Journal of Chromatography, 370 (1986) 355–376
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 043

RETENTION STUDIES OF ALKYL- AND HALOGEN-SUBSTITUTED AROMATICS ON NORMAL-PHASE SILICA AND ALUMINA COLUMNS

I. ALKYLBENZENES AND HALOGENOALKYLBENZENES

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(First received June 20th, 1986; revised manuscript received August 26th, 1986)

SUMMARY

Normal-phase liquid chromatography has been applied to alkylbenzenes and compounds with mixed halogen–alkyl substitution. Experiments were performed on both silica gel and alumina packed columns. With *n*-hexane as the mobile phase good peak differentiations were possible. Many of the derived log(capacity factors) could be correlated with structural features and predictions could be made. Substituent bulk and mesomeric effects are of major importance in regulating the transport of the investigated compounds. In addition, however, symmetry conditions seem to play a distinct role; group dipole moment values can therefore serve as suitable parameters in a number of instances.

INTRODUCTION

Several years ago some studies[1–5] were devoted to the chromatographic behaviour of over 200 compounds in the systems *n*-hexane–silica gel and *n*-hexane–alumina in order to obtain information on optimal separation techniques and the possible relationship between structure and retention. In addition to alkyl and halogenoalkyl aromatics, the series contained polychlorobiphenyls (PCBs), polybromobiphenyls (PBBs), polymethylbiphenyls (PMeBs), polychloronaphthalenes (PCNs) and polymethylnaphthalenes (PMeNs). The principle of the work described in this and forthcoming papers was to find parameters that describe effectively the transfer of the compounds. In a way, our studies link up with investigations performed by Snyder[6] on a number of similar structures on alumina columns, although Snyder's investi-

0021-9673/86/$03.50

gations were not intended to unravel the necessary parametrization of retention values. Also, the application of regression techniques was not in common use at the time.

EXPERIMENTAL

The compounds investigated were of several origins. All products were of sufficient purity with one main peak in the chromatogram.

n-Hexane (Baker, Deventer, The Netherlands)) was used throughout as the eluent, pre-treated with a suspension of sodium in solid paraffin[7], followed by drying over pre-heated molecular sieve 5A (200°C for at least 8 h[5]).

Retention times were determined on a Siemens high-performance liquid chromatographic (HPLC) apparatus, Type S 100, equipped with a Zeiss PM 2 UV absorbance detector, absorption was measured at 200–300 nm.

The silica gel column was packed with LiChrosorb Si 60, particle size 5 μm, column length 250 mm, I.D. 3.0 mm (Chrompack, Middelburg, The Netherlands). The alumina column was packed with LiChrosorb Alox T5, particle size 5 μm, column length 250 mm, I.D. 3.0 and 4.6 mm (Chrompack).

Sample concentrations were chosen so as to give a low but discernible signal from injection volumes of 10 μl.

Retention times are expressed in terms of log(capacity factors, k') using the equation

$$\log k' = \log(t_R - t_0)/t_0$$

where t_R is the retention time of the compound and t_0 the elution time of unretained *n*-hexane.

The flow-rate of the eluent was 2 ml/min for the silica gel column and 2 or 3.5 ml/min for the alumina column, depending on its diameter.

RESULTS AND DISCUSSION

Methylbenzenes on a silica gel column

The experimental log k' values are given in Table I for all methyl-substituted benzene derivatives and benzene.

Considering the general trend in the tabulated log k' values, we first tried to correlate log k' with the total number of methyl groups (n_{Me}), which resulted in the following equation (with 95% confidence intervals in parentheses):

$$\log k' = 0.088\ (\pm 0.010) n_{Me} + 0.378\ (\pm 0.035) \quad (1)$$

$$n = 13;\ r = 0.985;\ s = 0.027;\ F = 346$$

This equation accounts for 97% of the variances. Close inspection of the data points (Fig. 1) shows that seven out of the thirteen data points are slightly different from the others. They fit the following equation:

$$\log k' = 0.084\ (\pm 0.002) n_{Me} + 0.376\ (\pm 0.008) \quad (2)$$

$$n = 7;\ r = 0.9997;\ s = 0.004;\ F = 8280$$

These seven compounds (marked with asterisks in Fig. 1) will serve as a "backbone" for further improvement of the data correlation. The deviating behaviour of the six "non-asterisked" compounds in Fig. 1 seems to be connected with symmetry conditions in the methyl substitution pattern. For that reason, we decided to operate with n_{ortho} and n_{para} as additional parameters to n_{Me}. The two parameters denote the total number of methyl groups involved in *ortho* and *para* positions, respectively.

$$\log k' = 0.083\ (\pm 0.005)n_{Me} + 0.021\ (\pm 0.004)n_{ortho} - 0.020\ (\pm 0.003)n_{para} + 0.379\ (\pm 0.009) \quad (3)$$

$$n = 13;\ r = 0.9994;\ s = 0.006;\ F = 2840$$

Eqn. 3 has one drawback: it is slightly "under"-filled with data points (as a rule we recommend five data points for each independent parameter). The identity of the regressor values of n_{ortho} and n_{para} in eqn. 3 (with opposite algebraic sign), however, permits a parameter reduction by applying $n_{ortho} - n_{para}$ instead of n_{ortho} and n_{para} separately:

$$\log k' = 0.085\ (\pm 0.002)n_{Me} + 0.020\ (\pm 0.003)(n_{ortho} - n_{para}) + 0.377\ (\pm 0.007) \quad (4)$$

$$n = 13;\ r = 0.9994;\ s = 0.006;\ F = 4390$$

and this excellent result leaves no more than 0.2% of the variances unexplained.

Additional proof that symmetry conditions really are important and that the numerical difference in the *ortho* and *para* substitutions gives an adequate means of parametrizing this symmetry factor is demonstrated by eqn. 5 with the group dipole moment sum (μ) functioning as an additional parameter to n_{Me}:

$$\log k' = 0.088\ (\pm 0.005)n_{Me} + 0.083\ (\pm 0.029)\mu + 0.354\ (\pm 0.019) \quad (5)$$

$$n = 13;\ r = 0.997;\ s = 0.013;\ F = 785$$

Methylbenzenes on an alumina column

The experimental log k' values are given in Table II for all methyl-substituted benzene derivatives, including benzene. The following equation correlates log k' with the total number of methyl groups:

$$\log k' = 0.205\ (\pm 0.035)n_{Me} - 0.129\ (\pm 0.118) \quad (6)$$

$$n = 13;\ r = 0.969;\ s = 0.089;\ F = 169$$

The quality of this equation, which explains 94% of the variances, is significantly lower than that for the silica gel column (eqn. 1). Only five compounds are suitable to use as a "backbone" (Fig. 2) and are fitted by the equation

$$\log k' = 0.118\ (\pm 0.025)n_{Me} - 0.027\ (\pm 0.036) \quad (7)$$

$$n = 5;\ r = 0.994;\ s = 0.018;\ F = 230$$

TABLE I

CHROMATOGRAPHIC DATA FOR METHYLBENZENES ON A SILICA GEL COLUMN

n_{Me} = total number of methyl groups; the subscripts *o* and *p* denote *ortho* and *para*, respectively; μ = dipole moment in Debye units (calculated from that for a methyl group[8]).

