Improved method for prediction of gas chromatographic retention indices of C_9–C_{12} alkylbenzenes

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ABSTRACT

The positive identification of higher alkylbenzene isomers is a difficult task even with a mass spectral detector. A preliminary calculative identification could serve for a better orientation in the obtained mass spectra as well as acting as a complementary and independent identification tool. An accurate equation for the prediction of retention indices of C_9–C_{12} alkylbenzenes and their temperature coefficients, dI/dT, on OV-101 is given. The basic parameter is the molecular mass, while tuning parameters include the kind of substitution and the carbon chain of the substituents. The correlation coefficient obtained for 94 alkylbenzenes is 0.9995 and the mean standard deviation is 2.7 units. The predictive possibilities of the equation are demonstrated by inter- and extrapolative calculations of the retention indices of certain isomers with experimentally measured retention data, but without the mass spectral assignment of the positions of substituents.

INTRODUCTION

Aromatic hydrocarbons are important in the petrochemical and related industries and in the environment. C_6–C_{15} aromatics represent the major part of the mono-aromatic fraction of natural and synthetic hydrocarbon mixtures [1]. The positive identification of higher hydrocarbon isomers is difficult even with mass spectral detection. The role of capillary gas chromatography (GC) and combiend GC–mass spectrometry (GC–MS) for the identification of alkylbenzenes in multi-component hydrocarbon mixtures has been discussed in a recent review [2]. In that paper much space was devoted to the interlaboratory reproducibility of retention data. The best reproducibility was achieved on non-polar squalane and silicone stationary phases. However, owing to the low-temperature stability of squalane and therefore the long analysis times of alkylbenzenes above C_9, non-polar silicones such as SE-30, OV-101 and DB-1 are much more preferable. The limited number of practically significant non-polar stationary phases with very similar chromatographic properties makes the need for tabulated correct retention data (retention indices, I) of greater importance.

Isothermal retention indices on OV-101 [3–9] and SE-30 [10,11] for alkylbenzenes up to C_{10} have been published. Whereas for C_6–C_8 and even C_9 arenes the different published data agree very well, for higher alkylbenzenes, particularly alkylbenzenes with short alkyl chains in the aromatic ring, the published retention data on OV-101 [3,6,7,9] are very far complete and the determination of reproducibility is not possible.

The most widely used combined technique, capillary GC–MS with electron impact ionization, can unambiguously identify alkylbenzenes of lower molecular mass. However, because of some drawbacks of this technique in the differentiation of higher structural isomers and the lack of standard materials, a preliminary, calculative identification seemed to be of great benefit. The so-called "chemometric" identification can contribute to identification and/or to a better understanding of quantitative structure–retention relationship of alkylbenzenes [10,12–20]. Some of the calculative methods are valid for homologous series only. The most accurate [21,22] need at least four members, which is almost impossible for higher isomers. The homomorphic factor [23], used in several papers, also shows ambiguous results for the higher isomers. The use of topological and/or electronic indices [15,16,19,20,24–26] has mostly applied to C_6–C_{10} alkylbenzenes.

A more versatile calculation method which could cover a large number of different isomers would be of greater importance. The aim of this paper is to present an accurate calculation method for the prediction of retention indices, I, and their temperature gradients, dI/dT, for C_9–C_{12} alkylbenzenes. The adequacy of the equation is assessed by comparison with experimentally measured retentions on an OV-101 capillary column [9] and is proved by comparison of inter- and extrapolative calculations of I values for certain isomers with experimentally measured retention data, but without the assignment of the positions of substituents. The most possible structures of these compounds are proposed.

THEORY

To overcome the lack of standard substances, the alkylation of benzene and its homologous under fixed conditions was performed [27]. The compound identification was based on combination of GC with MS, taking into account quantum-chemical kinetic calculations of the yields of different isomers and using homomorphic factors.

