</i> -PrB	1176.5	0.371
1,2-DiMe-4- <i>iso</i> -PrB	1130.4	0.287	1,3,5-TriMe-2-EtB	1182.8	0.324
1,3-DiMe-5- <i>n</i> -PrB	1132.6	0.235	1,2,5-TriMe-3-EtB	1184.3	0.329
1-Et-2- <i>n</i> -PrB	1133.5	0.284	1,2,3-TriMe-5-EtB	1193.2	0.340
1-Me-3- <i>n</i> -BuB	1140.1	0.249	1,2,4-TriMe-3-EtB	1215.1	0.431
1,4-DiEt-2-MeB	1143.7	0.300	PentaMeB	1259.9	0.435
1-Me-4- <i>n</i> -BuB	1145.5	0.280	1,2,3-TriMe-4-EtB	1222.4	—
C_{12}					
1- <i>iso</i> -Pr-2- <i>n</i> -PrB	1179.8	0.275	1-Me-2- <i>n</i> -PeB	1248.7	0.310
1-Et-4- <i>sec.</i> -BuB	1184.6	0.310	1,3-DiMe-4- <i>n</i> -BuB	1248.8	0.280
1- <i>iso</i> -Pr-4- <i>n</i> -PrB	1190.1	0.268	1,2,4-TriMe-5- <i>n</i> -PrB	1251.7	0.340
1,4-DiMe-2- <i>sec.</i> -BuB	1190.6	0.260	1,2-DiMe-4- <i>n</i> -BuB	1254.0	—
1,2-DiMe-4- <i>tert.</i> -BuB	1192.4	0.310	1,3-DiMe-2- <i>n</i> -BuB	1258.3	0.293
1,3-DiMe-4- <i>sec.</i> -BuB	1198.4	0.312	1,3,5-TriMe-2- <i>n</i> -PrB	1263.2	0.346
1,3,5-TriEtB	1206.2	0.118	1,2-DiMe-3- <i>n</i> -BuB	1273.6	0.311
1,3-Di- <i>n</i> -PrB	1209.2	0.260	1,2,5-TriMe-3- <i>n</i> -PrB	1276.6	0.354
1,2-DiMe-4- <i>sec.</i> -BuB	1209.7	0.285	1,2,3-TriMe-5- <i>n</i> -PrB	1278.8	0.397
1,4-Di- <i>n</i> -PrB	1220.6	0.297	1,2,3-TriMe-4- <i>n</i> -PrB	1297.0	0.422

TABLE II (continued)

Compound	<i>I</i>	dI/dT	Compound	<i>I</i>	dI/dT
1-Et-3- <i>n</i> -BuB	1220.6	0.250	1,2,3,4-TetraMe-5-EtB	1344.2	—
1,3-Di- <i>iso</i> -PrB	1140.8	0.208	1,2,4-TriEtB	1222.7	0.294
1,2-Di- <i>iso</i> -PrB	1150.2	0.255	1,3-DiMe-5- <i>n</i> -BuB	1229.1	0.208
1,3-DiMe-5- <i>tert.</i> -BuB	1151.9	0.230	1-Et-4- <i>n</i> -BuB	1231.9	0.302
1,4-Di- <i>iso</i> -PrB	1159.6	0.248	1,2,4-TriMe-5- <i>iso</i> -PrB	1232.7	0.250
1,4-DiMe-2- <i>tert.</i> -BuB	1164.4	0.180	1-Me-3- <i>n</i> -PeB	1235.1	0.245
1,3-DiMe-4- <i>tert.</i> -BuB	1168.3	0.280	1,3,5-TriMe-2- <i>iso</i> -PrB	1238.5	0.265
1-Et-3- <i>sec.</i> -BuB	1170.5	0.272	1-Me-4- <i>n</i> -PeB	1241.5	0.267
1- <i>iso</i> -Pr-3- <i>n</i> -PrB	1175.7	0.238	1,4-DiMe-2- <i>n</i> -BuB	1243.2	0.257
1-Et-2- <i>sec.</i> -BuB	1177.5	—	1,2,3-TriEtB	1245.7	0.310
1,3-DiMe-5- <i>sec.</i> -BuB	1179.4	0.227	1,2,3-TriMe-5- <i>iso</i> -PrB	1245.5	0.295

the mutual interactions with the molecules of the stationary phase. According to the literature and our results, the following conclusions can be drawn about the retention of alkylbenzenes on OV-101.