No.	*Compound*	*Log* k'_{obs}	n_{Me}	n_o	n_p	$n_o - n_p$	μ	*Log* k'_{ext}		
								Eqn. 3	*Eqn. 4*	*Eqn. 5*
1	Benzene	0.375	0	0	0	0	0	0.379	0.377	0.354
2	Toluene	0.461	1	0	0	0	0.37	0.462	0.462	0.472
3	1,2-Dimethylbenzene	0.585	2	2	0	2	0.64	0.587	0.587	0.583
4	1,3-Dimethylbenzene	0.548	2	0	0	0	0.37	0.545	0.546	0.560
5	1,4-Dimethylbenzene	0.512	2	0	2	−2	0	0.506	0.506	0.529
6	1,2,3-Trimethylbenzene	0.690	3	3	0	3	0.74	0.691	0.692	0.679
7	1,2,4-Trimethylbenzene	0.633	3	2	2	0	0.37	0.631	0.631	0.648
8	1,3,5-Trimethylbenzene	0.621	3	0	0	0	0	0.628	0.631	0.617
9	1,2,3,4-Tetramethylbenzene	0.767	4	4	2	2	0.64	0.756	0.756	0.758
10	1,2,3,5-Tetramethylbenzene	0.736	4	3	2	1	0.37	0.735	0.736	0.736
11	1,2,4,5-Tetramethylbenzene	0.716	4	4	4	0	0	0.717	0.716	0.705
12	Pentamethylbenzene	0.820	5	5	4	1	0.37	0.821	0.821	0.823
13	Hexamethylbenzene	0.881	6	6	6	0	0	0.886	0.885	0.881

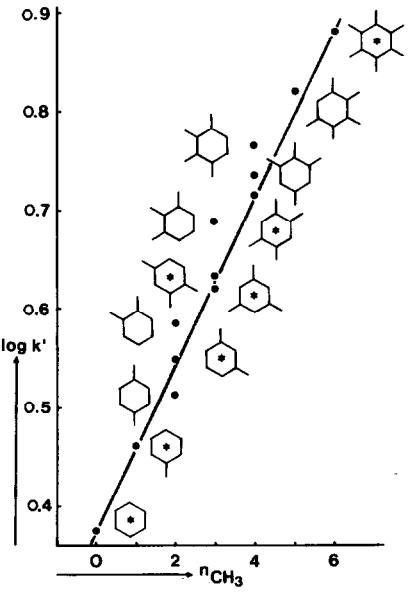


Fig. 1. Plot of log *k' versus* the number of methyl groups in methylbenzenes. Column: silica gel. The straight line correlates data obtained on the structures marked with asterisks; see eqn. 2.

Close inspection of Figs. 1 and 2, in particular the situation of the heavier methyl-substituted benzenes with regard to the two "backbones", suggests that symmetry conditions acting in the retention behaviour on an alumina column are different from those on a silica gel column. The non-equivalence of *para-* and *ortho-*

TABLE II

CHROMATOGRAPHIC DATA FOR METHYLBENZENES ON AN ALUMINA COLUMN

n_{ME} = Total number of methyl groups; the subscript *o* denotes *ortho*; n_{o-o} = number of ortho pairs.

No.	*Compound*	*Log* k'_{obs}	n_{Me}	n_o	n_{o-o}	*Log* k'_{est}*	
						Eqn. 8	*Eqn. 9*
1	Benzene	−0.032	0	0	0	*−0.035*	−0.004
2	Toluene	0.093	1	0	0	*0.083*	0.111
3	1,2-Dimethylbenzene	0.350	2	2	1	*0.351*	0.316
4	1,3-Dimethylbenzene	0.233	2	0	0	0.201	*0.226*
5	1,4-Dimethylbenzene	0.193	2	0	0	*0.201*	0.226
6	1,2,3-Trimethylbenzene	0.591	3	3	2	*0.545*	0.521
7	1,2,4-Trimethylbenzene	0.433	3	2	1	0.470	*0.432*
8	1,3,5-Trimethylbenzene	0.318	3	0	0	*0.319*	0.342
9	1,2,3,4-Tetramethylbenzene	0.778	4	4	3	*0.738*	0.727
10	1,2,3,5-Tetramethylbenzene	0.643	4	3	2	0.663	*0.637*
11	1,2,4,5-Tetramethylbenzene	0.625	4	4	2	0.738	*0.637*
12	Pentamethylbenzene	0.929	5	5	4	0.932	0.932
13	Hexamethylbenzene	1.176	6	6	6	1.125	1.227

* Estimates in italics indicate the best fitting of both values.

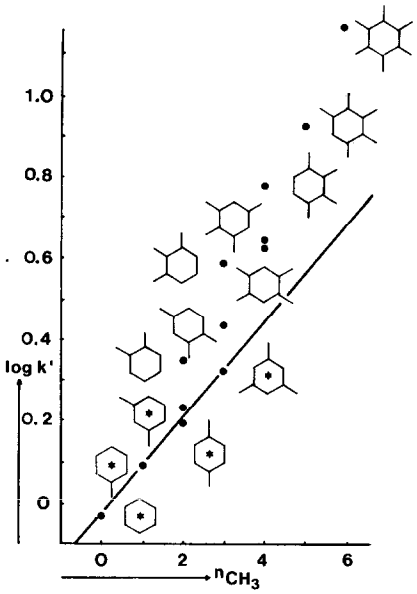


Fig. 2. Plot of log k' *versus* the number of methyl groups in methylbenzenes. Column: alumina. The straight line correlates data obtained on the structures marked with asterisks; see eqn. 7.

methyl substitution is especially evident. Compare, for instance, the location of hexamethylbenzene in Figs. 1 and 2. A good data fit could therefore be obtained by means of the exclusive use of n_{ortho} as additional parameter.

$$\log k' = 0.118\ (\pm 0.040)n_{Me} + 0.075\ (\pm 0.031)n_{ortho} - 0.035\ (\pm 0.073) \quad (8)$$

$$n = 13;\ r = 0.992;\ s = 0.047;\ F = 320$$

A different parametrization of the *ortho*-effect is applied in eqn. 9. The parameter n_{o-o} denotes the number of *ortho* pairs present in the considered structure. The statistics of the new equation are slightly improved over those of eqn. 8. Comparison of the log k'_{est} values (Table II) shows that eqn. 8 seems to be more effective with restricted methyl substitution and eqn. 9 seems to be more effective when more extended methyl substitution is involved. Eqn. 9 accounts for 99% of the variances and eqn. 8 for 98% of the variances.

$$\log k' = 0.115\ (\pm 0.032)n_{Me} + 0.090\ (\pm 0.028)n_{o-o} - 0.004\ (\pm 0.063) \quad (9)$$

$$n = 13;\ r = 0.995;\ s = 0.039;\ F = 500$$

The application of group dipole moments was not successful. This emphasizes that symmetry conditions are less important on alumina than on silica gel columns.

