

CHROM. 14,233

DEPENDENCE OF RETENTION INDICES OF ALKYL BENZENES ON THEIR MOLECULAR STRUCTURE

JIŘÍ MACÁK*

Institute of Chemical Technology, Prague (Czechoslovakia)

VALENTIN NABIVACH

Institute of Chemical Technology, Dniepropetrovsk (U.S.S.R.)

and

PETR BURYAN and STANISLAV ŠINDLER

Institute of Chemical Technology, Prague (Czechoslovakia)

(Received July 3rd, 1981)

SUMMARY

An open tubular column coated with squalane was used for the measurement of the retention of approximately 70 alkyl derivatives of benzene and naphthalene at two temperatures. Steric factors were shown to have a decisive effect on the elution sequence of isomers and on the retention index increment when the same alkyl groups were introduced at different positions of the hydrocarbon molecule. The increase in the Kováts index was higher when the alkyl groups were introduced in the ring than in a side chain. Proportionality factors proposed for calculating differences in the retention indices of aromatic isomers on the basis of differences in their boiling points varied in the range 3.9-4.5.

INTRODUCTION

The gas chromatographic (GC) retention parameters of hydrocarbons are usually determined in particular by intermolecular Van der Waals forces and by dispersion forces, if the separation occurs in a column containing a non-polar liquid stationary phase. The fact that the interaction forces are additive led Kováts¹ to suggest a retention index, which in its quantitative form reflects the incremental contributions to the free energy of interaction from the individual structural groups of a molecule. Thus, the value of this retention index is determined by the structural characteristics of the compounds analyzed, by the types and positions of the functional groups and the positions of the double bonds and by steric effects²⁻²⁰. There is a linear correlation between the Kováts index and the free energy of dissolution, as well as other thermodynamic functions of dissolution²⁻²⁶. Attention has been focused on the study of the laws of retention of aromatic hydrocarbons characterized by particular molecular structures.

The measurement of Kováts' indices for aromatic hydrocarbons and the prob-

lems of qualitative evaluation of actual commercial mixtures have been the subject of a great number of studies²⁷⁻³⁶. The dependence of the retention indices and their increments on column temperature, structure and physicochemical properties of alkylbenzenes have been reported^{32,36-39}.

In the present study Kováts' indices were measured for aromatic hydrocarbons in chemical products of thermal treatment of lignite and bituminous coal. On the basis of the data obtained, the relation of the retention indices and their increments to the structural characteristics of the aromatic hydrocarbons was investigated.

EXPERIMENTAL

The measurements were made on a Chrom 41 chromatograph (Laboratory Instruments, Prague, Czechoslovakia) equipped with a flame ionization detector. Conditions: column, stainless-steel coated open capillary (50 m × 0.25 mm); stationary phase, squalane; temperatures, column 86.96°C, evaporation cell 260°C; carrier gas (nitrogen) inlet pressure, 103,950 Pa; splitting ratio, 1:100; flow-rates, hydrogen 30 ml/min, air 350 ml/min; sample volume, $0.1 \cdot 10^{-3}$ – $0.2 \cdot 10^{-3}$ ml; column efficiency, 71,500 theoretical plates (with respect to *m*-xylene).

The hydrocarbons studied were injected by means of a Terumo (Japan) microsyringe in the form of mixtures of five to seven compounds. The retention times of the hydrocarbons were obtained at a known chart speed (20 mm/min) from at least three measurements for each compound. After correction for the retention time of methane, the values were employed for the calculation of the Kováts indices using a special program and a Hewlett-Packard calculator 9830A. The experimental results and variations in the retention indices per °C, $\bar{\epsilon}I/\bar{\epsilon}T$, are listed in Table I.

RESULTS AND DISCUSSION

The values of $\bar{\epsilon}I/\bar{\epsilon}T$ for the aromatic hydrocarbons studied and their isomers vary over a fairly wide range: monoalkylbenzenes, 0.21–0.49; dialkylbenzenes, 0.15–0.33; trialkylbenzenes, 0.17–0.27; tetramethylbenzenes, 0.31–0.35; naphthalene and its derivatives, 0.32–0.58. It is to be noted that the corresponding values for many cycloparaffins and cycloolefins⁹ are comparable with the values of some aromatic hydrocarbons, which complicates group identification in multi-component mixtures.

The investigation of intermolecular interactions in squalane, which lacks a dipole moment, induction forces and hydrogen bonding, led to the conclusion that these interactions are determined by dispersion forces, the distinguishing feature of which is their additivity. The extent and the importance of the dispersion forces depends on the shapes and volumes of the molecules of the substances separated, and on the stereochemistry of the substituents in the aromatic ring.

The retention indices (Table I) vary with the boiling points of alkylbenzenes, which in turn are a function of vapour pressure. Fig. 1 shows the linear relationship of the retention indices and logarithms of vapour pressure of alkylbenzenes. Similar relationships were found for numerous isomers, the elution sequence for the particular group of hydrocarbons being dependent on the structure and mutual position of the substituents in the benzene ring (Table II).

The replacement of one methyl group of dimethylbenzene with an arbitrary

TABLE I

RETENTION INDICES OF ALKYL BENZENES ON SQUALANE AND THEIR TEMPERATURE COEFFICIENTS

Compound	Temperature ($^{\circ}\text{C}$)		$\partial I/\partial T \cdot 10$
	86	96	
Benzene	648.0	650.22	2.2
Methylbenzene	755.0	757.1	2.1
Phenylacetylene	830.4	834.1	3.7
Ethylbenzene	845.3	847.7	2.4
<i>p</i> -Dimethylbenzene	859.0	861.2	2.3
<i>m</i> -Dimethylbenzene	861.0	863.2	2.2
<i>o</i> -Dimethylbenzene	880.8	883.0	2.2
Isopropylbenzene	904.1	906.7	2.6
Allylbenzene	917.8	920.0	2.2
<i>n</i> -Propylbenzene	932.7	935.1	2.4
Styrene	872.0	874.5	2.5
α -Methylstyrene	957.8	960.0	2.2
2-Methylstyrene	972.1	974.2	2.1
3-Methylstyrene	976.3	978.7	2.4
4-Methylstyrene	978.6	980.3	1.7
1-Methyl-3-ethylbenzene	945.9	947.4	1.5
1-Methyl-4-ethylbenzene	948.2	950.4	2.2
1-Methyl-2-ethylbenzene	961.1	963.4	2.3
1,3,5-Trimethylbenzene	965.0	967.1	2.1
1,2,4-Trimethylbenzene	982.0	985.3	2.5
1,2,3-Trimethylbenzene	1007.8	1010.5	2.7
<i>tert.</i> -Butylbenzene	969.9	972.5	2.6
Isobutylbenzene	985.5	988.3	2.8
<i>sec.</i> -Butylbenzene	986.4	989.1	2.7
<i>n</i> -Butylbenzene	1032.3	1034.9	2.6
1-Methyl-3-isopropylbenzene	1000.3	1001.8	1.5
1-Methyl-4-isopropylbenzene	1007.7	1009.9	2.2
1-Methyl-2-isopropylbenzene	1013.5	1015.8	2.3
2,3-Dihydroindene	1011.2	1014.5	3.3
Indene	1011.8	1015.7	3.9
2-Methylindene	1054.1	1057.7	3.6
1,2-Dimethylhydrindene	1124.7	1128.8	4.1
5-Ethylindene	—	1203.6	—
1,3-Diethylbenzene	1025.7	1028.1	2.4
1,2-Diethylbenzene	1034.8	1038.1	3.3
1,4-Diethylbenzene	1036.8	1039.3	2.5
1-Methyl-3- <i>n</i> -propylbenzene	1030.4	1032.8	2.4
1-Methyl-4- <i>n</i> -propylbenzene	1035.9	1038.8	2.9
1-Methyl-2- <i>n</i> -propylbenzene	1042.0	1045.4	3.4
<i>trans</i> -Decahydronaphthalene	1064.7	1069.3	4.6
<i>cis</i> -Decahydronaphthalene	1101.4	1106.2	4.8
<i>tert.</i> -Pentylbenzene	1065.9	1069.5	3.6
<i>sec.</i> -Pentylbenzene	1074.7	1077.8	3.1
Isopentylbenzene	1094.9	1098.4	3.5
<i>n</i> -Pentylbenzene	1131.3	1136.2	4.9
1-Methyl-3- <i>tert.</i> -butylbenzene	1053.6	1056.1	2.6
1-Methyl-4- <i>tert.</i> -butylbenzene	1072.3	1074.7	2.4