In this investigation we use another approximation of quantitative structure–retention relationships, published elsewhere [28]. The calculation is based on the following concepts:

(1) there are solute properties with the most significant influence on the retention on non-polar stationary phases; usually these are molecular mass (M_m), boiling point (T_b), vapour pressure (p_i), topological indices and other more or less extensive properties;

(2) there are specific solute properties (structure, charges, etc.), which tune the value of calculated basic retention and approximate it to the experimental value

$$R = f(B_i, T_j) \qquad (1)$$

where R is the corresponding retention (in this study I), B_i are basic contributors (in

this study M_m) and T_j are tuning contributors (in this study the number, positions and C-chain of the substituents in the alkylbenzenes studied). Every statistically significant deviation of $I_{calc.}$ from $I_{exp.}$ is considered as the result of some tuning effects that have not been taken into account. Therefore, one is able to search for very specific solute feature(s) such as the known from practice *ortho* effect or the so-called propyl effect.

The experiments and the experimentally obtained retention data used in this investigation have been published elsewhere [9,27].

RESULTS AND DISCUSSION

The formulation of the regression equations was based on a linear model [28]. The molecular mass, M_m, is the only available extensive property of the higher isomers studied, which is why it is accepted as the B factor in eqn. 1. Structural parameters instead of topological and/or quantum-chemical indices are preferred as tuning contributors as the chemical interpretation in this instance is easier and clearer. Therefore, ten tuning parameters presenting all possible substitutions in the benzene ring (mono-, *o*-, *m*-, *p*-, etc.) are added as T factors in eqn. 1. The presence of a given substitution is denoted by 1 and its absence by 0. The regression analysis now shows the important influence of C-chain branching [9]. An eleventh tuning parameter accounting for this effect was also added. The general appearance of the final equation is

$$I_{calc.} = b_o + b_1 \cdot M_m + \Sigma b_n \cdot (i,j, ..., s) + b_{12} \cdot (\text{Corr.}) \tag{2}$$

where b_o–b_{12} are parameter estimates, M_m is the molecular mass of the corresponding alkylbenzene, $i,j, ..., s$ are the corresponding positions of the substituents in the benzene ring (mono-, 1,2-, ..., 1,2,3,4-, etc.) and the last tuning correction, Corr., is calculated on the basis of the following rules:

(1) the presence of one *tert.*-butyl group diminishes the relative retention expected on a M_m basis and instead of 1 for parameter evaluation a value of -4 is arbitrarily assigned. The presence of one isopropyl or sec.-butyl group is denoted by -2, for the same reason;

(2) the *ortho* location of the above groups with respect to an existing substituent demands additionally an increase in the correction and it becomes -5 and -3 respectively;

(3) the presence of normal-chain substituents increases the expected relative retention and for an ethyl group the necessary correction is $+0.3$, for an *n*-propyl group $+1$, for an *n*-butyl group $+3$ and for an *n*-pentyl group $+5$;

(4) additionally a correction of -1 is necessary if the normal-chain substituents have an inner *ortho*-location in a multi-substituted benzene.

The following examples illustrate the rules. 1,3-Diethyl-4-methylbenzene has two ethyl groups and the correction is $0.3 + 0.3 = 0.6$. One of the ethyl groups is between two other substituents and in an *ortho* position with respect to one of them; therefore, -1 is added. The final correction is -0.4. 1,3,5-Triethylbenzene has three ethyl groups and the correction is $3 \times 0.3 = 0.9$. 1-Ethyl-3-isopropylbenzene has one ethyl group ($+0.3$) and one isopropyl group, which need a correction of -2. The

final correction is -1.7. 1-Ethyl-4-n-butylbenzene has one ethyl and one butyl substituent and the correction is $0.3 + 3 = 3.3$.

Eqn. 2 has a correlation coefficient $r = 0.998$, variance $s^2 = 26$ and $F = 29\ 226$. The greatest discrepancy was found to be 10.5 i.u. This equation, hoewever, is not correct from a mathematical point of view, because the presence of a given substitution eliminates the other possibilities. That is why the values of the parametric estimates are constants only for M_m and Corr. factors while the values for the substitution factor depend on the number of compounds included in the regression.