Alkylbenzenes on a silica gel column

Table III gives the experimentally derived log k' values of 38 alkylbenzenes. Comparison of these data shows that ethyl, propyl and higher alkyl substituents have a reducing effect on the capacity factor. In order to establish whether this effect could

be assigned a constant value, we correlated log k' with the total number of substituent carbons for toluene, ethylbenzene, isopropylbenzene and *n*-butylbenzene. This led to the following equation:

$$\log k' = -0.049\ (\pm 0.029)n_C + 0.508\ (\pm 0.079) \qquad (10)$$
$$n = 4;\ r = 0.982;\ s = 0.015;\ F = 52.8$$

The statistics are acceptable and the straight line is shown in Fig. 3b. The *tert.*-butyl-substituted compound had to be omitted from the regression on account of its bad fit ($\log k'_{obs} = 0.389$, $\log k'_{est} = 0.312$). The reason for this is discussed later.

Comparison of lines b and a in Fig. 3 (the latter represents the same line as that in Fig. 1) led to the choice of the following parametrization: n_1 is the total number of carbon atoms in the alkyl substituents, irrespective of branching or ring position, and n_2 is n_1 minus the total number of alkyl substituents. After removal of all non-fitting outliers, the following equation was obtained for eighteen (encircled) data points:

$$\log k' = 0.085\ (\pm 0.008)n_1 - 0.137\ (\pm 0.010)n_2 + 0.366\ (\pm 0.025) \qquad (11)$$
$$n = 18;\ r = 0.991;\ s = 0.022;\ F = 414$$

Included in this equation were the seven data points from eqn. 2. After completion of the regression analysis it appeared that four of the omitted data points might as well have been included in the equation. The total number of fitting structures is then 22. The residuals of the sixteen non-fitting compounds range from +0.121 to −0.238 and are at least partly connected with uncorrected symmetry conditions. Different from the transfer of eqn. 2 into eqn. 4 or 5, it is not simple to find an equation that includes all 38 compounds. This problem is as yet unsolved. The observed phenomenon may be attributed, partly, to the absence of adsorptivity of bulky alkyl groups on silica gel, resulting in an apparent lift of the adsorbed aromatic[9]. In the next section alumina is shown to behave in an identical manner. Similar suggestions were made by Snyder and Poppe[10] and by Popl *et al.*[11].

Alkylbenzenes on an alumina column

Table IV gives the experimentally derived log k' values of 38 alkylbenzenes. The regression study of the data was similar to that described above for the silica gel data. The analogues of eqns. 10 and 11 are the following equations, with identical parametrizations:

$$\log k' = -0.095\ (\pm 0.028)n_C + 0.180\ (\pm 0.076) \qquad (12)$$
$$n = 4;\ r = 0.995;\ s = 0.014;\ F = 217$$

and

$$\log k' = 0.117\ (\pm 0.011)n_1 - 0.214\ (\pm 0.015)n_2 - 0.027\ (\pm 0.021) \qquad (13)$$
$$n = 12;\ r = 0.996;\ s = 0.015;\ F = 555$$

TABLE III

CHROMATOGRAPHIC DATA FOR ALKYLBENZENES ON A SILICA GEL COLUMN

No.	*Compound*	*Log k'_{obs}*	n_1*	n_2**	*Log k'_{est} (eqn. 11)****	
					Fitting compounds	*Non-fitting compounds*
1	Benzene	0.375	0	0	0.366 (0.009)	
2	Methylbenzene	0.461	1	0	0.452 (0.009)	
3	1,2-Dimethylbenzene	0.585	2	0	*0.537* (0.048)	
4	1,3-Dimethylbenzene	0.548	2	0	0.537 (0.011)	
5	1,4-Dimethylbenzene	0.512	2	0	*0.537* (−0.025)	
6	1,2,3-Trimethylbenzene	0.690	3	0		0.623 (0.067)
7	1,2,4-Trimethylbenzene	0.633	3	0	0.623 (0.010)	
8	1,3,5-Trimethylbenzene	0.621	3	0	0.623 (−0.002)	
9	1,2,3,4-Tetramethylbenzene	0.767	4	0		0.708 (0.059)
10	1,2,3,5-Tetramethylbenzene	0.736	4	0	*0.708* (0.028)	
11	1,2,4,5-Tetramethylbenzene	0.716	4	0	0.708 (0.008)	
12	Pentamethylbenzene	0.820	5	0	*0.794* (0.026)	
13	Hexamethylbenzene	0.881	6	0	0.879 (0.002)	
14	1-Methyl-4-ethylbenzene	0.435	3	1	0.486 (−0.051)	
15	1,3-Dimethyl-5-isopropylbenzene	0.524	5	2	0.521 (0.003)	
16	1-Methyl-4-*tert.*-butylbenzene	0.407	5	3	0.384 (0.023)	
17	1,4-Dimethyl-2-*tert.*-butylbenzene	0.591	6	3		0.470 (0.121)
18	1,3-Dimethyl-5-*tert.*-butylbenzene	0.544	6	3		0.407 (0.074)
19	1,2,3-Trimethyl-5-*tert.*-butylbenzene	0.562	7	3	0.555 (0.007)	
20	1,2-Dimethyl-5-*tert.*-butylbenzene	0.462	6	3	0.470 (−0.008)	

21	1-Methyl-3,4-di-*tert.*-butylbenzene	0.334	9	6	0.317 (0.017)	
22	Ethylbenzene	0.398	2	1	0.401 (−0.003)	
23	1,3-Diethylbenzene	0.398	4	2	0.435 (−0.037)	
24	1,4-Diethylbenzene	0.326	4	2		0.435 (−0.109)
25	1,2,4-Triethylbenzene	0.386	6	3		0.470 (−0.084)
26	1,3,5-Triethylbenzene	0.332	6	3		0.470 (−0.138)
27	1-Ethyl-3,5-di-*tert.*-butylbenzene	0.137	10	7		0.266 (−0.129)
28	Isopropylbenzene	0.377	3	2	0.350 (0.027)	
29	1,3-Diisopropylbenzene	0.303	6	4	0.333 (−0.030)	
30	1,4-Diisopropylbenzene	0.176	6	4		0.333 (−0.157)
31	1,2,4-Triisopropylbenzene	0.086	9	6		0.317 (−0.231)
32	1,3,5-Triisopropylbenzene	0.079	9	6		0.317 (−0.238)
33	1,2,4,5-Tetraisopropylbenzene	0.079	12	8		0.300 (−0.221)
34	1-Isopropyl-3,5-di-*tert.*-butylbenzene	0.013	11	8		0.215 (−0.202)
35	*n*-Butylbenzene	0.305	4	3	0.299 (0.006)	
36	*tert.*-Butylbenzene	0.389	4	3		0.299 (0.090)
37	1,4-Di-*tert.*-butylbenzene	0.086	8	6		0.231 (−0.145)
38	1,3,5-Tri-*tert.*-butylbenzene	−0.027	12	9		0.164 (−0.191)

* n_1 = Total number of carbon atoms in alkyl substituents.