(Continued on p. 288)

TABLE I (continued)

Compound	Temperature ($^{\circ}\text{C}$)		$\bar{c}l/\bar{c}T \cdot 10$
	86	96	
1-Methyl-2- <i>tert.</i> -butylbenzene	1088.4	1090.9	2.5
2,4-Dimethylstyrene	1080.9	1084.2	3.3
1-Methyl-4- <i>sec.</i> -butylbenzene	1088.7	1091.0	2.3
1-Ethyl-3-isopropylbenzene	1074.3	1076.5	2.2
1-Ethyl-2-isopropylbenzene	1076.9	1079.8	2.9
1-Ethyl-4-isopropylbenzene	1094.5	1097.3	2.8
1,2,4,5-Tetramethylbenzene	1102.8	1105.9	3.1
1,2,3,5-Tetramethylbenzene	1108.4	1111.4	3.0
1,2,3,4-Tetramethylbenzene	1129.2	1132.7	3.5
1-Ethyl-3- <i>n</i> -propylbenzene	1108.4	1111.1	2.7
1-Ethyl-2- <i>n</i> -propylbenzene	1116.7	1119.2	2.5
1-Ethyl-4- <i>n</i> -propylbenzene	1121.9	1125.2	3.3
1,3-Diisopropylbenzene	1116.3	1118.8	2.5
1,2-Diisopropylbenzene	1118.1	1120.3	2.2
1,4-Diisopropylbenzene	1151.2	1153.4	2.2
1,2-Dihydronaphthalene	1127.9	1133.2	5.3
1,2,3,4-Tetrahydronaphthalene	1133.2	1137.6	4.4
Naphthalene	1146.0	1151.8	5.8
1-Ethyl-4- <i>tert.</i> -butylbenzene	1158.5	1161.0	2.5
1,4-Dimethyl-2- <i>n</i> -butylbenzene	1165.3	1167.1	1.8
1,3,5-Triethylbenzene	1189.1	1190.8	1.7
1,2,4-Triethylbenzene	1206.3	1208.0	1.7
<i>n</i> -Hexylbenzene	1225.4	1228.8	3.4
Pentamethylbenzene	1253.9	1258.6	4.7
1-Methylnaphthalene	1264.7	1267.9	3.2
2-Methylnaphthalene	1265.5	1271.1	5.6
1,3,5-Trisopropylbenzene	1285.7	1287.5	1.8

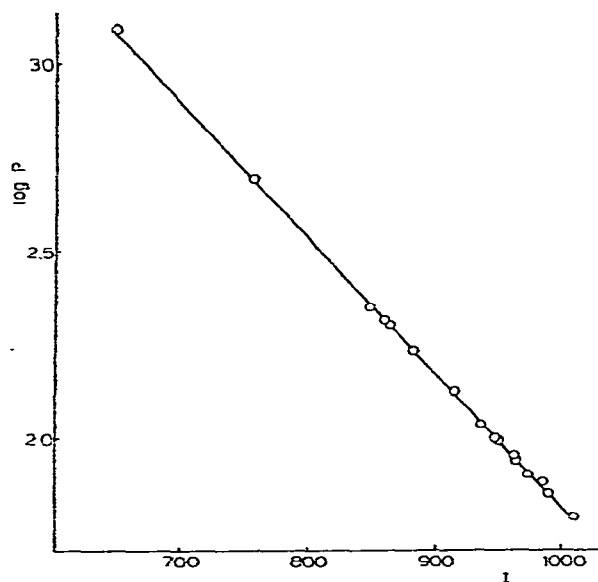


Fig. 1. Dependence of the retention indices on the logarithms of the vapour pressure of alkylbenzenes at 96 C.

TABLE II

ELUTION ORDER OF DIALKYL BENZENES ON SQUALANE IMPREGNATED OPEN TUBULAR COLUMN

No. of hydrocarbon group	Group constituents	Elution sequence
I	Dimethylbenzenes	1 <i>para</i> 2 <i>meta</i> 3 <i>ortho</i>
II	Methylethylbenzenes Methylpropylbenzenes Methylisopropylbenzenes Methylbutylbenzenes Methylpentylbenzenes	1 <i>meta</i> 2 <i>para</i> 3 <i>ortho</i>
III	Ethylpropylbenzenes Ethylisopropylbenzenes Diethylbenzenes Diisopropylbenzenes Ethylbutylbenzenes	1 <i>meta</i> 2 <i>ortho</i> 3 <i>para</i>

alkyl radical C_2-C_5 results in enhanced elution of the *meta* isomer as compared with that of the *para* isomer (Fig. 2a). Replacement of the other methyl group with an alkyl radical C_2-C_3 further retards the *para* isomer, which in this case leaves the column after the *meta* and *ortho* isomers (Fig. 2b). In Fig. 3 both these effects are shown within one homologous series of alkylbenzenes.

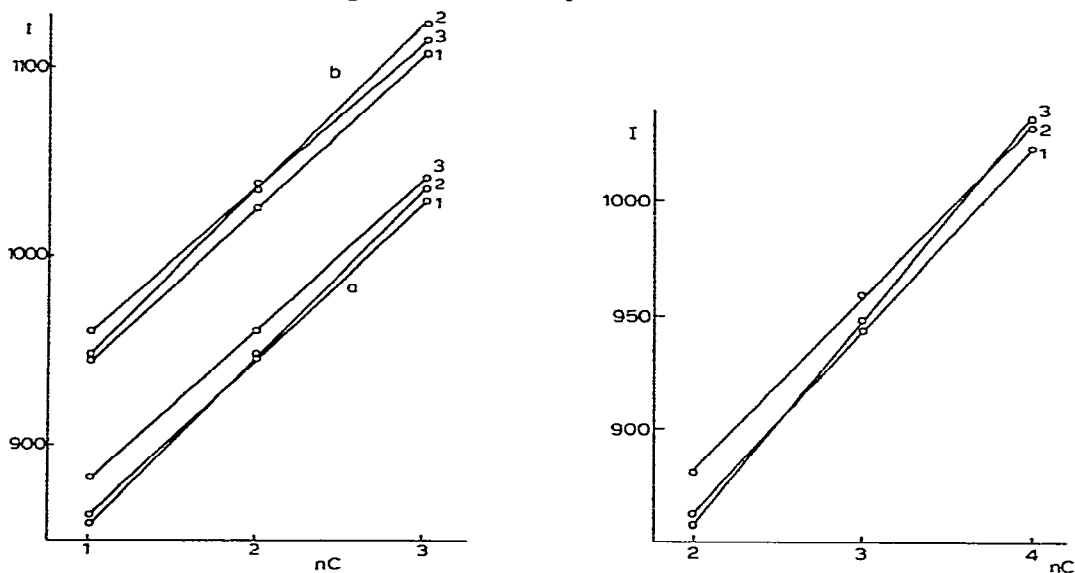


Fig. 2. Dependence of the retention indices of monosubstituted isomers of methylbenzene (a) and ethylbenzene (b) on the number of carbon atoms of the substituents. 1 = *meta*; 2 = *para*; 3 = *ortho* isomers.

Fig. 3. Dependence of the retention indices and elution sequences of isomers on the number of carbon atoms of the alkyl group of C_3-C_{10} alkylbenzenes. 1 = *meta*; 2 = *ortho*; 3 = *para* isomers.