To overcome this shortcomming, we introduce the relative value of the substitution factor, called the relative contribution, RC. Independent on the number of the compounds included in the regression, this relative contribution to the retention always shows the same importance of the different substitution positions. For 94 alkylbenzenes, the values of the relative contributions (monosubstitution taken as 1.0) are: 1,2-substitution $= 1.892$; 1,2,3-substitution $= 3.242$ and 1,2,3,4-substitution $= 4.761$. For *meta* substitution the value is 1.446 and for 1,3,5-substitution it is 1.8. *Para*-substitution has a distinct differentiation; for methylalkyl substituents it is 1.55 (alkyl means here number of C atoms in the substituent >2) and for alkylalkyl substituents, it is 1.7.

For 1,2,4- and 1,3,4-trisubstituted benzenes the value of RC is 2.532, for 1,2,3,5-tetrasubstituted benzenes 3.828 and for 1,2,4,5-tetrasubstituted benzenes 3.615. The following exact equation is created with the above-mentioned values of RC:

$$I_{calc.} = 237.33 + 5.5898 M_m + 32.384 RC + 9.249 \text{Corr.} \tag{3}$$

with $r = 0.9995$ ($F = 108\ 157$), variance $s^2 = 7.3$ and standard deviation only 2.7 i.u.

Using the corrections calculated above for 1,3-diethyl-4-methylbenzene, 1-ethyl-3-isopropylbenzene, 1,3,5-triethylbenzene and 1-ethyl-4-n-butylbenzene the following values of $I_{calc.}$ are obtained: 1,3-diethyl-4-methylbenzene (No. 55, Table I), $M_m = 148$, Corr. $= -0.4$, 1,3,4-substitution $RC = 2.532$, $I_{calc.} = 1143$, $I_{exp.} = 1149$; 1-ethyl-3-isopropylbenzene (No. 20, Table I), $M_m = 148$, Corr. $= -1.7$, *meta* substitution $RC = 1.446$, $I_{calc.} = 1095.7$, $I_{exp.} = 1092$; 1,3,5-triethylbenzene (No. 71, Table I), $M_m = 162$, Corr. $= 0.9$, 1,3,5-substitution $RC = 1.8$, $I_{calc.} = 1209.4$, $I_{exp.} = 1206$; 1-ethyl-4-n-butylbenzene (No. 39, Table I), $M_m = 162$, Corr. $= 3.3$, *para*-substitution $RC = 1.7$, $I_{calc.} = 1228.4$, $I_{exp.} = 1232$. The calculated results are compared with the experimental data in Table I. The highest discrepancy in all instances studied is 6 i.u.

The accuracy of the calculated indices is extremely good. Obviously the values obtained for the relative contribution to the retention represent clearly and in a quantitative manner the well known from practice *ortho* effect. Additionally, there is a linear regression between the values of RC for *ortho* substitution and the number of *ortho*-positions in the benzene ring. This allows us to calculate the RC value for pentasubstituted benzenes, -6.165 ± 0.002, and we are able to predict the I values of 1,2,3,4,5-pentamethylbenzene and 1,2,3,4-tetramethyl-5-ethylbenzene by extrapolation. The $I_{calc.}$ values coincide well with the experimental values (see Nos. 93 and 94 in Table I).

The values of the relative contributions show that there are also other effects: (i) a *meta* effect is clearly evident; (ii) branching of the substituent C-chain markedly

TABLE I

COMPARISON OF $I_{exp.}$ AND $dI/dT_{exp.}$ WITH $I_{calc.}$ AND $dI/dT_{calc.}$ VALUES AND THE DIFFERENCE $\Delta = I_{exp.} - I_{calc.}$

The experimental values are rounded to 1.0 and the calculated data to 0.1.