** $n_2 = n_1 -$ number of alkyl substituents.

*** In parentheses: differences between observed and estimated log k' values; data in italics were not included in regression eqn. 11 as they did not fit eqn. 6 accurately; after all, there is no reason to exclude them from being ranged in the last column but one with compounds fitting eqn. 11.

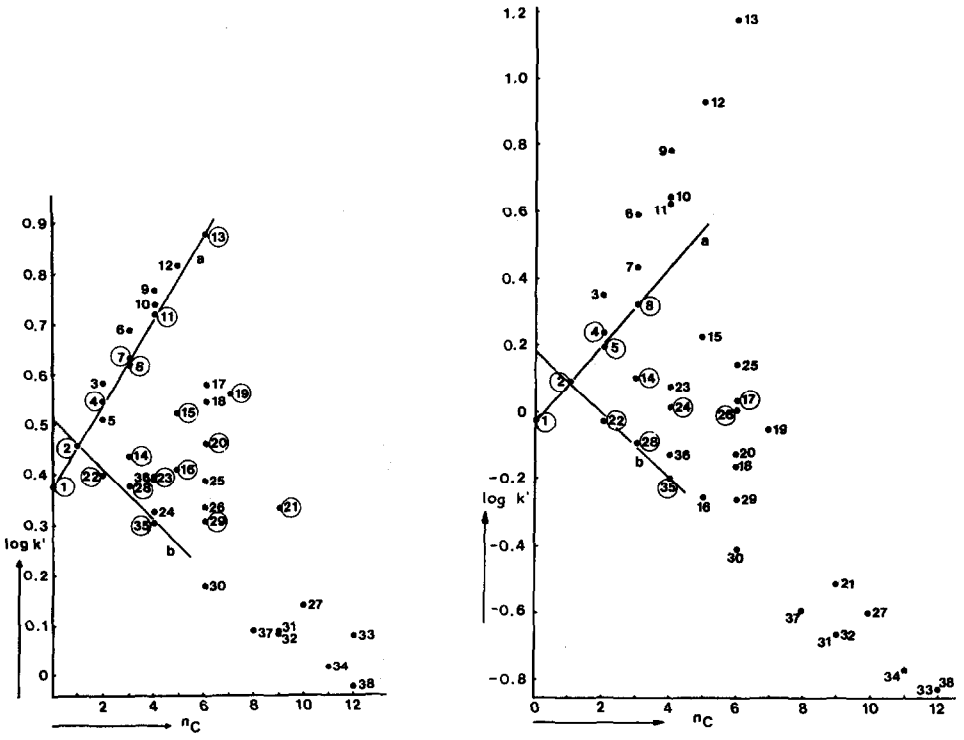


Fig. 3. Plot of log k' *versus* the number of alkyl carbon atoms (n_C) in alkylbenzenes. Column: silica gel. Numbering as in Table III. Straight line a comprises data points 1, 2, 4, 7, 8, 11 and 13 and corresponds with the straight line in Fig. 1 (see eqn. 2); straight line b comprises data points 2, 22, 28 and 35 (see eqn. 10); the encircled data points (1, 2, 4, 7, 8, 11, 13, 14, 15, 16, 19, 20, 21, 22, 23, 28, 29 and 35) can be included in regression eqn. 11.

Fig. 4. Plot of log k' *versus* the number of alkyl carbon atoms (n_C) in alkylbenzenes. Column: alumina. Numbering as in Table IV. Straight line a comprises data points 1, 2, 4, 5 and 8 and corresponds with the straight line drawn in Fig. 2 (see eqn. 7); straight line b comprises data points 2, 22, 28 and 35 (see eqn. 12); the encircled data points (1, 2, 4, 5, 8, 14, 17, 22, 24, 26, 28 and 35) can be included in regression eqn. 13.

The total number of fitting data points (encircled in Fig. 4) is strongly reduced with regard to the equation for silica gel data (eqn. 11). The total number of outliers is now 26 with residuals ranging from $+0.504$ to -0.480.

Comparison of eqns. 11 and 13, guided by the schematized line pattern given in Fig. 5, reveals the following trends for alkyl substitution, independent of whether the column packing is silica gel or alumina.

(1) Methyl-substitution increases log k' with a uniform pattern; independent of whether the methyl groups are introduced in benzene (toluene) or in ethylbenzene, propylbenzene, etc., the introduction of one methyl group is accompanied by a constant log k' increase of:

for silica gel columns: 0.084 (eqn. 2), 0.085 (eqn. 11);

for alumina columns: 0.118 (eqn. 7), 0.117 (eqn. 13).

There is a constant upward movement along the straight lines denoted by a'_0, a_2, a_3,..., in Fig. 5.

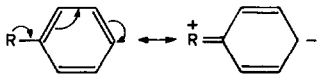
(2) Alkyl substitution decreases log k' along the straight lines b_0, b_1, b_2 in Fig. 5. These log k' decreases can easily be derived from eqns. 11 and 13 and are 0.052 for silica gel columns and 0.097 for alumina columns.

(3) Changes in the symmetry pattern cause large differences between the predicted and observed log k' values (see relevant columns in Tables III and IV). Attempts to make the necessary corrections as performed for methylbenzenes (eqns. 4, 5, 8 and 9) proved ineffectual.

(4) The effect of alkyl substitution on log k' seems to consist of two distinguishable factors, one being attributable to the substituent bulk and the other to mesomeric effects of the alkyl substituent on the phenyl nucleus. The following calculation enables some detailed information to be obtained:

	SiO_2		Al_2O_3	
Toluene: log k'_{obs}	0.461		0.093	
"CH_2 bulk" factor	−0.052	−	−0.097	−
Benzene: log k'_{pred}	0.513		0.190	
Benzene: log k'_{obs}	0.375	−	−0.032	−
Δ =	0.138		0.222	

The observed log k' values for benzene are 0.138 and 0.222, respectively, lower than predicted. These deviations can be attributed to the mesomeric impact of methyl and other alkyl groups on the benzene ring according to



where R represents an aliphatic hydrocarbon residue. These mesomeric effects are fairly consistent, as follows from their Hammett σ-values (-0.152 ± 0.015 for an *n*-alkyl group[12]). An isopropyl group is not different ($\sigma = -0.15$) but a *tert.*-butyl group with $\sigma = -0.20$ has a significantly higher mesomeric effect on a benzene ring. This is probably the reason why an isopropyl group fits correctly the b-line equation, whereas the *tert.*-butyl group has a significantly increased log k' value*.

(5) The basic values for log k' moving along the a lines by a mesomeric effect and along the b lines by the introduction of bulk [see the values in paragraphs (1) and (4) above, respectively] permit predictions of log k' values. The following examples can be given for 1,3-diethylbenzene and 1-methyl-4-ethylbenzene.

