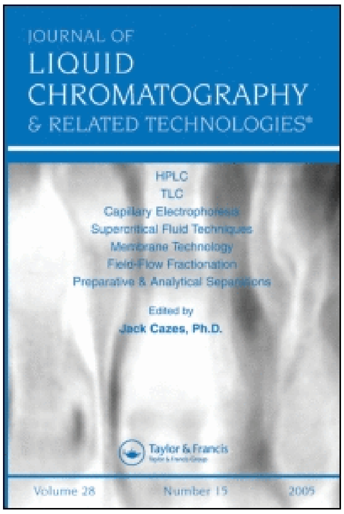

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Retention Studies of Alkyl- and Halogen-Substituted Aromatics on Normal-Phase Silica and Alumina Columns. IV. Effect of the Mobile Phase Structure on Retention Data

G. De Vries[a]; R. F. Rekker[b]
[a] Department of Analytical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands [b] Department of Pharmacochemistry, Vrije Universiteit, Amsterdam, The Netherlands

To cite this Article De Vries, G. and Rekker, R. F.(1993) 'Retention Studies of Alkyl- and Halogen-Substituted Aromatics on Normal-Phase Silica and Alumina Columns. IV. Effect of the Mobile Phase Structure on Retention Data', Journal of Liquid Chromatography & Related Technologies, 16: 2, 383 — 402

To link to this Article: DOI: 10.1080/10826079308020920

URL: http://dx.doi.org/10.1080/10826079308020920

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(2), 383-402 (1993)

RETENTION STUDIES OF ALKYL- AND HALOGEN-SUBSTITUTED AROMATICS ON NORMAL-PHASE SILICA AND ALUMINA COLUMNS. IV. EFFECT OF THE MOBILE PHASE STRUCTURE ON RETENTION DATA

G. DE VRIES[1] AND R. F. REKKER[2*]
[1]Department of Analytical Chemistry
[2]Department of Pharmacochemistry
Vrije Universiteit
De Boelelaan 1083
1081 HV Amsterdam, The Netherlands

ABSTRACT

Normal-phase liquid chromatography has been applied to five series of compounds: chlorobenzenes, chloronaphthalenes, chlorobiphenyls, methylbenzenes and methylbiphenyls. Experiments were performed on silica with n-octane, n-decane, iso-octane and cyclo-hexane as the mobile phases.

The data obtained are compared with previously published n-hexane retention data. Mutual differences are significant and they are apparently associated with differences in bulk and mobility of the molecules of the eluent. Moreover, the substitution pattern in the investigated series seems to be of due importance.

INTRODUCTION

Ample inspection of the literature brings to light that the choice of the mobile phase in retention studies on normal-

---

* to receive all correspondence

phase HPLC columns mainly restricts itself to n-hexane. Other hydrocarbons such as pentane, heptane, etc., are much less frequently used. Any purposeful search into the effect of chain-length, branching or cyclisation of the hydrocarbon used for elution seems lacking.

We considered it to be useful to extend our previously published material on the retention of alkyl- and halogen-substituted aromatics - with an exclusive usage of n-hexane as the eluent - with a set of measurements on a silica column in which n-octane, n-decane, iso-octane (2,2,4-trimethylpentane) and cyclo-hexane were used as the mobile phase. The new data do not cover completely the old ones with n-hexane elution since a number of items were no longer available. An extension to eluents with longer chains and/or branchings was rather considered but finally abandoned because matters of viscosity and obtainability presented insuperable objections.

EXPERIMENTAL

Retention data, except those with cyclo-hexane, were obtained during earlier experiments together with those on n-hexane (1 - 6), largely performed by one of the present authors(dV).

Regarding materials, apparatus and further experimental conditions, reference is made to the first paper in the present series (7).

RESULTS AND DISCUSSION

Table 1 collects the experimental log k' - values for three series of compounds: chlorobenzenes, chloronaphthalenes and chlorobiphenyls. The table compares data obtained on silica columns using n-hexane, n-octane, n-decane, iso-octane and cyclo-hexane as the mobile phase, respectively.

Careful comparison of the tabulated data will reveal fairly close parallels between the observed retention-values for the three unbranched hydrocarbonacious eluents, whereas some obvious irregularities for the branched octane and the cyclic hexane phases become evident.

This made us decide to treat the retention data for the unbranched mobile phases separated from the others.