No.	Alkylbenzene[a]	$I_{exp.}$	$I_{calc.}$	Δ	$dI/dT_{exp.}$	$dI/dT_{calc.}$
1	iPrB	920	921.9	−1.9	0.280	0.281
2	nPrB	949	949.7	−0.7	0.265	0.300
3	tertBuB	987	981.7	5.3	0.310	0.300
4	secBuB	1005	1000.2	4.8	0.310	0.300
5	nBuB	1047	1046.4	0.6	0.270	0.300
5a	12DMB	−	−	−	0.290	0.310
6	1M2EB	973	972.1	0.9	0.305	0.310
7	12DEB	1051	1053.1	−2.1	0.310	0.310
8	1M2nPrB	1057	1056.8	0.2	0.334	0.310
8a	1M2iPrB	−	−	−	0.292	0.291
9	1E2iPrB	1098	1100.9	−2.9	0.314	0.291
9a	1E2PrB	−	−	−	0.284	0.310
10	1M2nPrB	1134	1137.9	−3.9	−	−
11	1M2nBB	1153	1153.6	−0.6	0.328	0.310
12	1iPrB2nPrB	1180	1185.6	−5.6	0.275	0.310
13	1M2nPeB	1249	1250.3	−1.3	0.310	0.310
14	12DiPrB	1150	1148.6	1.4	0.255	0.272
15	1E2secBuB	1177	1179.1	−2.1	−	−
15a	13DMB	−	−	−	0.245	0.259
16	1M3EB	955	957.7	−2.7	0.250	0.259
17	1M3iPrB	1013	1014.6	−1.6	0.235	0.240
18	1M3nPrB	1042	1042.4	−0.6	0.272	0.259
19	13DEB	1040	1038.7	1.3	0.244	0.259
20	1E3iPrB	1092	1095.7	−3.7	0.230	0.240
21	1M3secBuB	1093	1092.9	0.1	0.281	0.259
23	1M3nBuB	1140	1139.2	0.8	0.249	0.259
24	13DnPrB	1209	1208.2	0.8	0.260	0.259
25	1E3nBuB	1221	1220.2	0.8	0.250	0.259
26	1E3secBuB	1170	1173.9	−3.9	0.272	0.259
27	1nPr3iPrB	1176	1180.4	−4.4	0.238	0.240
28	1M3nPeB	1235	1235.9	−0.9	0.245	0.259
28a	14DMB	−	−	−	0.250	0.279
30	1M4iPrB	1016	1018	−2	0.263	0.260
31	1M4nPrB	1046	1045.8	0.2	0.280	0.279
32	14DEB	1046	1046.9	−0.9	0.265	0.279
33	1M4secBuB	1100	1096.3	3.7	0.282	0.279
34	1E4iPrB	1103	1103.9	−0.9	0.260	0.260
35	1M4nBuB	1146	1142.5	3.5	0.280	0.279
36	1E4secBuB	1185	1182.2	2.8	0.310	0.279
37	1nPr4iPrB	1190	1188.6	1.4	0.268	0.260
38	14DiPrB	1160	1160.9	−0.9	0.248	0.241
39	1E4nBuB	1232	1228.4	3.6	0.302	0.279
40	1M4nPeB	1241	1239.3	1.7	0.267	0.279
40a	14DnPrB	−	−	−	0.297	0.279
41	123TMB	1015	1013.1	1.9	0.370	0.341
42	12DM3EB	1094	1094.1	−0.1	0.360	0.341
42a	13DM2nPrB	−	−	−	0.303	0.341
43	12DE3MB	1170	1165.9	4.1	−	−
44	12DM3nPrB	1177	1178.8	−1.8	0.371	0.341

TABLE I (*continued*)