1,3-Diethylbenzene: starting from log k' (benzene), two moves upwards along a_0 and two moves downwards along b_1 are required, resulting in the following calculations:

log $k'(SiO_2) = 0.375 + 2 \cdot 0.085 - 2 \cdot 0.052 = 0.441$ (fit eqn. 11, 0.435; obs., 0.398)
log $k'(Al_2O_3) = -0.032 + 2 \cdot 0.117 - 2 \cdot 0.097 = 0.008$ (fit eqn. 13, 0.010; obs., 0.083)

* A Hammett σ-value describes the total electronic substituent effect, but for an alkyl group it represents the proper mesomeric effect as the inductive counterpart of an alkyl mesomeric effect is zero, independent of length, branching or cyclization of the alkyl group[13].

TABLE IV

CHROMATOGRAPHIC DATA FOR ALKYLBENZENES ON AN ALUMINA COLUMN

No.	*Compound*	*Log k'_{obs}*	n_1*	n_2**	*Log k'_{est} (eqn. 13)****	
					Fitting compounds	*Non-fitting compounds*
1	Benzene	−0.032	0	0	−0.027 (−0.005)	
2	Methylbenzene	0.093	1	0	0.089 (0.004)	
3	1,2-Dimethylbenzene	0.350	2	0		0.206 (0.144)
4	1,3-Dimethylbenzene	0.233	2	0	0.206 (0.027)	
5	1,4-Dimethylbenzene	0.193	2	0	0.206 (−0.013)	
6	1,2,3-Trimethylbenzene	0.591	3	0		0.322 (0.269)
7	1,2,4-Trimethylbenzene	0.433	3	0		0.322 (0.111)
8	1,3,5-Trimethylbenzene	0.318	3	0	0.322 (−0.004)	
9	1,2,3,4-Tetramethylbenzene	0.778	4	0		0.439 (0.339)
10	1,2,3,5-Tetramethylbenzene	0.643	4	0		0.439 (0.204)
11	1,2,4,5-Tetramethylbenzene	0.625	4	0		0.439 (0.186)
12	Pentamethylbenzene	0.929	5	0		0.555 (0.374)
13	Hexamethylbenzene	1.176	6	0		0.672 (0.504)
14	1-Methyl-4-ethylbenzene	0.104	3	1	0.108 (−0.004)	
15	1,3-Dimethyl-5-isopropylbenzene	0.225	5	2		0.127 (0.098)
16	1-Methyl-4-*tert.*-butylbenzene	−0.252	5	3		−0.088 (−0.164)
17	1,4-Dimethyl-2-*tert.*-butylbenzene	0.037	6	3	0.029 (0.008)	
18	1,3-Dimethyl-5-*tert.*-butylbenzene	−0.161	6	3		0.029 (−0.180)
19	1,2,3-Trimethyl-5-*tert.*-butylbenzene	−0.051	7	3		0.146 (−0.197)
20	1,2-Dimethyl-5-*tert.*-butylbenzene	−0.119	6	3		0.029 (−0.148)

21	1-Methyl-3,4-di-*tert.*-butylbenzene	−0.509	9	6		−0.264 (−0.245)
22	Ethylbenzene	−0.027	2	1	−0.008 (−0.019)	
23	1,3-Diethylbenzene	0.083	4	2		0.010 (0.073)
24	1,4-Diethylbenzene	0.021	4	2	0.010 (0.011)	
25	1,2,4-Triethylbenzene	0.152	6	3		0.029 (0.123)
26	1,3,5-Triethylbenzene	0.013	6	3	0.029 (−0.016)	
27	1-Ethyl-3,5-di-*tert.*-butylbenzene	−0.602	10	7		−0.362 (−0.240)
28	Isopropylbenzene	−0.097	3	2	−0.106 (0.009)	
29	1,3-Diisopropylbenzene	−0.260	6	4		−0.185 (−0.075)
30	1,4-Diisopropylbenzene	−0.409	6	4		−0.185 (−0.224)
31	1,2,4-Triisopropylbenzene	−0.658	9	6		−0.264 (−0.394)
32	1,3,5-Triisopropylbenzene	−0.658	9	6		−0.264 (−0.394)
33	1,2,4,5-Tetraisopropylbenzene	−0.824	12	8		−0.344 (−0.480)
34	1-Isopropyl-3,5-di-*tert.*-butylbenzene	−0.770	11	8		−0.770 (−0.460)
35	*n*-Butylbenzene	−0.201	4	3	−0.204 (0.003)	
36	*tert.*-Butylbenzene	−0.125	4	3		−0.204 (0.079)
37	1,4-Di-*tert.*-butylbenzene	−0.585	8	6		−0.381 (−0.204)
38	1,3,5-Tri-*tert.*-butylbenzene	−0.824	12	9		−0.557 (−0.267)

* n_1 = total number of carbon atoms in alkyl substituents.
** $n_2 = n_1$ − number of alkyl substituents.
*** In parentheses: differences between observed and estimated log k' values.

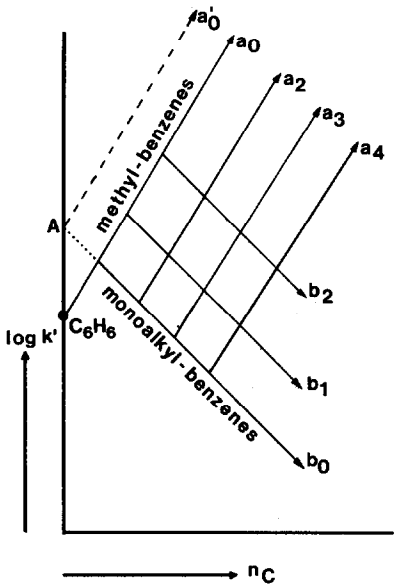


Fig. 5. Schematized log k' *versus* n_C plot for alkylbenzenes on silica gel or alumina columns. The a lines depict the effect of methyl substitution in a monoalkylbenzene, the subscripts denoting the number of carbon atoms in the alkyl group; a'_0 is the hypothetical a_0 line with exclusion of mesomeric methyl effects; A indicates the hypothetical location of benzene. The b lines depict the effect of alkyl substitution in a methylbenzene, the subscripts denoting the number of methyl groups.

1-Methyl-4-ethylbenzene: starting from log k' (benzene), two moves upwards along a_0 and one move downwards along b_1 are required, resulting in the following calculations:

$\log k'(SiO_2) = 0.375 + 2 \cdot 0.085 - 1 \cdot 0.052 = 0.493$ (fit eqn. 11, 0.486; obs., 0.435)
$\log k'(Al_2O_3) = -0.032 + 2 \cdot 0.117 - 1 \cdot 0.097 = 0.105$ (fit eqn. 13, 0.108; obs., 0.104)

(6) Lengthening of the aliphatic chain in an alkylbenzene will gradually decrease log k' on both silica gel and alumina columns. An aliphatic behavioural pattern will finally dominate, first on an alumina and then on a silica gel column.