UNBRANCHED MOBILE PHASES

Correlations were derived for *n*-octane and *n*-decane data *versus* those obtained for *n*-hexane.

a. Chlorobenzenes

$$\log k'(n\text{-oct}) = 1.007(\pm 0.046)\ \log k'(n\text{-hex}) + 0.021(\pm 0.013)^{*}$$

$n = 13 \quad r = 0.998 \quad s = 0.016 \quad F = 2200$ (eq.1)

$$\log k'(n\text{-dec}) = 0.930(\pm 0.044)\ \log k'(n\text{-hex}) + 0.045(\pm 0.013)$$

$n = 13 \quad r = 0.996 \quad s = 0.036 \quad F = 455$ (eq.2)

b. Chloronaphthalenes

$$\log k'(n\text{-oct}) = 1.018(\pm 0.020)\ \log k'(n\text{-hex}) + 0.017(\pm 0.005)$$

$n = 8 \quad r = 1.000 \quad s = 0.004 \quad F = 17400$ (eq.3)

$$\log k'(n\text{-dec}) = 0.997(\pm 0.017)\ \log k'(n\text{-hex}) + 0.037(\pm 0.005)$$

$n = 8 \quad r = 1.000 \quad s = 0.006 \quad F = 10600$ (eq.4)

c. Chlorobiphenyls

$$\log k'(n\text{-oct}) = 0.986(\pm 0.027)\ \log k'(n\text{-hex}) + 0.031(\pm 0.012)$$

$n = 32 \quad r = 0.996 \quad s = 0.019 \quad F = 6200$ (eq.5)

$$\log k'(n\text{-dec}) = 1.008(\pm 0.019)\ \log k'(n\text{-hex}) + 0.057(\pm 0.009)$$

$n = 32 \quad r = 0.995 \quad s = 0.029 \quad F = 2970$ (eq.6)

All three series include the unsubstituted parent compound: benzene, naphthalene and biphenyl, respectively. The close mutual resemblance of the equation sets (1-3-5) and (2-4-6) allow the inclusion of the investigated material into the following two equations:

$$\log k'(n\text{-oct}) = 1.002(\pm 0.014)\ \log k'(n\text{-hex}) + 0.024(\pm 0.006)$$

$n = 53 \quad r = 0.999 \quad s = 0.016 \quad F = 21900$ (eq.7)

$$\log k'(n\text{-dec}) = 1.001(\pm 0.020)\ \log k'(n\text{-hex}) + 0.055(\pm 0.010)$$

$n = 53 \quad r = 0.997 \quad s = 0.030 \quad F = 7430$ (eq.8)

---

* in brackets the 95% confidence intervals.

TABLE 1

Chromatographic Data of Chlorobenzenes, Chloronaphthalenes and Chlorobiphenyls on Silica Columns using *n*-Hexane, *n*-Octane, *n*-Decane, *iso*-Octane and *cyclo*-Hexane as the Mobile Phase

No	compound	log k'(obs)				
		n-hex	*n*-oct	*n*-dec	*i*-oct	*c*-hex
	chlorobenzenes					
1	unsubst.	0.375	0.371	0.320	0.61	0.624
2	1-	0.033	0.072	0.111	0.41	0.295
3	1,2-di	-0.027	0.009	0.037	0.29	0.176
4	1,3-di	-0.187	-0.149	-0.086	0.15	0.074
5	1,4-di	-0.149	-0.119	-0.071	0.23	0.106
6	1,2,3-tri	-0.086	-0.060	-0.022	0.17	0.116
7	1,2,4-tri	-0.194	-0.194	-0.149	0.08	n
8	1,3,5-tri	-0.432	-0.409	-0.357	0.10	-0.117
9	1,2,3,4-tetra	-0.180	-0.161	-0.125	0.10	0.054
10	1,2,3,5-tetra	-0.387	-0.357	-0.328	-0.05	-0.064
11	1,2,4,5-tetra	-0.337	-0.328	-0.276	0.11	-0.044
12	penta	-0.409	-0.387	-0.347	-0.07	-0.085
13	hexa	-0.523	-0.538	-0.509	-0.24	n
	chloronaphthalenes					
14	unsubst.	0.582	0.613	0.619	1.09	n
15	1-	0.258	0.281	0.297	0.70	n
16	2-	0.344	0.364	0.384	0.83	n
17	1,2-di	0.201	0.215	0.228	0.60	n
18	1,3-di	0.021	0.045	0.064	0.46	n
19	1,4-di	-0.036	-0.022	0.000	0.34	n
20	1,5-di	-0.036	-0.018	0.000	0.33	n
21	1,8-di	0.354	0.377	0.384	0.75	n
	chlorobiphenyls					
22	unsubst.	0.967	0.978	1.041	1.46	1.423
23	2-	0.804	0.839	0.885	1.20	1.175
24	3-	0.663	0.672	0.705	1.15	1.086

TABLE 1 (continued)