The explanation of these relationships is to be found in the structural characteristics and the electron density distribution of the molecules studied. The introduction of substituents affects the electron distribution and density of the delocalized π -orbital of benzene. The presence of two alkyl groups produces effects dependent on their character and mutual position. The greatest asymmetry of the *o*-dimethylbenzene in group I of the isomers causes the maximum retention due to the hindered rotation of this isomer in the squalane lattice. In addition, the *ortho* isomers in the group of dialkylbenzenes are characterized by a more compact arrangement of atoms, which is confirmed by their higher density, dielectric constant, coefficient of refraction and boiling point. As a result of the very near mutual position of the alkyl groups in the *ortho* isomers, the σ/π conjugation of the C-H bond of a carbon atom α to the aromatic ring is disturbed, leading to a decrease in the electron mobility of *ortho* isomers compared with other isomers. It is obvious that the observed relationships have a decisive influence on the elution sequence of isomers of groups I and II, one alkyl group of which is methyl. The elution order of isomers of group III, the alkyl constituents of which contain two or more carbon atoms, is in agreement with that of group II as regards the *meta* isomer, and has nothing in common with group I.

Since the alkyl substituents have practically equal "polarities", the above features can be accounted for in terms of the respective alkyl chain lengths. Indeed, extension of the substituent chain results in an increase in the number of sites in the molecules which are capable of mutual attraction. The degree of attraction, and consequently of the dispersion forces, is a maximum, provided the linear alkyl radical can form a "bent" or zigzag configuration, thus assisting in intimate contact of the dialkylbenzene molecules with the stationary phase. This interaction mechanism is confirmed by the relative retention data of the isomers studied (Table III). The relative retention of *p*-dialkylbenzenes (Table III), the lowest value of which is characteristic of methylbenzenes, increases with increasing alkyl chain length, and exceeds the retention of *m*-dialkylbenzenes by 0.8% (group II) and that of *o*-dialkylbenzenes by 2.3% (group III). The stronger retention of *para* isomers is directly connected with the length of the end alkyl groups which have two micropoles in contrast to the *meta* and *ortho* isomers characterized by a common dipole moment. It is to be noted that in this particular case the attractive forces of the alkyl groups predominate over the steric factors, *p*-diisopropylbenzene exhibiting the greatest retention relative to the *ortho* isomers of the hydrocarbons in group III.

If the retention of the *para* isomers of groups II and III is determined by the interaction of the alkyl groups with the molecules of the stationary phase, then the

TABLE III

MEAN VALUES OF RETENTION INDEX DIFFERENCES IN COMPARISON WITH BENZENE (%)

Dialkylbenzenes	Group of isomers		
	I	II	III
<i>para</i> Isomers	32.5	53.8	69.9
<i>meta</i> Isomers	32.8	53.0	66.9
<i>ortho</i> Isomers	35.9	55.2	67.6

TABLE IV
STRUCTURAL INCREMENTS OF ALKYL BENZENES ON SQUALANE

Compound	Temperature (°C)	
	86	96
Toluene	55.0	57.1
1,4-Dimethylbenzene	59.0	61.2
1,3-Dimethylbenzene	61.0	63.2
1,2-Dimethylbenzene	80.8	83.0
1,3,5-Trimethylbenzene	65.0	67.1
1,2,4-Trimethylbenzene	82.8	85.3
1,2,3-Trimethylbenzene	107.8	110.5
1,2,4,5-Tetramethylbenzene	102.8	105.9
1,2,3,5-Tetramethylbenzene	108.4	111.4
1,2,3,4-Tetramethylbenzene	129.2	132.7
Pentamethylbenzene	153.9	158.6
Ethylbenzene	45.3	47.7
1,3-Diethylbenzene	25.7	28.1
1,2-Diethylbenzene	34.8	38.1
1,4-Diethylbenzene	36.8	39.3
1,3,5-Triethylbenzene	-11.9	-9.2
1,2,4-Triethylbenzene	6.3	8.0
<i>n</i> -Propylbenzene	32.7	35.1
Isopropylbenzene	4.1	6.7
1,3-Diisopropylbenzene	-83.7	-81.2
1,2-Diisopropylbenzene	-81.9	-79.7
1,4-Diisopropylbenzene	-48.8	-46.6
1,3,5-Triisopropylbenzene	-214.3	-212.5
<i>tert.</i> -Butylbenzene	-30.1	-27.5
Isobutylbenzene	-14.5	-11.7
<i>sec.</i> -Butylbenzene	-13.6	-10.9
<i>n</i> -Butylbenzene	32.3	34.9
<i>tert.</i> -Pentylbenzene	-34.1	-30.5
<i>sec.</i> -Pentylbenzene	-25.3	-22.2
Isopentylbenzene	-5.1	-1.6
<i>n</i> -Pentylbenzene	31.3	36.2
<i>n</i> -Hexylbenzene	25.4	28.8
1-Methyl-3-ethylbenzene	45.9	47.4
1-Methyl-4-ethylbenzene	48.2	50.4
1-Methyl-2-ethylbenzene	61.1	63.4
1-Methyl-3- <i>n</i> -propylbenzene	30.4	32.8
1-Methyl-4- <i>n</i> -propylbenzene	35.9	38.8
1-Methyl-2- <i>n</i> -propylbenzene	42.0	45.4
1-Methyl-3-isopropylbenzene	0.3	1.8
1-Methyl-4-isopropylbenzene	7.7	9.9
1-Methyl-2-isopropylbenzene	13.5	15.8
1-Methyl-4- <i>sec.</i> -butylbenzene	-11.3	-9.0
1-Methyl-3- <i>tert.</i> -butylbenzene	-46.4	-43.9
1-Methyl-4- <i>tert.</i> -butylbenzene	-27.7	-25.3
1-Methyl-2- <i>tert.</i> -butylbenzene	-11.6	-9.1
1-Ethyl-3- <i>n</i> -propylbenzene	8.4	11.1
1-Ethyl-2- <i>n</i> -propylbenzene	16.7	19.2
1-Ethyl-4- <i>n</i> -propylbenzene	21.9	25.2
1-Ethyl-3-isopropylbenzene	-25.7	-23.5
1-Ethyl-2-isopropylbenzene	-23.1	-20.2
1-Ethyl-4-isopropylbenzene	-5.5	-2.7
1-Ethyl-4- <i>tert.</i> -butylbenzene	-41.5	-39.0

elution order of the other isomers is closely associated with the steric effects. Thus, increasing of one of the two alkyls in dialkylbenzene results in an increase in steric hindrances, weakening the dispersion interaction of *meta*- compared with *para* isomers by approximately 1.0%, and enhancing the elution of *meta* isomers with respect to the dialkylbenzenes of group II (Table III). Increasing chain length of the other alkyl substituent causes an additional intensification of the steric hindrance, resulting in elution of the *ortho* before the *para* isomers of the hydrocarbons of group III.

The experimental values of the retention indices can be used to calculate values of the homomorphous factor, H

$$H = I_{ab} - I_p$$

where I_{ab} and I_p are the retention indices of an alkylbenzene and of an n -alkane with the same number of carbon atoms, respectively. The values obtained, which permit an evaluation of the effect of the molecular structure of the alkylbenzene on the retention index, are given in Table IV.

The homomorphous factor increases with increasing methyl substitution from methylbenzene to pentamethylbenzene. The introduction of one methyl group in the benzene ring results in an increase in H on average by 25–30%. In all the other cases the values of H decrease with the increasing number of carbon atoms in a molecule, including the introduction of a methyl group in the side chain of a ring. A sudden decrease in H occurs from n -alkylbenzenes to their respective *iso* derivatives (n -propylbenzene–isopropylbenzene, n -butyl- and n -pentylbenzenes and their isomers) and in a number of derivatives of isopropylbenzene. In a homologous series of n -alkylbenzenes the decrease in H is insignificant. It is to be noted that the H value for n -propylbenzene does not fit the approximately linear dependence (line 1 in Fig. 4) of the homomorphous factor on the number of carbon atoms. It is possible to deduce from this figure another dependence involving the points corresponding to C_9 and C_{11} alkylbenzenes (broken line in Fig. 4). The anomalously low retention indices of n -propylbenzene and its dialkyl derivatives has been treated in detail by Soják and co-workers^{39,40}.