It is interesting that the essential features of the relationships between log k' and the number of carbon atoms in an alkylbenzene as shown in Figs. 3–5 can also be found in the papers by Ageev *et al.*[14] and Kříž and co-workers[15,16]. Ageev *et al.* gave a line pattern corresponding to lines a and b in Fig. 3 for the retention of methylbenzenes (a) and monoalkylbenzenes on a silica gel column. Kříž *et al.* extend the plot to more and heavier substituted alkylbenzenes[15] and to alkylnaphthalenes[16]. Neither group used alumina packed columns and the scope of their work was restricted to qualitative considerations.

Silica gel versus alumina in alkylbenzene retention

Careful comparison of Tables III and IV reveals a close parallel between the observed retention values for at least some of the investigated alkylbenzenes. The

correlation of alumina data *versus* those obtained on silica gel for the complete data set is given by

$$\log k'(Al_2O_3) = 1.996\ (\pm 0.224)\log k'\ (SiO_2) - 0.847\ (\pm 0.107) \qquad (14)$$
$$n = 38;\ r = 0.949;\ s = 0.156;\ F = 324$$

The sensitivity for alkylbenzenes on an alumina column is twice that on a silica gel column. Eqn. 14 confirms our findings that retentions obtained on both silica gel and alumina are mainly regulated by bulk factors in the transported hydrocarbons (see eqns. 1, 6, 11 and 13) and that any specific factor on alkylbenzene retention originating from the applied column packing is of only secondary importance.

Straight line A in Fig. 6 clearly reflects the mutual relationships in the investigated series. It is of interest how all ethyl compounds (marked with asterisks in Fig. 6) are clustered on the left side of line A and that especially the higher methylated benzenes tend to follow a deviating pattern. This led us to check some non-linear fits. All thirteen methylbenzenes could be correctly fitted by a "pit" parabola:

$$\log k'(Al_2O_3) = 1.857\ (\pm 0.127)[\log k'(SiO_2)]^2 - 0.314\ (\pm 0.059) \qquad (15)$$
$$n = 13;\ r = 0.995;\ s = 0.037;\ F = 1020$$

The six ethylbenzenes could be fitted by this equation (details in Table V) and the complete methyl- and ethylbenzene set (thirteen data points) could be correlated as follows:

$$\log k'(Al_2O_3) = 3.152\ (\pm 0.918)[\log k'(SiO_2)]^2 - 1.728\ (\pm 1.078)\log k'(SiO_2) + 0.242\ (\pm 0.295) \qquad (16)$$
$$n = 19;\ r = 0.992;\ s = 0.048;\ F = 501$$

This equation is represented by curve B in Fig. 6 and it puts all alkylbenzenes higher than ethyl benzenes aside. Their retention values on alumina remain considerably lower than those obtained on silica gel and the effect depends to some extent on (a) the number and (b) the size of the alkyl groups.

Halogenomethylbenzenes on a silica gel column

Table VI gives the experimentally derived log k' values of a series of 28 halogenomethylbenzenes. Simple comparisons of analogous trios (1–10–25, 2–11–26, etc.) clearly indicate an effect of increasing halogen bulk on the capacity factor. We decided to account for this effect by the application of a suitable set of indicator values (dummy parameters). For chloro compounds $D_1 = 0, D_2 = 0$, for bromo compounds $D_1 = 1$ and $D_2 = 0$ and for iodo compounds $D_1 = 0$ and $D_2 = 1$. The simplest parametrization gives the following equation:

$$\log k' = 0.034\ (\pm 0.038)n_{Me} + 0.034\ (\pm 0.015)D_1 + 0.057\ (\pm 0.051)D_2 + 0.037\ (\pm 0.076) \qquad (17)$$
$$n = 28;\ r = 0.747;\ s = 0.043;\ F = 11.6$$

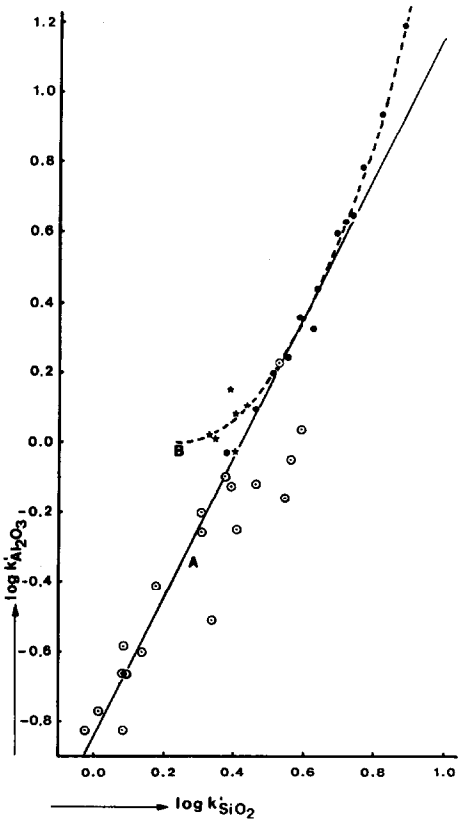


Fig. 6. Plot of log k' (alumina) *versus* log k' (silica gel) for 38 alkylbenzenes (data taken from Tables III and IV). Curve A, eqn. 14; curve B; eqn. 16. ●, Methylbenzenes; ★, ethylbenzenes; ⊙, higher alkylbenzenes.

This equation is far from significant. It can be improved by the replacement of n_{Me} by the parameters $n_{meta+para}$, n_{ortho} and n_{para}:

$$\log k' = 0.051\ (\pm 0.007)n_{meta+para} + 0.034\ (\pm 0.008)D_1 + 0.062\ (\pm 0.011)D_2 + \\ + 0.022\ (\pm 0.005)n_{ortho} - 0.013\ (\pm 0.004)n_{para} + 0.040\ (\pm 0.007) \quad (18)$$

$$n = 28;\ r = 0.990;\ s = 0.010;\ F = 245$$

There is a striking correspondence between the parametrizations of eqns. 3 and 18. The algebraic signs of the n_{ortho} and n_{para} regressors are the same, although their values are no longer statistically equal. It is therefore justified to try the introduction of a summed group dipole moment μ as an additional parameter to eqn. 17. For detailed information we refer to Table VI. The results of this calculation are given in eqn. 19.

TABLE V

CHROMATOGRAPHIC DATA FOR ETHYLBENZENES ON AN ALUMINA COLUMN

Benzene and toluene data have been added for comparison.