25	4-	0.702	0.708	0.723	1.16	1.103
26	2,3-di	0.720	0.748	0.790	1.08	n
27	2,4-di	0.578	0.597	0.634	0.95	0.931
28	2,5-di	0.553	0.584	0.627	0.94	n
29	2,6-di	0.734	0.792	0.845	1.04	1.065
30	3,4-di	0.602	0.592	0.616	1.02	n
31	3,5-di	0.411	0.408	0.444	0.87	0.826
32	2,3,4,5-tetra	0.432	0.444	0.477	n	n
33	2,3,4,5,6-penta	0.381	0.403	0.444	n	n
34	2,2'-di	0.741	0.792	0.845	1.05	n
35	3,3'-di	0.426	0.439	0.467	0.91	n
36	2,4,6,3'-tetra	0.230	0.255	0.305	n	0.564
37	4,4'-di	0.459	0.455	0.477	0.86	0.807
38	2,4,6,4'-tetra	0.190	0.210	0.238	n	n
39	2,3,2',3'-tetra	0.542	0.572	0.604	0.81	n
40	2,3,2',4'-tetra	0.373	0.415	0.450	n	n
41	2,4,2',4'-tetra	0.212	0.238	0.272	0.51	n
42	2,5,2',5'-tetra	0.305	0.350	0.389	0.62	0.598
43	2,4,5,2',5'-penta	0.188	0.228	0.246	n	0.461
44	2,6,2',6'-tetra	0.573	0.641	0.693	0.72	0.781
45	2,5,3',4'-tetra	0.266	0.281	0.312	0.60	n
46	3,4,3',4'-tetra	0.371	0.377	0.384	0.70	n
47	3,5,3',5'-tetra	-0.027	0.029	0.072	0.45	n
48	2,3,4,2',3',4'-hexa	0.332	0.350	0.364	n	0.524
49	2,3,6,2',3',6'-hexa	0.349	0.389	0.433	n	0.550
50	2,4,5,2',4',5'-hexa	0.063	0.079	0.111	0.33	0.318
51	3,4,5,3',4',5'-hexa	0.176	0.190	0.199	0.46	0.394
52	2,3,4,5,2',3',4',5'-octa	-0.027	0.000	0.029	0.30	0.204
53	deca	-0.332	-0.276	-0.252	0.04	-0.072

Note: n = not available

TABLE 2

Tentatively Proposed Δlog k' - values for Chain-elongations of the Mobile Phase (relative to n-hexane)

mobile phase	log k'
n-pentane	-0.013
n-hexane	0.000
n-heptane	0.013
n-octane	0.026
n-nonane	0.039
n-decane	0.052

The slopes of equations 7 and 8 are equal to unity but their intercepts - though rather small - differ significantly from zero. Especially against the background of the intercept - values of the equations 1 - 6, the difference between 0.055 and 0.024 has to be considered of sufficient significance to allow an inter- and extrapolation-scheme as given in Table 2*.

Figure 1 gives the graphical representations of eqns 7 and 8. We have to point at the marked similarities in the deviation pattern of the data points around the two parallel straight lines A and B. More attention will be given to this phenomenon in one of the following sections.

BRANCHING AND CYCLIZATION OF THE MOBILE PHASE

Iso-octane (2,2,4-trimethylpentane)

Forty five compounds in total were available for retention studies with iso-octane as the mobile phase. The data are reported in Table 1 and due comparison with the data obtained with unbranched hydrocarbon elution shows an obvious lack in interconsistency. Following regression equations were derived:

a. Chlorobenzenes

$$\log k'(i\text{-oct}) = 0.847(\pm 0.205)\ \log k'(n\text{-hex}) + 0.309(\pm 0.061)$$

$$n = 13 \quad r = 0.940 \quad s = 0.077 \quad F = 83.4 \qquad (eq.9)$$

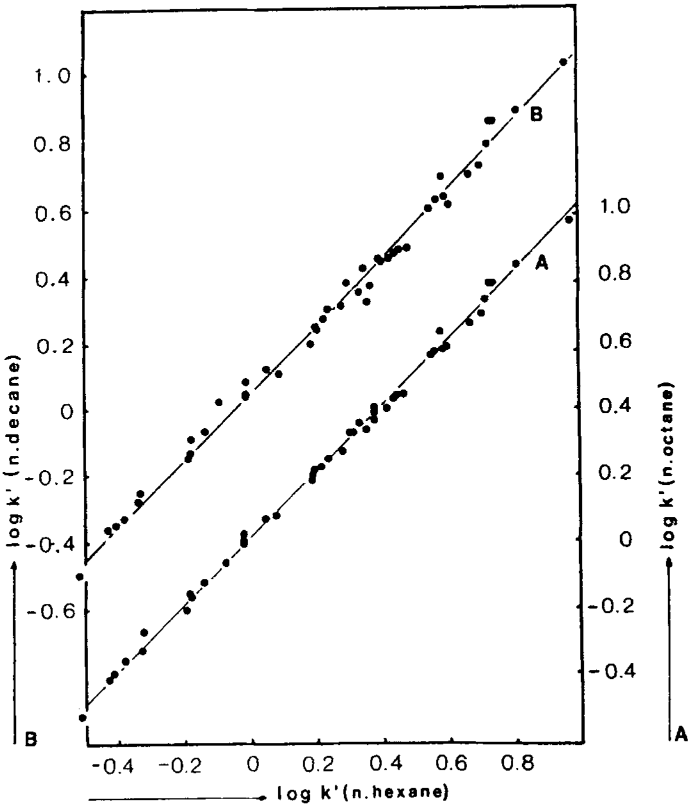

FIGURE 1. Retention plots of polychlorobenzenes, polychloronaphthalenes and polychlorobiphenyls.
A: *n*-octane *versus* *n*-hexane;
B: *n*-decane *versus* *n*-hexane;
Column: silicagel.