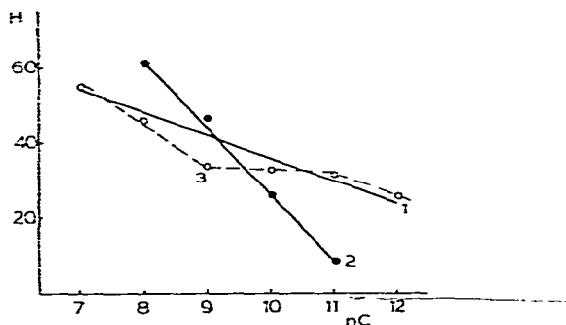


Fig. 4. Dependence of H on the number of carbon atoms for homologous series of alkylbenzenes at 86°C. 1 = Monosubstituted n -alkylbenzenes; 2 = 1,3-dialkylbenzenes; 3 = a different interpretation of dependence 1.

TABLE V

CONTRIBUTION OF ONE METHYLENE GROUP TO THE RETENTION INDICES OF HOMOLOGOUS SERIES OF ALKYL BENZENES

B = Benzene; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; Hex = hexyl; Hep = heptyl; Oct = octyl; Non = nonyl; *i* = *iso*; *s* = *sec*; *t* = *tert*.

Series and compounds		No. of carbon atoms	Temperature (°C)	
Basic compound	CH ₂ group incorporated		86	96
B	MeB	C ₆ -C ₇	107.0	106.9
MeB	1,2-Di-MeB	C ₇ -C ₈	125.8	125.9
EtB	1-Me-2-EtB	C ₈ -C ₉	115.8	115.7
<i>n</i> -PrB	1-Me-2- <i>n</i> -PrB	C ₉ -C ₁₀	109.3	110.3
<i>i</i> -PrB	1-Me-2- <i>i</i> -PrB	C ₉ -C ₁₀	109.4	109.1
<i>n</i> -BuB	1-Me-2- <i>n</i> -BuB	C ₁₀ -C ₁₁	—	106.5*
<i>n</i> -PeB	1-Me-2- <i>n</i> -PeB	C ₁₁ -C ₁₂	—	102.3*
<i>n</i> -HexB	1-Me-2- <i>n</i> -HexB	C ₁₂ -C ₁₃	—	104.1*
<i>n</i> -HepB	1-Me-2- <i>n</i> -HepB	C ₁₃ -C ₁₄	—	103.6*
<i>n</i> -OctB	1-Me-2- <i>n</i> -OctB	C ₁₄ -C ₁₅	—	103.2*
<i>n</i> -NonB	1-Me-2- <i>n</i> -NonB	C ₁₅ -C ₁₆	—	102.6*
MeB	1,4-Di-MeB	C ₇ -C ₈	104.0	104.2
EtB	1-Me-4-EtB	C ₈ -C ₉	102.9	102.7
<i>n</i> -PrB	1-Me-4- <i>n</i> -PrB	C ₉ -C ₁₀	103.2	103.7
<i>i</i> -PrB	1-Me-4- <i>i</i> -PrB	C ₉ -C ₁₀	103.6	103.2
<i>n</i> -BuB	1-Me-4- <i>n</i> -BuB	C ₁₀ -C ₁₁	103.1	102.3**
<i>t</i> -BuB	1-Me-4- <i>t</i> -BuB	C ₁₀ -C ₁₁	102.4	102.2
<i>s</i> -BuB	1-Me-4- <i>s</i> -BuB	C ₁₀ -C ₁₁	102.3	101.9
<i>n</i> -PeB	1-Me-4- <i>n</i> -PeB	C ₁₁ -C ₁₂	103.2	103.3**
<i>n</i> -HexB	1-Me-4- <i>n</i> -HexB	C ₁₂ -C ₁₃	101.3	102.1**
MeB	1,3-Di-MeB	C ₇ -C ₈	106.0	106.1
EtB	1-Me-3-EtB	C ₈ -C ₉	100.6	99.7
<i>n</i> -PrB	1-Me-3- <i>n</i> -PrB	C ₉ -C ₁₀	97.7	97.7
<i>n</i> -BuB	1-Me-3- <i>n</i> -BuB	C ₁₀ -C ₁₁	—	93.0****
<i>n</i> -PeB	1-Me-3- <i>n</i> -PeB	C ₁₁ -C ₁₂	—	91.3****
1-Me-3-EtB	1,2-Di-Me-3-EtB	C ₉ -C ₁₀	138.3	139.2*
1-Me-4-EtB	1,2-Di-Me-4-EtB	C ₉ -C ₁₀	119.8	120.0*
1-Me-4-EtB	1,3-Di-Me-4-EtB	C ₉ -C ₁₀	115.2	115.3*
1-Me-2-EtB	1,3-Di-Me-2-EtB	C ₉ -C ₁₀	106.8	107.1*
1-Me-2-EtB	1,4-Di-Me-2-EtB	C ₉ -C ₁₀	95.8	95.6*
<i>i</i> -PrB	1-Me-3- <i>i</i> -PrB	C ₉ -C ₁₀	96.2	95.1
<i>t</i> -BuB	1-Me-3- <i>t</i> -BuB	C ₁₀ -C ₁₁	83.7	83.6
1,3-Di-MeB	1,2,3-Tri-MeB	C ₈ -C ₉	146.8	147.3
1,2-Di-MeB	1,2,3-Tri-MeB	C ₈ -C ₉	127.0	127.5
1,4-Di-MeB	1,2,4-Tri-MeB	C ₈ -C ₉	123.8	124.0
1,3-Di-MeB	1,3,5-Tri-MeB	C ₈ -C ₉	104.0	103.9
1,2-Di-MeB	1,2,4-Tri-MeB	C ₈ -C ₉	102.0	102.3
1,2,4-Tri-MeB	1,2,3,4-Tetra-MeB	C ₉ -C ₁₀	146.4	147.4
1,3,5-Tri-MeB	1,2,3,5-Tetra-MeB	C ₉ -C ₁₀	143.4	144.3
1,2,3-Tri-MeB	1,2,3,4-Tetra-MeB	C ₉ -C ₁₀	121.4	122.2
1,2,4-Tri-MeB	1,2,4,5-Tetra-MeB	C ₉ -C ₁₀	120.0	120.2
1,2,3-Tri-MeB	1,2,3,5-Tetra-MeB	C ₉ -C ₁₀	100.6	100.9

(Continued on p. 294)

TABLE V (continued)