No.	Alkylbenzene[a]	$I_{exp.}$	$I_{calc.}$	Δ	$dI/dT_{exp.}$	$dI/dT_{calc.}$
45	12DM3nBuB	1274	1275.6	−1.6	0.311	0.341
46	123TEB	1246	1246.9	−0.9	0.310	0.341
47	124TMB	987	990.1	−3.1	0.310	0.290
48	14DM2EB	1067	1061.8	5.2	0.300	0.290
49	13DM4EB	1069	1071.1	−2.1	0.310	0.290
50	12DM4EB	1074	1071.1	2.9	0.318	0.290
51	14DM2iPrB	1119	1118.8	0.2	0.255	0.270
52	13DM4iPrB	1123	1118.8	4.2	0.285	0.270
53	12DM4iPrB	1130	1128.1	1.9	0.287	0.270
54	14DM2nPrB	1148	1146.6	1.4	0.297	0.290
55	13DE4MB	1149	1143	6	0.305	0.290
56	13DM4nPrB	1152	1155.8	−3.8	0.302	0.290
56a	12DE4MB	−	−	−	0.300	0.290
56b	14DE2MB	−	−	−	0.305	0.290
57	12DM4nPrB	1158	1155.8	2.2	−	−
58	14DM2secBuB	1191	1197.1	−6.2	0.260	0.290
59	12DM4tertBuB	1192	1187.8	4.2	0.310	0.290
60	13DM4secBuB	1198	1197.1	0.9	0.312	0.290
61	12DM4secBuB	1210	1206.3	3.7	0.285	0.290
62	13DM4nBuB	1249	1252.6	−3.6	0.280	0.290
63	12DM4nBuB	1254	1252.6	1.4	−	−
64	124TEB	1223	1223.9	−0.9	0.288	0.290
65	14DM2nBuB	1243	1243.3	−0.3	−	−
66	135TMB	963	966.4	−3.6	0.240	0.228
67	13DM5EB	1048	1047.4	−0.6	0.240	0.228
68	13DM5iPrB	1103	1104.4	−1.6	0.215	0.209
69	13DE5MB	1130	1128.4	1.6	0.240	0.228
70	13DM5nPrB	1133	1132.1	0.9	0.235	0.228
71	135TEB	1206	1209.4	−3.4	0.195	0.228
72	13DM5secBuB	1179	1182.6	−3.6	0.227	0.228
73	13DM5nBuB	1229	1228.9	0.1	0.208	0.228
74	1234tMB	1139	1140.5	−1.5	0.440	0.424
75	124TM3EB	1215	1212.3	2.7	0.431	0.424
75a	124TM3nPrB	−	−	−	0.422	0.424
76	123TM4EB	1222	1221.5	0.5	−	−
77	1235tMB	1109	1110.3	−1.3	−	−
78	135TM2EB	1183	1182.1	0.9	0.324	0.331
79	125TM3EB	1184	1182.1	1.9	0.327	0.331
80	123TM5EB	1193	1191.3	1.7	0.340	0.331
81	135TM2nPrB	1263	1266.8	−3.8	0.346	0.331
82	125TM3nPrB	1277	1276	1	0.335	0.331
83	123TM5nPrB	1279	1276	3	−	−
84	135TM5iPrB	1238	1239	−1	−	−
85	123TM5iPrB	1246	1248.3	−2.3	0.295	0.312
86	1245tMB	1106	1103.4	2.5	0.347	0.352
87	124TM5iPrB	1233	1232.2	0.8	−	−
87a	124TM5EB	−	−		0.355	0.352
87b	124TM5nPrB	−	−		0.347	0.352
88	13DnPrB	1209	1208.2	0.8	−	−
89	14DnPrB	1221	1216.4	4.6	−	−
90	12DM35DEB	1264	1263.1	0.9	0.315	0.331
91	124TM3nPrB	1297	1297	0	−	−

TABLE I (*continued*)

No.	Alkylbenzene[a]	$I_{exp.}$	$I_{calc.}$	Δ	$dI/dT_{exp.}$	$dI/dT_{calc.}$
92	12DEEMB	1170	1165.9	4.1	–	–
93	12345pMB	1260	1264.2	−4.2	–	–
94	1234tM5EB	1344	1345.3	−1.3	–	–

[a] M = Methyl; E = ethyl; Pr = propyl; Bu = butyl; B = benzene; i = iso-; n = *n*-; sec = *sec*.-; tert = *tert*.-; D = di-; T = tri-; t = tetra-.

influences the retention (see also ref. 29); and (iii) the presence of an *ortho* substitution decreases the relative retention in both branched or normal C-chains equally.