b. Chloronaphthalenes

$$\log k'(\underline{i}\text{-oct}) = 1.178(\pm 0.152) \log k'(\underline{n}\text{-hex}) + 0.389(\pm 0.044)$$

$n = 8 \quad r = 0.992 \quad s = 0.036 \quad F = 358$ (eq. 10)

c. Chlorobiphenyls

$$\log k'(\underline{i}\text{-oct}) = 1.051(\pm 0.120) \log k'(\underline{n}\text{-hex}) + 0.342(\pm 0.064)$$

$n = 24 \quad r = 0.968 \quad s = 0.087 \quad F = 325$ (eq. 11)

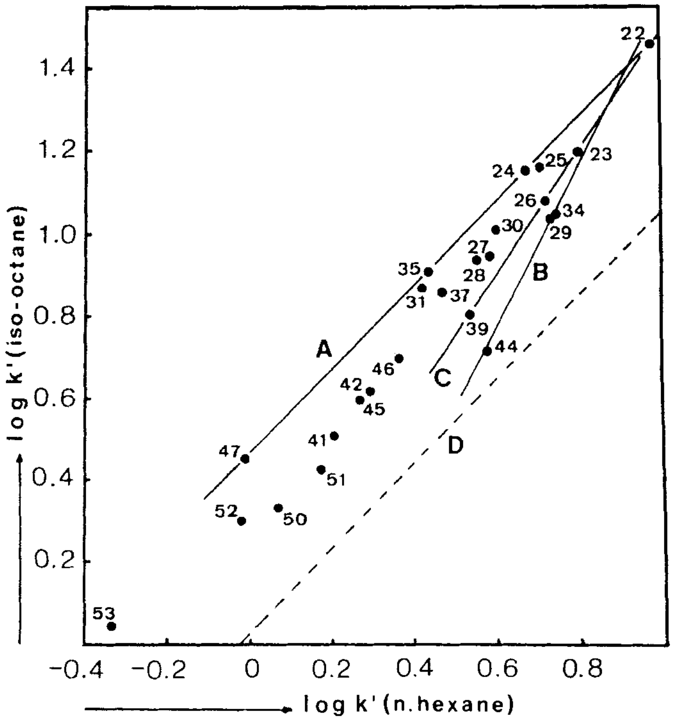

FIGURE 2. Retention plots of polychlorobiphenyls; log k'(*i*-oct) *versus* log k'(*n*-hex). Numbering: see table 1.
A: exclusive *meta*-substitution (eqn. 12);
B: exclusive *ortho*-substitution (eqn. 13);
C: *para*-substituted PCB's (eqn. 14);
D: location of straight line A as drawn in fig. 1.
Column: silicagel.

The statistical merits of the eqns 9, 10 and 11 are less striking than those of eqns 1 - 6 so that we left a combined equation including 9, 10 and 11 out of consideration.

Meta-chlorobiphenyls: The separate chlorobiphenyl-series (eqn 11) invites for some further unraveling. Figure 2 picturizes all 25 *data points* and it clearly indicates the bordering function of the *meta*-substituted derivatives (straight line A). Together with the unsubstituted biphenyl they yield following highly significant regression equation (Nos 22, 24, 31, 35 and 47):

$$\log k'(\underline{i}\text{-oct}) = 1.019(\pm 0.054)\log k'(\underline{n}\text{-hex}) + 0.471(\pm 0.032)$$
$$n = 5 \quad r = 1.000 \quad s = 0.013 \quad F = 3450 \qquad \text{(eq. 12)}$$

The slope of this equation equals that observed for equation 7 (<u>n</u>-oct <u>vs</u> <u>n</u>-hex) but its intercept strongly surpasses that of latter equation; a visualization is presented in fig.2 (compare the straight lines A and D). The intercept-value of eqn.12 would indicate that <u>iso</u>-octane, relative to <u>n</u>-hexane, behaves as if it had an unseemly long unbranched chain of more than 40 C-atoms ! Compare for that purpose the data from Table 2. None of the physical properties of <u>iso</u>-octane appear responsible for this phenomenon, except perhaps its bulky shape.