Series and compounds		No. of carbon atoms	Temperature (°C)	
Basic compound	CH ₂ group incorporated		86	96
1,2,4,5-Tetra-MeB	1,2,3,4,5-Penta-MeB	C ₁₀ -C ₁₁	151.1	152.7
1,2,3,5-Tetra-MeB	1,2,3,4,5-Penta-MeB	C ₁₀ -C ₁₁	145.5	147.2
1,2,3,4-Tetra-MeB	1,2,3,4,5-Penta-MeB	C ₁₀ -C ₁₁	124.7	125.9
Penta-MeB	Hexa-MeB	C ₁₁ -C ₁₂	152.1	154.1**
Styrene	4-Me-Styrene	C ₈ -C ₉	106.6	105.8
Styrene	3-Me-Styrene	C ₈ -C ₉	104.3	104.2
Styrene	2-Me-Styrene	C ₉ -C ₉	100.1	99.7
Styrene	α -Me-Styrene	C ₈ -C ₉	85.0	85.5
Indene	2-Me-Indene	C ₉ -C ₁₀	42.3	42.0
2-Me-Styrene	2,4-Di-Me-Styrene	C ₉ -C ₁₀	108.8	110.0
4-Me-Styrene	2,4-Di-Me-Styrene	C ₉ -C ₁₀	102.3	103.9
Naphthalene	2-Me-Naphthalene	C ₁₀ -C ₁₁	119.5	119.3
Naphthalene	1-Me-Naphthalene	C ₁₀ -C ₁₁	118.7	116.1
<i>Introduction of CH₂ into side chain</i>				
MeB	EtB	C ₇ -C ₈	90.0	90.6
EtB	<i>n</i> -PrB	C ₈ -C ₉	87.4	87.4
<i>n</i> -PrB	<i>n</i> -BuB	C ₉ -C ₁₀	99.6	99.8
<i>n</i> -BuB	<i>n</i> -PeB	C ₁₀ -C ₁₁	99.0	101.3
<i>n</i> -PeB	<i>n</i> -HexB	C ₁₁ -C ₁₂	94.1	92.6
1,4-Di-MeB	1-Me-4-EtB	C ₈ -C ₉	89.2	89.1
1-Me-4-EtB	1-Me-4- <i>n</i> -PrB	C ₉ -C ₁₀	87.7	88.4
1-Me-4- <i>n</i> -PrB	1-Me-4- <i>n</i> -BuB	C ₁₀ -C ₁₁	99.6	98.9**
1-Me-4- <i>n</i> -BuB	1-Me-4- <i>n</i> -PeB	C ₁₁ -C ₁₂	96.4	97.2**
1-Me-4- <i>n</i> -PeB	1-Me-4- <i>n</i> -HexB	C ₁₂ -C ₁₃	95.8	96.7**
1-Me-4- <i>n</i> -HexB	1-Me-4- <i>n</i> -HepB	C ₁₃ -C ₁₄	103.0	101.2**
1-Me-4- <i>i</i> -PrB	1-Et-4- <i>i</i> -PrB	C ₁₀ -C ₁₁	86.8	87.4
1-Et-4- <i>i</i> -PrB	1- <i>n</i> -Pr-4- <i>i</i> -PrB	C ₁₁ -C ₁₂	83.8	83.6**
1-Me-4-EtB	1,4-Di-EtB	C ₉ -C ₁₀	88.6	88.9
1,4-Di-EtB	1-Et-4- <i>n</i> -PrB	C ₁₀ -C ₁₁	85.1	85.9
1-Et-4- <i>n</i> -PrB	1-Et-4- <i>n</i> -BuB	C ₁₁ -C ₁₂	100.1	100.5**
1-Et-4- <i>n</i> -BuB	1-Et-4- <i>n</i> -PeB	C ₁₂ -C ₁₃	95.2	95.1**
1-Et-4- <i>n</i> -PeB	1-Et-4- <i>n</i> -HexB	C ₁₃ -C ₁₄	101.3	99.6**
1-Me-4- <i>n</i> -PrB	1-Et-4- <i>n</i> -PrB	C ₁₀ -C ₁₁	86.0	86.4
1-Et-4- <i>n</i> -PrB	1,4-Di- <i>n</i> -PrB	C ₁₁ -C ₁₂	85.1	85.8**
1,4-Di- <i>n</i> -PrB	1- <i>n</i> -Pr-4- <i>n</i> -BuB	C ₁₂ -C ₁₃	99.1	98.7**
1- <i>n</i> -Pr-4- <i>n</i> -BuB	1- <i>n</i> -Pr-4- <i>n</i> -PeB	C ₁₃ -C ₁₄	110.4	108.6**
1-Me-4- <i>n</i> -BuB	1-Et-4- <i>n</i> -BuB	C ₁₁ -C ₁₂	86.6	87.8**
1-Et-4- <i>n</i> -BuB	1- <i>n</i> -Pr-4- <i>n</i> -BuB	C ₁₂ -C ₁₃	84.1	84.0**
1- <i>n</i> -Pr-4- <i>n</i> -BuB	1,4-Di- <i>n</i> -BuB	C ₁₃ -C ₁₄	101.3	100.2**
1-Me-4- <i>t</i> -BuB	1-Et-4- <i>t</i> -BuB	C ₁₁ -C ₁₂	86.2	86.3**

TABLE V (continued)

Series and compounds		No. of carbon atoms	Temperature (°C)	
Basic compound	CH ₂ group incorporated		86	96
1,3-Di-MeB	1-Me-3-EtB	C ₈ -C ₉	84.9	84.2
1-Me-3-EtB	1-Me-3- <i>n</i> -PrB	C ₉ -C ₁₀	84.5	85.4
1,3-Di-EtB	1-Et-3- <i>n</i> -PrB	C ₁₀ -C ₁₁	82.7	83.0
1-Et-3- <i>n</i> -PrB	1,3-Di- <i>n</i> -PrB	C ₁₁ -C ₁₂	83.0	83.2**
1-Me-3-EtB	1,3-Di-EtB	C ₉ -C ₁₀	79.8	80.7
1-Me-3- <i>n</i> -PrB	1-Et-3- <i>n</i> -PrB	C ₁₀ -C ₁₁	78.0	78.3
1-Me-3- <i>i</i> -PrB	1-Et-3- <i>i</i> -PrB	C ₁₀ -C ₁₁	74.0	74.7
1,2-Di-MeB	1-Me-2-EtB	C ₈ -C ₉	80.3	80.4
1-Me-2-EtB	1-Me-2- <i>n</i> -PrB	C ₉ -C ₁₀	80.9	82.0
1-Me-2- <i>n</i> -PrB	1-Me-2- <i>n</i> -BuB	C ₁₀ -C ₁₁	—	96.3*
1-Me-2- <i>n</i> -BuB	1-Me-2- <i>n</i> -PeB	C ₁₁ -C ₁₂	—	95.0*
1-Me-2- <i>n</i> -PeB	1-Me-2- <i>n</i> -HexB	C ₁₂ -C ₁₃	—	96.8*
1-Me-2- <i>n</i> -HexB	1-Me-2- <i>n</i> -HepB	C ₁₃ -C ₁₄	—	99.2*
1-Me-2- <i>i</i> -PrB	1-Et-2- <i>i</i> -PrB	C ₁₀ -C ₁₁	63.4	64.0
1-Me-2-EtB	1,2-Di-EtB	C ₉ -C ₁₀	73.7	74.7
1,2-Di-EtB	1-Et-2- <i>n</i> -PrB	C ₁₀ -C ₁₁	81.9	81.1
1-Et-2- <i>n</i> -PrB	1-Et-2- <i>n</i> -BuB	C ₁₁ -C ₁₂	—	93.2*
1-Et-2- <i>n</i> -BuB	1-Et-2- <i>n</i> -PeB	C ₁₂ -C ₁₃	—	94.2*
1-Et-2- <i>n</i> -PeB	1-Et-2- <i>n</i> -HexB	C ₁₃ -C ₁₄	—	97.0*
1-Et-2- <i>n</i> -HexB	1-Et-2- <i>n</i> -HepB	C ₁₄ -C ₁₅	—	97.3*
1-Et-2- <i>n</i> -HepB	1-Et-2- <i>n</i> -OctB	C ₁₅ -C ₁₆	—	98.6*
1-Me-2- <i>n</i> -PrB	1-Et-2- <i>n</i> -PrB	C ₁₀ -C ₁₁	74.7	73.8
1-Et-2- <i>n</i> -PrB	1,2-Di- <i>n</i> -PrB	C ₁₁ -C ₁₂	—	72.8*
1,2-Di- <i>n</i> -PrB	1- <i>n</i> -Pr-2- <i>n</i> -BuB	C ₁₂ -C ₁₃	—	91.8*
1- <i>n</i> -Pr-2- <i>n</i> -BuB	1- <i>n</i> -Pr-2- <i>n</i> -PeB	C ₁₃ -C ₁₄	—	92.6*
1- <i>n</i> -Pr-2- <i>n</i> -PeB	1- <i>n</i> -Pr-2- <i>n</i> -HexB	C ₁₄ -C ₁₅	—	94.9*
1- <i>n</i> -Pr-2- <i>n</i> -HexB	1- <i>n</i> -Pr-2- <i>n</i> -HepB	C ₁₅ -C ₁₆	—	97.5*
1-Me-4- <i>n</i> -BuB	1-Et-2- <i>n</i> -BuB	C ₁₁ -C ₁₂	—	67.6*
1-Et-2- <i>n</i> -BuB	1- <i>n</i> -Pr-2- <i>n</i> -BuB	C ₁₂ -C ₁₃	—	71.4*
1- <i>n</i> -Pr-2- <i>n</i> -BuB	1,2-Di- <i>n</i> -BuB	C ₁₃ -C ₁₄	—	90.7*

* According to measurements by Soják *et al.*³⁹.