Compound	*Log k'_{obs}*	*Log k'_{est}*					
		Eqn. 14	*Δ*	*Eqn. 15*	*Δ*	*Eqn. 16*	*Δ*
1-Methyl-4-ethylbenzene	0.104	0.021	0.083	0.037	0.067	0.086	0.018
Ethylbenzene	−0.027	−0.053	0.026	−0.021	−0.006	0.052	−0.079
1,3-Diethylbenzene	−0.083	−0.053	0.136	−0.021	−0.062	0.052	0.031
1,4-Diethylbenzene	0.021	−0.197	0.218	−0.117	0.138	0.013	0.008
1,2,4-Triethylbenzene	0.152	−0.077	0.229	−0.037	0.189	0.045	0.107
1,3,5-Triethylbenzene	0.013	−0.185	0.198	−0.110	0.123	0.015	−0.002
Benzene	−0.032	−0.099	0.067	−0.052	0.020	0.038	−0.070
Toluene	0.093	0.073	0.020	0.081	0.012	0.117	−0.024

$$\log k' = 0.030\ (\pm 0.007)n_{Me} + 0.055\ (\pm 0.019)D_1 + \\ + 0.068\ (\pm 0.025)D_2 + 0.141\ (\pm 0.033)\mu - 0.221\ (\pm 0.062) \quad (19)$$

$$n = 28;\ r = 0.947;\ s = 0.021;\ F = 55.8$$

in which the correlation coefficient r has increased significantly from 0.747 in eqn. 17 to 0.947.

Halogenomethylbenzenes on an alumina column

The experimentally derived log k' values are given in Table VI. A regression equation with a parametrization identical with that of eqn. 17 is

$$\log k' = 0.156\ (\pm 0.027)n_{Me} + 0.154\ (\pm 0.067)D_1 + \\ + 0.385\ (\pm 0.091)D_2 - 0.001\ (\pm 0.063) \quad (20)$$

$$n = 28;\ r = 0.950;\ s = 0.075;\ F = 81.1$$

In contrast with eqn. 17, the statistics of eqn. 20 are acceptable, although the addition of n_{para} and n_{o-o} as extra parameters gives a substantial improvement:

$$\log k' = 0.082\ (\pm 0.014)n_{Me} + 0.156\ (\pm 0.021)D_1 + 0.380\ (\pm 0.029)D_2 + \\ + 0.034\ (\pm 0.020)n_{para} + 0.112\ (\pm 0.016)n_{o-o} + 0.071\ (\pm 0.023) \quad (21)$$

$$n = 28;\ r = 0.995;\ s = 0.025;\ F = 526$$

The introduction of the sum group dipole moment in eqn. 20 was unsuccessful.

Comparison between methylbenzenes and halogenomethylbenzenes

From the preceding sections, it is obvious that the chromatographic behaviour of methylbenzenes and halogenomethylbenzenes on both silica gel and alumina has distinct points of concurrence. Close observation of the obtained regression equations (compare eqns. 3 and 4 with eqns. 18 and 8 and compare eqn. 9 with eqn. 20) reveals,

TABLE VI

CHROMATOGRAPHIC DATA FOR HALOGENOMETHYLBENZENES ON SILICA GEL AND ALUMINA COLUMNS

n_{Me} = total number of methyl groups; D_1 and D_2 = indicator values (dummy parameters); for chloro compounds $D_1 = D_2 = 0$, for bromo compounds $D_1 = 1$ and $D_2 = 0$ and for iodo compounds $D_1 = 0$ and $D_2 = 1$; the subscripts *m*, *p* and *o* denote *meta*, *para* and *ortho*, respectively; n_{o-o} = number of *ortho*-methyl pairs; μ = dipole moment in Debye units (calculated from group moments).

No.	*Compound*	*Log* k'_{obs}		n_{Me}	$n_{m,p}$	n_o	n_p	n_{o-o}	D_1	D_2	μ	*Log* k'_{est}			
		SiO_2	Al_2O_3									SiO_2 *(eqn. 15)*	Al_2O_3 *(eqn. 18)*	SiO_2 *(eqn. 16)*	Al_2O_3 *(eqn. 19)*
	Chlorobenzenes														
1	Unsubstituted	0.033	0.061	0	0	0	0	0	0	0	1.76	0.040	0.071	0.028	0.033
2	2-Methyl	0.045	0.143	1	0	0	0	0	0	0	1.61	0.040	0.152	0.037	0.109
3	3-Methyl	0.090	0.143	1	1	0	0	0	0	0	1.97	0.091	0.152	0.088	0.242
4	4-Methyl	0.086	0.176	1	1	0	0	0	0	0	2.13	0.091	0.186	0.110	0.161
5	2,3-Dimethyl	0.137	0.380	2	1	2	0	1	0	0	1.87	0.134	0.346	0.104	0.293
6	2,4-Dimethyl	0.090	0.283	2	1	0	0	0	0	0	1.97	0.091	0.268	0.118	0.242
7	2,6-Dimethyl	0.037	0.250	2	0	0	0	0	0	0	1.39	0.040	0.234	0.036	0.221
8	3,4-Dimethyl	0.188	0.384	2	2	2	0	1	0	0	2.34	0.185	0.380	0.170	0.370
9	2,5-Dimethyl	0.072	0.201	2	1	0	2	0	0	0	1.76	0.065	0.234	0.088	0.349
	Bromobenzenes														
10	Unsubstituted	0.079	0.243	0	0	0	0	0	1	0	1.64	0.074	0.226	0.065	0.208
11	2-Methyl	0.083	0.307	1	0	0	0	0	1	0	1.49	0.074	0.308	0.074	0.285
12	3-Methyl	0.127	0.297	1	1	0	0	0	1	0	1.85	0.125	0.308	0.125	0.418

13	4-Methyl	0.127	0.332	1	1	0	0	0	1	0	2.01	0.125	0.342	0.148	0.336
14	2,4-Dimethyl	0.127	0.436	2	1	0	0	0	1	0	1.85	0.125	0.424	0.125	0.418
15	3,5-Dimethyl	0.170	0.346	2	2	0	0	0	1	0	2.01	0.176	0.389	0.178	0.336
16	3,4-Dimethyl	0.223	0.526	2	2	2	0	1	1	0	2.22	0.219	0.536	0.208	0.546
17	2,3-Dimethyl	0.164	0.538	2	1	2	0	1	1	0	1.76	0.168	0.501	0.143	0.464
18	2,6-Dimethyl	0.079	0.410	2	0	0	0	0	1	0	1.27	0.074	0.389	0.074	0.397
19	2,5-Dimethyl	0.104	0.350	2	1	0	2	0	1	0	1.64	0.098	0.389	0.126	0.525
20	2,4,6-Trimethyl	0.114	0.528	3	1	0	0	0	1	0	1.64	0.125	0.505	0.156	0.525
21	2,3,6-Trimethyl	0.130	0.598	3	1	2	2	1	1	0	1.49	0.142	0.583	0.135	0.601
22	2,3,4,6-Tetramethyl	0.210	0.825	4	2	3	2	2	1	0	1.85	0.214	0.811	0.216	0.734
23	2,3,5,6-Tetramethyl	0.190	0.782	4	2	4	4	2	1	0	1.64	0.210	0.776	0.187	0.841
24	2,3,4,5,6-Pentamethyl	0.303	1.086	5	3	5	4	4	1	0	2.01	0.282	1.116	0.269	0.970
	Iodobenzenes														
25	Unsubstituted	0.097	0.465	0	0	0	0	0	0	1	1.71	0.103	0.450	0.088	0.417
26	2-Methyl	0.114	0.542	1	0	0	0	0	0	1	1.56	0.103	0.532	0.097	0.493
27	3-Methyl	0.146	0.516	1	1	0	0	0	0	1	1.92	0.153	0.532	0.148	0.626
28	2,4-Dimethyl	0.155	0.639	2	1	0	0	0	0	1	1.92	0.153	0.648	0.178	0.626

however, that mutual similarities are not such as to allow the incorporation of both series in one regression equation.