<u>Ortho-chlorobiphenyls</u>: Taken together with biphenyl (No 22) the four <u>ortho</u>-substituted derivatives (Nos 23, 29, 34 and 44) present themselves as a second bordering line (B) in fig.2. The equation is of reasonable quality:

$$\log k'(\underline{i}\text{-oct}) = 1.891(\pm 0.241)\log k'(\underline{n}\text{-hex}) - 0.350(\pm 0.167)$$
$$n = 5 \quad r = 0.998 \quad s = 0.022 \quad F = 613 \qquad \text{(eq. 13)}$$

Compared with the <u>meta</u>-line A, line B has made a turn to the right around biphenyl (No 22) as a hinge-point. All remaining derivatives find themselves in the field bordered by the lines A and D and biphenyl persists in maintaining its rather exclusive position as clearly shown by straight line C which comprises all chlorobiphenyls with any para-chlorosubstitution: Nos 25, 27, 30, 37, 41, 45, 46, 50 - 53:

$$\log k'(\underline{i}\text{-oct}) = 1.140(\pm 0.098)\log k'(\underline{n}\text{-hex}) + 0.316(\pm 0.047)$$
$$n = 12 \quad r = 0.993 \quad s = 0.051 \quad F = 677 \qquad \text{(eq. 14)}$$

<u>Cyclo-hexane</u>

Although the available data was fairly restricted we tried to construe, partially qualitatively, some overview in order to

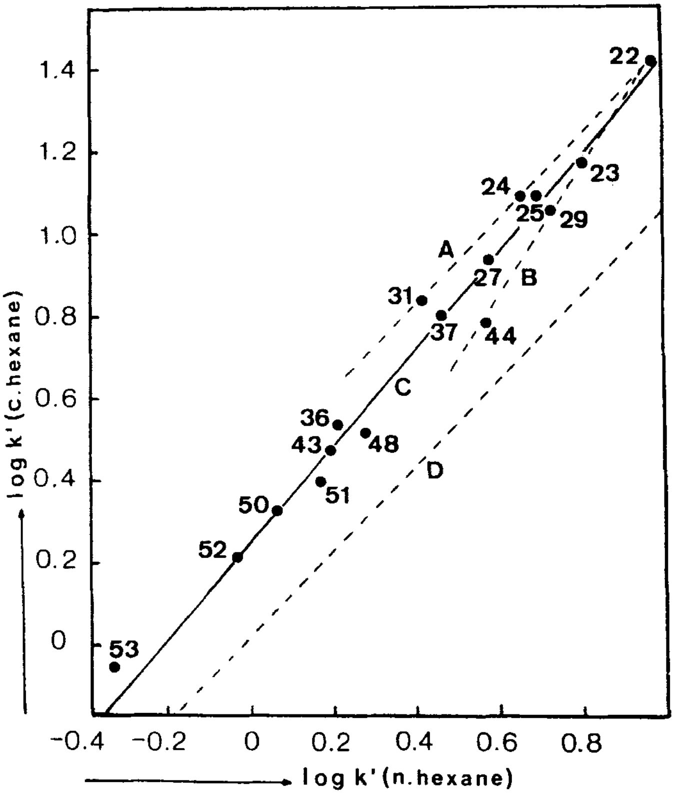

FIGURE 3. Retention plots of polychlorobiphenyls; log k'(*c*-hex) *versus* log k'(*n*-hex). Numbering: see table 1.
A: exclusive *meta*-substitution (hand-drawn line);
B: exclusive *ortho*-substitution (hand-drawn line);
C: *para*-substituted PCB's (eqn.17);
D: location of straight line A as drawn in fig. 1.
Column: silicagel.

make some comparison between *c*-hexane and *i*-octane retentions. Following regression equations were derived:

a. Chlorobenzenes

$$\log k'(\underline{c}\text{-hex}) = 0.880(\pm 0.106)\ \log k'(\underline{n}\text{-hex}) + 0.246(\pm 0.029)$$

$n = 11 \quad r = 0.966 \quad s = 0.035 \quad F = 354$ (eq.15)

TABLE 3

Mutual Comparison of Mobile Phases iso-Octane and cyclo-Hexane

mob. phase	comp. class	eqn	n	slope	intercept	r	s	F	fig.
i-oct.	ClBzs	9	13	0.847	0.309	0.940	0.077	83.4	
c-hex.	do.	15	11	0.880	0.246	0.988	0.035	354	
i-oct.	ClBPs	11	24	1.051	0.342	0.968	0.087	325	
c-hex.	do.	16	18	1.164	0.244	0.986	0.067	544	
i-oct.	do.^{m}	12	5	1.019	0.471	1.000	0.013	3450	2 A
c-hex.	do.^{m}	*	3	(1.1)	(0.4)				3 A
i-oct.	do.^{o}	13	5	1.891	-0.350	0.998	0.022	613	2 B
c-hex.	do.^{o}	*	4	(1.65)	(-0.15)				3 B
i-oct.	do.^{p}	14	12	1.140	0.316	0.993	0.051	677	2 C
c-hex.	do.^{p}	17	11	1.178	0.248	0.993	0.055	610	3 C