** According to measurements by Engewald and Wennrich³⁸.

*** According to measurements by Döring *et al.*³².

The overall effect of the number and position of the alkyl groups in the benzene ring was evaluated by means of the increment δI

$$\delta I = I_2 - I_1$$

where I_1 and I_2 are the retention indices of alkylbenzenes differing by one or several structural groups, respectively. The values of the increments δI_{CH_2} are listed in Table V. This increment is dependent primarily on the site of introduction of the structural element. If an alkylbenzene molecule is extended by a $-\text{CH}_2-$ group, the value of δI

usually exceeds 100 I -units, if substitution occurs in the benzene ring. If, however, the CH_2 group is introduced in the side chain of the ring, the δI value is lower than 100.

Introduction of a methyl group in the ring

The values of δI_{CH_2} for isomeric dialkylbenzenes increase in the order: *meta* < *para* < *ortho*. The δI_{CH_2} values for *m*- and *p*-dimethyl benzenes, being mutually comparable, slightly differ from the δI_{CH_2} value characterizing the introduction of a CH_2 group in an unsubstituted benzene ring, which shows there are no obstacles to the introduction of the methyl group in the *meta* and *para* positions. The *ortho* position is associated with the greatest electron density, consequently the introduction of a methyl group results in an increase in δI_{CH_2} compared with the other isomers. The anomalous retention behaviour of various *ortho*-substituted compounds has been dealt with in many papers⁴¹⁻⁴⁴. One study⁴² indicates that in the *ortho* position the free rotation of the methyl groups is made more difficult and is changed to rotational-vibrational motion. Increasing the length of the alkyl chain counterbalances these effects, and for C_{11} - C_{12} *o*-dialkylbenzenes the values of δI_{CH_2} decrease to 102-106 units, comparable with the values for *p*-dialkylbenzenes (Fig. 5).

The lowest δI_{CH_2} values (< 100 units) are characteristic for *m*-dialkylbenzenes, which permits to consider the differences in the retention indices (or δI_{CH_2}) between the extreme substituents of the corresponding isomers (in this case *ortho* and *meta*) as a quantitative measure of the screening effect of the substituents.

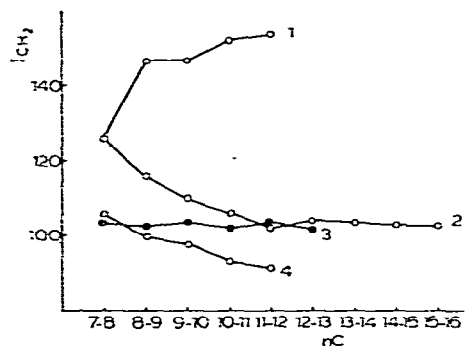


Fig. 5. Dependence of δI_{CH_2} on the number of carbon atoms for homologous series of alkylbenzenes at 96°C. 1 = Methyl-substituted benzenes; 2 = 1-methyl-2-alkylbenzenes; 3 = 1-methyl-4-alkylbenzenes; 4 = 1-methyl-3-alkylbenzenes.

The decisive influence of the methyl group on the size of the retention index increment can be well demonstrated by trialkylbenzenes (Table V). The increase in δI_{CH_2} for isomeric dimethylbenzenes is directly associated with the mutual position of the methyl groups in the ring: 1,4 < 1,3 < 1,2.

Increasing the number of methyl groups in the benzene rings increases the degree of its screening. The highest δI_{CH_2} value is achieved when a methylene group is introduced in the *ortho* position with respect to methyl groups already occupying *ortho* positions with respect to each other (a double *ortho*-effect): 1,2,4,5-tetramethylbenzene-1,2,3,4,5-pentamethylbenzene, and pentamethylbenzene-hexamethylbenzene (Fig. 5).

It is interesting that for styrols with a methyl substituent and for indenenes the lowest δI_{CH_2} value is that for the *ortho*-isomers. The anomalies observed for *n*-propylbenzene and its derivatives, in the case of side chains of the aromatic ring³⁹, do not appear when the CH_2 group is introduced in a ring containing a propyl group (e.g., in *meta* position to the *n*-propyl).

Introduction of a methylene group in the side chain

In this case the values of δI_{CH_2} for isomeric alkylbenzenes increase in the sequence *ortho* < *meta* < *para*. In each group of isomers the value of δI_{CH_2} with increasing length of side chains approaches 100, this value being attained by *para* isomers with a lower number of carbon atoms in comparison with other isomers.

The increments δI_{CH_2} in the case of *ortho* isomers are higher for introduction of the CH_2 group into the longer side chain: with increasing length of the longer chain the increments δI_{CH_2} for the introduction in the shorter side chain decrease, and *vice versa* — the extension of the shorter side chain produces a decrease in the δI_{CH_2} value for the introduction of an alkyl group in the longer side chain.

For *p*-dialkylbenzenes such a distinct pattern does not exist (Table VI). In each of the homologous series studied there are differences with respect to the general dependences and trends, which defy interpretation. The value δI_{CH_2} is determined by the length, mutual position and the structure of the alkyls. In a homologous series with a branched alkyl group, δI_{CH_2} is smaller than in a series with an analogous *n*-alkyl group (i.e., alkylpropylbenzenes—alkylisopropylbenzenes). The influence of the isoalkyl group (branched alkyls) increases with increasing length of the other alkyl group, and with decreasing distance between the side chain alkyls. The minimum value of δI_{CH_2} was found for *ortho* isomers with one isoalkyl group and increased in the sequence: *ortho* < *meta* < *para*. The dependence discussed here results from all the steric hindrances in the molecule.

TABLE VI

δI_{CH_2} VALUES FOR VARIOUS ALKYL CHAIN LENGTHS IN *p*-DIALKYL BENZENES

No. of C atoms		1-X-4-MeB to 1-X-4-EtB	1-X-4-EtB to 1-X-4-PrB	1-X-4-PrB to 1-X-4-BuB	1-X-4-BuB to 1-X-4-PeB	1-X-4-PeB to 1-X-4-HexB
Basic aromatic	+CH ₂ group					
7	8	90.0				
8	9	89.2	87.4			
9	10	88.6	87.7	99.6		
10	11	86.0	85.1	99.6	99.0	
11	12*	86.6	85.1	100.1	96.4	94.1
12	13*	85.4	84.1	99.1	95.2	95.8
13	14*	90.9	99.3	101.3	110.4	101.3

* Data from ref. 38.

Introduction of alkyl groups containing more than one carbon atom (C₂–C₅)

The changes in retention index due to the introduction of alkyl groups with two and more carbon atoms are characterized by systematic deviations from the