(1) For monoalkylbenzenes the retention indices increase with increasing alkyl chain length. Substitution of the benzene ring by a methyl group results in an increase in retention indices of greater than 100 i.u. compared to benzene owing to increased solute-stationary phase interaction. For C₈, C₉ alkylbenzenes the increment I_{CH_2} decreases and is lower than 100 i.u. For *n*-propylbenzene a considerable decrease in retention index is connected with the propyl effect^{25-27,44}. For C₁₀ and higher alkyl-

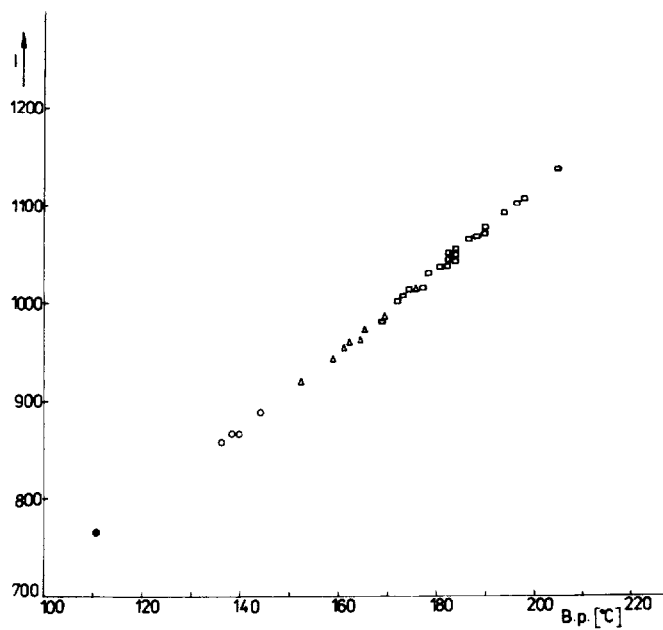


Fig. 6. The dependence of Kovats indices, *I*, on the boiling points for C₇ (●), C₈ (○), C₉ (△) and C₁₀ (□) alkylbenzenes.

benzenes the sorption process is dominated by the alkyl substituent and therefore the value of I_{CH_2} approximates to 100 i.u. With branched substituents there is a decrease in retention compared to straight chain ones, the order of elution being *tert.*- < *iso.*- < *sec.*- < *n*-alkyl. The temperature coefficients, dI/dT , slightly increase with increasing alkyl chain length, and are higher for branched substituents.

(2) For dialkylbenzenes the elution order corresponds to two groups of isomers. In the first group there are alkylbenzenes with one methyl substituent (dimethyl, methyl-ethyl, methyl-isopropyl, methyl-*n*-propyl, methyl-*sec.*-butyl, methyl-*n*-butyl, methyl-*n*-pentyl) and diethylbenzenes with the elution order of 1,3 < 1,4 < 1,2. The second group comprises alkylbenzenes with both alkyl substituents having $nC > 1$ (ethyl-isopropyl, ethyl-*n*-propyl, ethyl-*sec.*-butyl, ethyl-*n*-butyl, diisopropyl, isopropyl-*n*-propyl, di-*n*-propyl) with the elution order 1,3 < 1,2 < 1,4. These elution orders of the alkylbenzene isomers was explained by the change in electron density of the delocalized π -orbitals of the hydrocarbons studied upon substitution by the two alkyl groups³. On increasing the size of an alkylbenzene molecule by addition of a methyl group the increment I_{CH_2} is higher than 100 i.u., but on prolonging the alkyl chain length to C_5 the value of I_{CH_2} is lower than 100. For dialkylbenzene isomers, I_{CH_2} increases in the order of 1,3 < 1,4 < 1,2 when the substituent is methyl. Temperature coefficients of dialkylbenzene positional isomers with one methyl substituent and diethylbenzene increase in the order 1,3 < 1,4 < 1,2.

(3) For polyalkylbenzenes the number of possible isomers depends on the number and type of alkyl groups present in the benzene ring. As a general rule, among positional isomers, the most symmetrical molecules are eluted first; high retention is observed for molecules with adjacent substituents, the highest being for polymethylbenzenes with *ortho* methyl groups. In trialkylbenzenes with only one kind of substituents the order of elution of the three possible isomers is 1,3,5 < 1,2,4 < 1,2,3; the temperature coefficients increase in the same order, the highest values being found for trimethylbenzenes. Increase in the alkyl chain length results in decreasing I_{CH_2} and dI/dT values. For trialkylbenzenes with two different substituents, the order of elution of the six possible isomers is 1,3-5 < 1,4-2 < 1,3-4 < 1,2-4 < 1,3-2 < 1,2-3; the dI/dT values of these isomers increase in the same sequence.

For tetramethylbenzenes the retention indices increase in the order 1,2,4,5 < 1,2,3,5 < 1,2,3,4. Generally polymethylbenzenes have relatively high dI/dT values compared with other isomeric alkylbenzenes, the highest being those with the most methyl groups in *ortho* position. By prolonging one methyl group there is a slight decrease in the value of I_{CH_2} , dependent on its position. The retention of the six isomers increases in the order 1,2,4-5 < 1,3,5-2 < 1,2,5-3 < 1,2,3-5 < 1,3,4-2 < 1,2,3-4. The I_{CH_2} and dI/dT values of trimethylalkylbenzenes also increase in this order.

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