Notes: m, o, p indicate meta, ortho and para-series, respectively;
* the number of data points are insufficient for setting up sound correlations; values given in parenthesis are obtained from hand-drawn lines (given as broken lines in fig. 3).

b. Chlorobiphenyls

$$\log k'(c\text{-hex}) = 1.164(\pm 0.106) \log k'(n\text{-hex}) + 0.244(\pm 0.053)$$

$$n = 18 \quad r = 0.986 \quad s = 0.067 \quad F = 544 \qquad \text{(eq. 16)}$$

c. Para-chlorosubstituted biphenyls

$$\log k'(c\text{-hex}) = 1.178(\pm 0.109) \log k'(n\text{-hex}) + 0.248(\pm 0.048)$$

$$n = 11 \quad r = 0.993 \quad s = 0.055 \quad F = 610 \qquad \text{(eq. 17)}$$

Straight line C in figure 3 visualizes eqn 17 and the hand-drawn (broken) lines A and B denote the counterparts of lines A and B from figure 2, representing the bordering lines for meta and ortho-substitution, respectively, in the two figures. The agreement of these figures is striking and becomes even more conspicuous from Table 3 where the relevant equations can be directly compared.

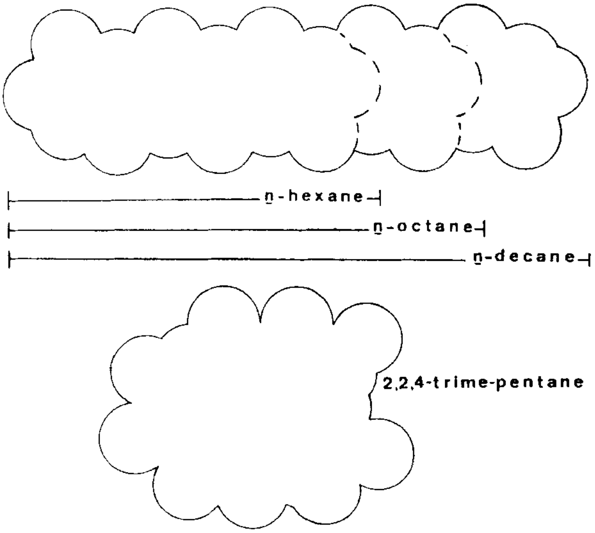

FIGURE 4: Profiles of n-hexane, n-octane, n-decane and 2,2,4-trimethylpentane (i-octane) obtained from projections of CPK - models.

The only difference between c-hexane and i-octane would seem that the first of the two mobile phases finds itself slightly closer to an unbranched mobile phase than the evidently more bulky i-octane (see figure 4).

COMMENTARIES CONCERNING SOME OF THE PRECEEDING SECTIONS

The eqns 7 and 8 derived for a series of 53 compounds including chlorobenzenes, chloronaphthalenes and chlorobiphenyls compare n-octane versus n-hexane elutions and n-decane versus n-hexane elutions, respectively. Both equations were of a perfect statistical quality, but close inspection of the two graphs (Fig.1), however, gave a clear indication of a faint dissimilarity pattern. In order to draw an optimal amount of information from our investigations we sketched the expanded line - pat-