TABLE VII
 ALKYL GROUP INCREMENTS FOR HOMOLOGOUS SERIES OF ALKYL BENZENES

<i>Series and compounds</i>		<i>No. of C atoms</i>	<i>Range of δI</i>
<i>Basic compound</i>	<i>Alkylene in- corporated</i>		
<i>Introduction of C₂H₄ into ring</i>			
B	EtB	C ₆ -C ₈	197
<i>n</i> -Alkyl-B	1-Et-2- <i>n</i> -Alkyl-B	C ₇ -C ₁₅	206-169
<i>n</i> -Alkyl-B	1-Et-4- <i>n</i> -Alkyl-B	C ₇ -C ₁₄	193-190
<i>n</i> -Alkyl-B	1-Et-3- <i>n</i> -Alkyl-B	C ₇ -C ₁₁	190-170
Di-EtB	Tri-EtB	C ₁₀ -C ₁₂	170-163
<i>Introduction of n-C₂H₅ into side chain</i>			
<i>n</i> -Alkyl-B*		C ₇ -C ₁₄	178-199
1,4-Di-MeB*	1-Me-4- <i>n</i> -Alkyl-B	C ₈ -C ₁₄	177-199
1,2-Di-MeB*	1-Me-2- <i>n</i> -Alkyl-B	C ₈ -C ₁₅	161-198
<i>Introduction of n-C₃H₇ into ring</i>			
B	<i>n</i> -PrB	C ₆ -C ₉	285
<i>n</i> -Alkyl-B*	1- <i>n</i> -Pr-2- <i>n</i> -Alkyl-B	C ₇ -C ₁₄	288-240
<i>n</i> -Alkyl-B*	1- <i>n</i> -Pr-4- <i>n</i> -Alkyl-B	C ₇ -C ₁₂	281-274
<i>n</i> -Alkyl-B*	1- <i>n</i> -Pr-3- <i>n</i> -Alkyl-B	C ₇ -C ₁₁	276-263
<i>Introduction of n-C₃H₇ into side chain</i>			
<i>n</i> -Alkyl-B		C ₇ -C ₁₅	277-299
1,4-Di-MeB	1-Me-4- <i>n</i> -Alkyl-B	C ₈ -C ₁₄	276-295
1,2-Di-MeB	1-Me-2- <i>n</i> -Alkyl-B	C ₈ -C ₁₅	259-295
<i>Introduction of i-C₃H₇ into ring</i>			
B	<i>i</i> -PrB	C ₆ -C ₉	256
<i>n</i> -Alkyl-B*	1- <i>i</i> -Pr-2- <i>n</i> -Alkyl-B	C ₇ -C ₁₂	259-214
<i>n</i> -Alkyl-B*	1- <i>i</i> -Pr-4- <i>n</i> -Alkyl-B	C ₇ -C ₁₂	253-244
<i>n</i> -Alkyl-B*	1- <i>i</i> -Pr-3- <i>n</i> -Alkyl-B	C ₇ -C ₁₁	245-229
1,3-Di- <i>i</i> -PrB	1,3,5-Tri- <i>i</i> -PrB	C ₁₂ -C ₁₅	169
<i>Introduction of i-C₃H₇ into side chain</i>			
MeB	<i>i</i> -BuB	C ₇ -C ₁₀	231
<i>Introduction of n-C₄H₉ into ring</i>			
B	<i>n</i> -BuB	C ₆ -C ₁₀	385
<i>n</i> -Alkyl-B*	1- <i>n</i> -Bu-4- <i>n</i> -Alkyl-B	C ₇ -C ₁₄	384-374**
<i>n</i> -Alkyl-B*	1- <i>n</i> -Bu-2- <i>n</i> -Alkyl-B	C ₇ -C ₁₅	385-327**
<i>Introduction of n-C₄H₉ into side chain</i>			
<i>n</i> -Alkyl-B*		C ₇ -C ₁₅	376-394***

TABLE VII (continued)

Series and compounds		No. of C atoms	Range of δI
<i>Basic compound</i>	<i>Alkylene in- corporated</i>		
<i>Introduction of $n\text{-C}_5\text{H}_{10}$ into ring</i>			
B	<i>n</i> -PeB	C ₆ -C ₁₁	485
<i>n</i> -Alkyl-B*	1- <i>n</i> -Pe-4- <i>n</i> -Alkyl-B	C ₇ -C ₁₄	476-483**
<i>n</i> -Alkyl-B*	1- <i>n</i> -Pe-2- <i>n</i> -Alkyl-B	C ₇ -C ₁₆	480-418***
<i>Introduction of $n\text{-C}_5\text{H}_{10}$ into side chain</i>			
<i>n</i> -Alkyl-B*		C ₇ -C ₁₅	470-493***

* The values are valid for a group of homologues and the compounds under the heading *Alkylene incorporated* are the final products of incorporation in the range of molecule sizes as determined by the number of C-atoms (indicated on the second place in the column *No. of C-atoms*). For example: by incorporation of the *i*-C₃H₆ group into the benzene ring of *n*-alkyl-B in the *ortho* position results in 1-*i*-Pr-2-*n*-alkyl-B with the molecule size from C₁₂₋₃ to C₁₂. The first datum under the heading *No. of C-atoms* is C₇, this means that the lowest member of the homologous series used as basic compound was in this case methylbenzene and the δI_{CH_2} -values decreased from 259 *I*-units (incorporation of *i*-Pr into methylbenzene) to 214 (incorporation of *i*-Pr into C₁₂₋₃ = C₉ *n*-alkylbenzene, *i.e.* *n*-propylbenzene, what gives 1-*i*-Pr-2-*n*-Pr-B.

** According to measurements by Engewald and Wennrich³⁸.

*** According to measurements by Soják *et al.*³⁹.

additivity principle. Independently of the site of substitution, the Kováts retention index increment is smaller than the value to be expected on the additivity principle, *i.e.*, for the group C₂H₅, $\delta I < 200$, for the group C₃H₆, $\delta I < 300$, etc. (Table VII).

For these groups the value of δI decreases as a result of introduction of the C₂-C₅ groups in the aromatic ring, but increases when the incorporation takes place in the side chain. However, the difference in retention indices due to the introduction of the same C₂-C₅ alkyl group in the aromatic ring and in the side chain is small, equal to 10-20 *I*-units, in contrast to the case of methylene groups which produce a difference of 30-40 *I*-units. Thus, the increase in alkyl chain length reduces the influence on δI of the position of incorporation.

The rôle of the steric factor is important especially in the systems 1,3-diisopropylbenzene-1,3,5-triisopropylbenzene where the introduction of the third isopropyl group produces an increment of only 169 *I* units (instead of the 300 units expected).

As has been reported by many authors^{44,45}, the Kováts rule

$$\delta I \approx 5 \cdot \bar{\epsilon} T_b$$

(where T_b = boiling point) for two isomers is not completely valid in all cases, *i.e.*, the proportionality factor, K_p , varies in a wider interval. From Table VIII it follows that the values of the proportionality factor calculated on the basis of experimental and theoretical data are smaller than 5. The proportionality factors for the other isomers are: trimethylbenzenes, 3.7-4.0; tetramethylbenzenes, 3.1-4.3; triethylbenzenes, 8.2; butylbenzenes, 3.9-4.6; pentylbenzenes, 3.4-5.8.

TABLE VIII
PROPORTIONALITY FACTORS FOR ISOMERS OF DIALKYLBENZENES

<i>Dialkylbenzenes</i>	86°C			96°C		
	<i>meta-ortho</i>	<i>meta-para</i>	<i>para-ortho</i>	<i>meta-ortho</i>	<i>meta-para</i>	<i>para-ortho</i>
Dimethylbenzenes	3.7	2.9	3.6	3.7	2.9	3.6
Dimethylbenzenes ^{27,28}	3.7	3.1	3.7	3.7	2.9	3.7
Methylethylbenzenes	3.9	3.3	4.0	4.1	4.3	4.1
Methylethylbenzenes ^{27,28}	4.0	3.4	4.1	4.1	2.9	4.4
Methylpropylbenzenes	3.9	3.2	4.7	4.2	3.5	5.1
Methylpropylbenzenes ^{27,28}	3.8	—	—	4.0	3.5	4.6
Methylisopropylbenzenes	4.2	3.6	5.3	4.4	4.0	5.4
Methylisopropylbenzenes ²⁷	—	—	—	4.1	3.9	4.8
Ethylpropylbenzenes	4.2	3.9	3.5	4.1	4.0	4.0
Ethylisopropylbenzenes	1.7	3.7	4.4	2.2	3.8	4.4
Diethylbenzenes	4.0	4.2	5.0	4.4	4.2	3.0

The comparison of the experimental results obtained (Table VIII) with the data in Table IX, which gives the average values of factors K_p in a temperature interval 80–115°C calculated on the basis of literature data^{27,28,33–35,38}, shows a satisfactory agreement. The proportionality factors for *para* and *ortho* isomers are somewhat higher than for the other pairs of isomers which have approximately identical values of K_p . The statistical analysis of the deviations in the case of alkylbenzenes showed that the numerous proportionality factors K_p calculated for particular groups and positions yielded no substantial improvement of accuracy. Therefore, the following values were deduced on the basis of literature data^{27,28,33–35,38} for the average proportionality factors of the alkylbenzenes studied: dialkyl- and trimethylbenzenes, 3.9; tetramethylbenzenes, 3.6; butylbenzenes, 4.4; pentylbenzenes, 4.5.