Eqn. 3 is the most accurate given so far in the literature and it can be applied for predictive calculations. To increase the probability of the identification, however, we studied also the regression between the temperature increment of I (dI/dT) and the structure. Applying the same approach the following equation is obtained:

$$dI/dT_{calc.} = 196.63 + 103.57RC - 19.2(iPr) \tag{4}$$

with $r = 0.93$, $F = 520$ and the mean standard deviation = 0.017 i.u. for 89 alkylbenzenes, where (iPr) accounts for the presence ($+1$) or absence (0) of an isopropyl group. As seen from eqn. 4, in this instance the molecular mass does not play a significant role and the kind of substitution is the most important factor.

Using eqns. 3 and 4 we shall create hypotheses for the structural assignment of the alkylbenzenes, as mass spectra do not allow a positive identification [27] of positional isomers. Such a group of alkylbenzenes is the dimethyldiethylbenzenes (DiMe-DiEtB). We found that all 1,2,3,4-tetrasubstituted DiMeDiEtB should have $I_{calc.}$ values between 1284 and 1302 i.u. and a dI/dT value of 0.424I/°C. None of the experimental index values correspond to these values. Hence, *ortho*-tetrasubstituted DiMeDiEtB are not present in the mixture.

Other experimental I values are assigned as in Table II.

The other examples are presented with unpublished retention data. Among methylethyl-*n*-propylbenzenes (MeEtnPrB), 1-Me-2-Et-3-nPrB, 1-Me-3-Et-2-nPrB and 1-Me-2-Et-6-nPrB have $I_{calc.}$ values higher than any of the $I_{exp.}$ values obtained.

TABLE II

I VALUES FOR DIMETHYLDIETHYLBENZENES

Compound	$I_{calc.}$	$I_{exp.}$	$dI/dT_{calc.}$	$dI/dT_{exp.}$
1,2-DiMe-3,5-DiEtB	1272	1274.7	0.33	0.38
1,3-DiMe-2,5-DiEtB	1263	1262.9	0.33	0.23
1,3-DiMe-4,5-DiEtB	1263	1263.6	0.33	0.30
1,4-DiMe-2,6-DiEtB	1263	1258.4	0.33	0.29
1,2-DiMe-4,5-DiEtB	1256	1255.7	0.35	0.31
1,4-DiMe-2,5-DiEtB	1256	1257.3	0.35	0.34
1,3-DiMe-4,6-DiEtB	1265	1263.9	0.35	0.30

TABLE III

I VALUES FOR METHYLETHYL-*n*-PROPYLBENZENES AND DIMETHYL-*tert.*-BUTYLBEN-ZENES

	$I_{calc.}$	$I_{exp.}$	$dI/dT_{calc.}$	$dI/dT_{exp.}$
1-Me-2-Et-4-nPrB	1228	1228.1	0.29	0.28
1-Me-3-Et-4-nPrB	1228	1232.2	0.29	0.28
1-Me-3-Et-6-nPrB	1236	1236.2	0.29	0.30
1-Me-4-et-2-nPrB	1228	1238.5	0.29	0.29
1-Me-4-Et-3-nPrB	1228	1228.1	0.29	0.28
1-Me-3-Et-5-nPrB	1213	1211.7	0.23	0.21
1,2-DiMe-3-tertBuB	1211	1211.2	0.34	0.47
1,3-DiMe-2-tertBuB	1211	1213.8	0.34	0.38
1,2-DiMe-4-tertBuB	1188	1192	0.29	0.31

Again, no *ortho*-trisubstituted MeEtPrB are present in the mixture. For the other isomers, the data in Table III are proposed. The greater difference in the case of 1-Me-4-Et-2-nPrB shows that either the experimental value or the proposed structure is uncorrect.

The illustrated coincidence between the calculated and experimental data for retention indices and the acceptable accuracy of the dI/dT values show that preliminary calculative identification is possible and we expect this to be of help in mass spectral identification. The proposed model evaluates quantitatively the relative influence of substitution in the benzene ring and branching in the alkyl substituent. Hence one can obtain both a qualitative and a quantitative understanding of the retentions of different alkylbenzenes in GC on non-polar stationary phases and can use the experimental data for structure elucidation.

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