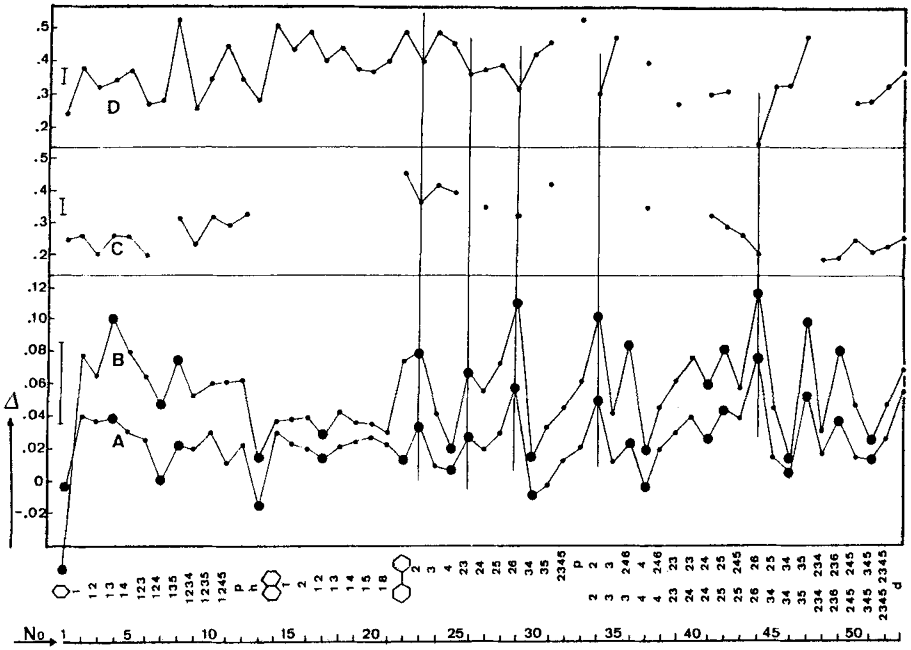

FIGURE 5. (opposite page) Graphical presentation of data from Table 1 on relative Δ-scales;
A: Δ = log k'(n-oct) - log k'(n-hex)
B: Δ = log k'(n-dec) - log k'(n-hex)
C: Δ = log k'(c-hex) - log k'(n-hex)
D: Δ = log k'(i-oct) - log k'(n-oct)
Evident extremes in A and B are given in heavy dots; these are interconnected by vertical lines for a number of ortho-substituted BPs;
Δ's for C and D are drawn on a five-fold contracted scale; p = penta; h = hexa; d = deca;

tern represented in Fig.5. This figure clearly facilitates the mutual comparison of some details "hidden" in Fig.1.

1. The A and B patterns closely follow each other as is easily observable by inspecting their evident extremes. In the PCB - series ortho - chlorine substitution effectuates a pronounced upward move in the curvatures A and B. In a number of cases we in-

TABLE 4

Chromatographic Data of Bromobenzenes, Iodobenzenes and Bromobiphenyls on Silica Columns using *n*-Hexane and *iso*-Octane as the Mobile Phase

No	compound	log k'(obs)	
		n-hex	*i*-oct
	bromobenzenes		
1	unsubst.	0.375	0.61
2	1-	0.079	0.50
3	1,2-di	0.072	0.39
4	1,3-di	-0.092	0.27
5	1,4-di	-0.060	0.32
6	1,2,4-tri	-0.076	0.26
7	1,3,5-tri	-0.310	0.09
8	hexa	-0.119	0.15
	iodobenzenes		
9	1-	0.097	0.57
10	1,3-di	-0.027	0.43
11	1,4-di	-0.004	0.45
	bromobiphenyls		
12	unsubst.	0.967	1.46
13	2-	0.838	1.38
14	3-	0.687	1.34
15	4-	0.717	1.35
16	2,2'-di	0.824	1.25
17	4,4'-di	0.520	1.13
18	2,5-di	0.620	1.18
19	3,5,3',5'-tetra	0.188	0.76
20	2,4,5,2',4',5'-hexa	0.322	0.75
21	3,4,5,3',4',5'-hexa	0.484	0.80

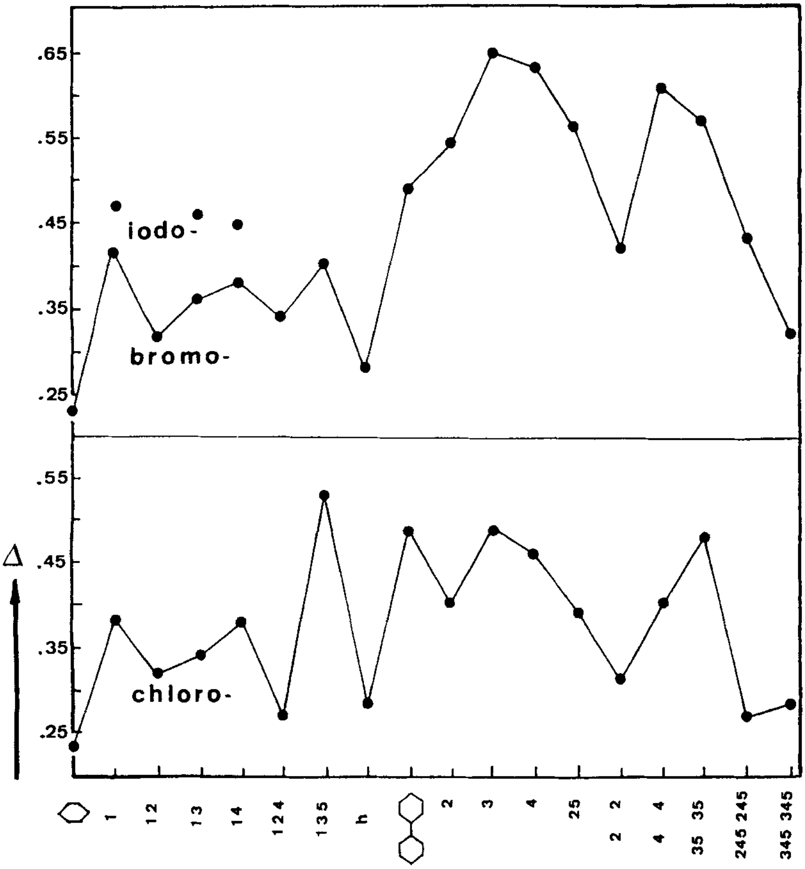

FIGURE 6. Graphical presentation of data from Table 1 (chloro-derivatives) and Table 4 (bromo- and iodo-derivatives) on relative Δ-scales;
Δ = log k'(i-oct) − log k'(n-hex)

terconnected the points in question by vertical lines. Para-chlorine substitution appears to have an opposite effect and the downward displacements happen to become partially compensated by suitable meta-chlorine substitution. The individual meta-chlorine effect is manifestly unveiled by No 47 – the 3,5,3',5'-tetrachloroderivative – with an upward effect fully comparable with that of No 29 – 2,2'-dichlorobiphenyl.