The boiling points and retention indices of alkylbenzenes, calculated by means of the values indicated here, are in good agreement with corresponding literature and experimental data. The maximum differences found do not exceed 1°C and 2.5–3.0 *l* units.

TABLE IX
AVERAGE VALUES OF PROPORTIONALITY FACTORS, K_p , FOR DIALKYLBENZENES

<i>Dialkylbenzenes</i>	<i>Meta-ortho</i>	<i>Meta-para</i>	<i>Para-ortho</i>
Dimethylbenzenes	3.8	2.8	3.7
Methylethylbenzenes	4.1	3.5	4.1
Methylpropylbenzenes	4.1	3.5	4.8
Methylisopropylbenzenes	4.2	3.8	5.2
Diethylbenzenes	4.0	4.8	2.8
Diisopropylbenzenes	—	4.6	4.1

CONCLUSIONS

The elution sequence of isomeric alkylbenzenes using a squalane coated open capillary column is determined by the length and by the mutual distribution and position of the alkyl groups. Thus, increase in the alkyl chain length increases the dispersion interaction of *para* isomers with the stationary phase. This leads to an increase in retention in the sequence: dimethyl-, methylalkyl- and ethyl-alkylbenzenes. In contrast, corresponding decreases occur for the retention sequence of *ortho* isomers.

The retention index variations studied show that the δI_{CH_2} value is determined primarily by the character of the site of introduction of the CH_2 group. For introduction into the ring of dialkylbenzenes the value δI for the first member of a homologous series is lower than 100 *I* units, and with increasing alkyl chain length it approaches 100. The presence of an isopropyl group in alkylbenzenes produces a decrease in δI_{CH_2} . The difference in retention indices corresponding to the introduction of a methylene group in the ring and in the side chain is 30–40 *I* units. This difference diminishes with increasing length of the group incorporated; in the case of C_2 – C_5 alkyl groups it is equal to 10–20 *I* units.

For the isomers investigated here, the proportionality factor in the equation

$$\delta I \approx K_p \cdot \bar{c} T_b$$

varies from 1.7 to 8.2. Average values of K_p calculated on the basis of both literature and experimental data enables in most cases a good correlation between physicochemical and chromatographic data of individual alkylbenzenes.

REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 A. Wehrli and E. Kováts, *Helv. Chim. Acta*, 42 (1959) 2709.
- 3 G. Schomburg, *J. Chromatogr.*, 14 (1964) 157.
- 4 G. Schomburg, *J. Chromatogr.*, 23 (1966) 118.
- 5 J. Jonas, J. Janák and M. Kratochvíl, *J. Gas Chromatogr.*, 4 (1966) 332.
- 6 A. V. Iogansen and G. N. Semina, *Gazov. Chromatographia*, No. 4 (1966) 17.
- 7 G. Schomburg, *Anal. Chim. Acta*, 38 (1967) 45.
- 8 D. A. Tourres, *J. Chromatogr.*, 30 (1967) 357.
- 9 R. A. Hively and R. E. Hinton, *J. Gas Chromatogr.*, 6 (1968) 203.
- 10 M. B. Evans, *Chromatographia*, 2 (1969) 397.
- 11 V. Martinů and J. Janák, *J. Chromatogr.*, 52 (1970) 69.
- 12 J. Takacz, C. Szita and G. Tarjan, *J. Chromatogr.*, 56 (1971) 1.
- 13 I. V. Butina and N. A. Shevchenko, *Gazov. Chromatographia*, No. 16 (1971) 40.
- 14 V. V. Kejko, B. V. Prokopiev, L. P. Kuzmenko, N. A. Kalinina and G. N. Bokova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 1 (1972) 111.
- 15 A. S. Leshchiner, L. M. Ugarova and B. A. Rudenko, *Gazov. Chromatographia*, No. 19 (1973) 37.
- 16 L. C. Ettore, *Chromatographia*, 7 (1974) 39.
- 17 F. Vernon, W. E. Sharples and T. W. Kyffin, *J. Chromatogr.*, 111 (1975) 117.
- 18 S. Rang, K. Kuningas, A. Orav and O. Eisen, *J. Chromatogr.*, 128 (1976) 59.
- 19 T. G. Paramonova, S. A. Reznikov, R. I. Sidorov and I. S. Borovskaia, *Zh. Anal. Khim.*, 31 (1976) 1743.
- 20 S. A. Fedoreev and O. B. Maximov, *Chim. Tverd. Topliva*, No. 1 (1977) 23.
- 21 S. S. Iufit, B. A. Rudenko, Iu. A. Krasnyia and V. F. Kucherov, *Dokl. Akad. Nauk USSR*, 188 (1969) 156.
- 22 R. V. Golovnyia and Iu. N. Arseniev, *Dokl. Akad. Nauk SSSR*, 192 (1970) 1064.
- 23 R. V. Golovnyia and Iu. N. Arseniev, *Chromatographia*, 3 (1970) 455.

- 24 W. E. Hammers and C. L. de Ligny, *Rec. Trav. Chim. Pays-Bas*, 90 (1971) 175.
- 25 M. S. Vigdergaus, V. V. Pomazanov, A. I. Bogdanchikov and E. I. Gunchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 3 (1973) 646.
- 26 J. Novák and J. Růžicková, *J. Chromatogr.*, 91 (1974) 79.
- 27 L. Soják and J. Hrivňák, *Ropa Uhlíe*, 11 (1969) 361.
- 28 L. Soják and A. Bučinská, *J. Chromatogr.*, 51 (1970) 75.
- 29 A. N. Denisenko, V. I. Lebedeva, I. N. Agapova and R. I. Sidorov, *Khim. Tekhnol. Topl. Masel*, No. 7 (1970) 54.
- 30 V. M. Nabivach and S. S. Isatsenko, *Chimicheskaya Tekhnologia*, No. 20 (1971) 77.
- 31 L. E. Cook and F. M. Raushel, *J. Chromatogr.*, 65 (1972) 556.
- 32 C. E. Döring, D. Estel and R. Fischer, *J. Prakt. Chem.*, 316 (1974) 1.
- 33 V. Švob and D. Deur-Šiftar, *J. Chromatogr.*, 91 (1974) 677.
- 34 N. Dimov, T. Petkova and D. Shopov, *J. Chromatogr.*, 91 (1974) 691.
- 35 L. Soják and J. A. Rijks, *J. Chromatogr.*, 119 (1976) 505.
- 36 M. Ryba, *J. Chromatogr.*, 123 (1976) 327.
- 37 J. Krupčík, O. Liška and L. Soják, *J. Chromatogr.*, 51 (1970) 119.
- 38 W. Engewald and L. Wennrich, *Chromatographia*, 9 (1976) 540.
- 39 L. Soják, J. Janák and J. A. Rijks, *J. Chromatogr.*, 135 (1977) 71; 138 (1977) 119.
- 40 L. Soják, P. Majer, J. Krupčík and J. Janák, *J. Chromatogr.*, 65 (1972) 143.
- 41 L. S. Bark and K. F. Clarke, *J. Chromatogr.*, 48 (1970) 418.
- 42 T. L. Kwa and C. Boelhouwer, *J. Chromatogr.*, 52 (1970) 21.
- 43 R. I. Sidorov, A. N. Denisenko and V. I. Lebedeva, *Zh. Anal. Khim.*, 26 (1971) 388.
- 44 E. Kovats, *Advan. Chromatogr.*, 1 (1965) 229.
- 45 L. Soják, J. Krupčík, K. Tesářík and J. Janák, *J. Chromatogr.*, 65 (1972) 93.