A comparison of both series, based on a replacement of one methyl group from a methylbenzene by a halogen atom, showed some striking parallels between the methylbenzene and halogenomethylbenzene series. These parallels are illustrated in Figs. 7 and 8. They also give the following set of equations:

(a) Bromomethylbenzenes with the bromine atom flanked by two methyl groups:

on silica gel columns:

$$\log k'_{\text{Br-Me}} = 1.152\ (\pm 0.316)\log k'_{\text{Me}} - 0.734\ (\pm 0.288) \qquad (22)$$

$n = 6$; $r = 0.975$; $s = 0.020$; $F = 76.4$

on alumina columns:

$$\log k'_{\text{Br-Me}} = 1.116\ (\pm 0.193)\log k'_{\text{Me}} - 0.234\ (\pm 0.167) \qquad (23)$$

$n = 6$; $r = 0.992$; $s = 0.034$; $F = 258$

(b) The whole bromomethylbenzene series were correlated by applying an extra parameter n_{ortho}, denoting the number of methyl groups in an *ortho* position with respect to bromine:

on silica gel columns:

$$\log k'_{\text{Br-Me}} = 0.932\ (\pm 0.205)\log k'_{\text{Me}} - 0.094\ (\pm 0.028)n_{ortho} - 0.374\ (\pm 0.114) \qquad (24)$$

$n = 15$; $r = 0.942$; $s = 0.023$; $F = 51.0$

on alumina columns:

$$\log k'_{\text{Br-Me}} = 1.047\ (\pm 0.159)\log k'_{\text{Me}} - 0.129\ (\pm 0.055)n_{ortho} + 0.077\ (\pm 0.053) \qquad (25)$$

$n = 15$; $r = 0.984$; $s = 0.045$; $F = 198$

(c) The integrated halogenomethylbenzene series coupled together by means of a set of dummy parameters, identical with the set presented in Table VI:

on silica gel columns:

$$\log k'_{\text{Hal-Me}} = 0.908\ (\pm 0.127)\log k'_{\text{Me}} - 0.093\ (\pm 0.016)n_{ortho} + 0.036\ (\pm 0.016)D_1 + 0.064\ (\pm 0.022)D_2 - 0.395\ (\pm 0.068) \qquad (26)$$

$n = 28$; $r = 0.958$; $s = 0.019$; $F = 72.6$

on alumina columns:

$$\log k'_{\text{Hal-Me}} = 1.033\ (\pm 0.118)\log k'_{\text{Me}} - 0.133\ (\pm 0.037)n_{ortho} + 0.161\ (\pm 0.037)D_1 + 0.392\ (\pm 0.050)D_2 - 0.071\ (\pm 0.039) \qquad (27)$$

$n = 28$; $r = 0.985$; $s = 0.043$; $F = 211$

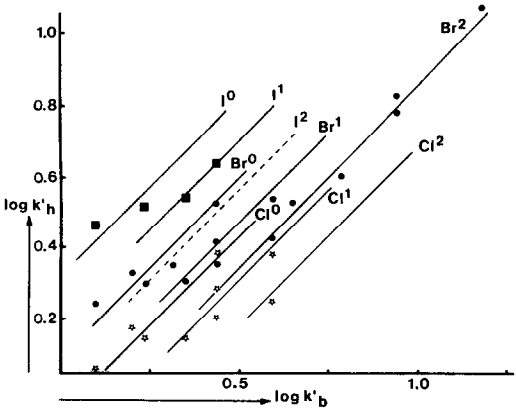


Fig. 7. Plot of log k' for halogenomethylbenzenes (log k'_h) on a silica gel column *versus* corresponding data for related methylbenzenes (log k'_b). ☆, Chloromethylbenzenes; ●, bromomethylbenzenes; ■, iodomethylbenzenes. The superscripts 0, 1 and 2 denote the number of methyl groups in an *ortho* position with respect to the halogen.

Eqns. 26 and 27 permit the nine parallel lines in Figs. 7 and 8 to be drawn. Each of these lines comprises the halogenomethylbenzenes indicated by Cl, Br and I; the superscripts 0, 1 and 2 denote the number of methyl groups in an *ortho* position with respect towards the halogen atom. The equivalence of both systems is surprisingly evident, especially if one considers the regressor values of the first right-hand terms in eqns. 26 and 27: they are not significantly differing from unity.

Owing to the difference between the weights of the halogen effects, as indicated by the computed dummy regressor values, part of the line pattern in Fig. 8 has moved compared with the pattern in Fig. 7, thus clearly demonstrating the difference between the two column packings.

CONCLUSION

Retention of methylbenzenes on silica (elution with *n*-hexane) is regulated by the number of methyl groups and to a lesser extent by symmetry conditions. This

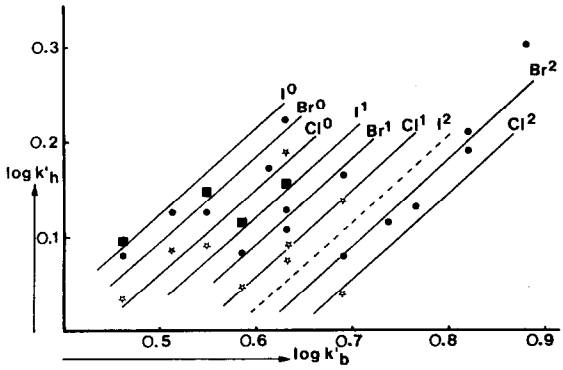


Fig. 8. Plot of log k' for halogenomethylbenzenes (log k'_h) on an alumina column *versus* corresponding data for related methylbenzenes (log k'_b). Symbols and superscripts as in Fig. 7.

can be correctly parametrized either by the $n_{ortho} - n_{para}$ number or by a summed group dipole moment. On alumina the number of methyl groups is equally important and, the additional parameter is the number of *ortho* pairs. Extension of a methyl group to a higher alkyl leads to a network plot of log k' *versus* the number of alkyl carbon atoms with an indication that larger alkyl groups give a "lift" to the adsorbed aromatics away from the packing material. Introduction of one halogen atom in the nucleus of methylbenzenes does not essentially change the features of retention, and indicated above for methylbenzenes, the observed retentions run largely parallel.

ACKNOWLEDGEMENT

The authors thank Prof. Dr. U. A. Th. Brinkman for commenting on the manuscript.

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