TABLE 5

Chromatographic Data of Methylbiphenyls on Silica Columns using *n*-Hexane, *n*-Octane and *n*-Decane as the Mobile Phase

No	compound	log k'(obs)		
		n-hex	*n*-oct	*n*-dec
1	unsubst.	0.967	0.978	1.041
2	2-	1.08	1.158	1.200
3	4-	1.08	1.097	1.099
4	2,2'-di	1.15	1.240	1.290
5	3,3'-di	1.15	1.203	1.203
6	4,4'-di	1.15	1.169	1.169
7	3,5-di	1.11	1.181	1.200
8	2,3,2',3'-tetra	1.34	1.437	1.466
9	2,4,2',4'-tetra	1.32	1.422	1.457
10	2,5,2',5'-tetra	1.23	1.328	1.380
11	3,4,3',4'-tetra	1.38	1.430	1.410
12	2,4,5,2',4',5'-hexa	1.43	1.561	1.545
13	2,4,6,2',4',6'-hexa	1.28	1.420	1.450

2. The overall effect of the rather bulky structures *iso*-octane and *cyclo*-hexane in comparison with the evidently less compact *n*-hydrocarbons consists in a significant lowering of the PCB patterns (C and D) in question.

3. Although the data-series with *iso*-octane and *cyclo*-hexane elutions are less complete, they allow the conclusion that the *ortho*-chlorine effect in the PCB-series is apparently inversed. The effect can easily be followed by observations along the vertical lines in Fig.5.

A clear physical picture of the effects signalized under 2 and 3 is as yet not available, however.

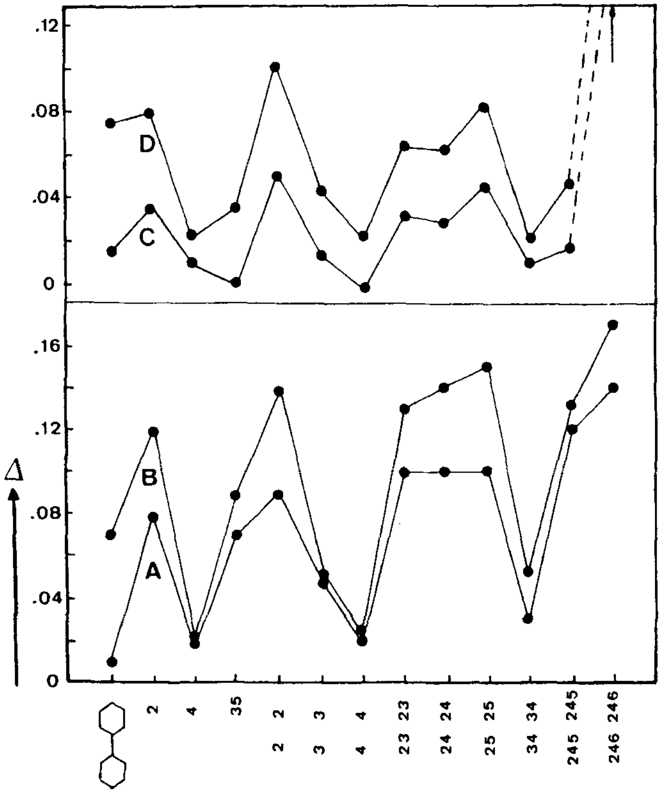

FIGURE 7. Graphical presentation of data from Table 5 (methyl-biphenyls) and Table 1 (chlorobiphenyls) on relative -scales;

A(me-BPs) : Δ = log k'(n-oct) - log k'(n-hex)
B(me-BPs) : Δ = log k'(n-dec) - log k'(n-hex)
C(Cl-BPs) : Δ = log k'(n-oct) - log k'(n-hex)
D(Cl-BPs) : Δ = log k'(n-dec) - log k'(n-hex)

Broken lines and arrow in the top-half denote the approximate location (outside the figure) of 2,4,6,2',4',6'-hexachloro-biphenyl.

THE EFFECT OF BROMO- AND METHYL-SUBSTITUTION IN THE PATTERNS OBSERVED ABOVE

Due reflection on the preceding section arises the question whether the observed phenomena are exclusive of the presence of other substituents.

Having available a (restricted) collection of bromo- and methyl - derivatives we decided to round off our study with the data collected in Tables 4 and 5. Table 4 presents the chromatographic data of bromobenzenes, iodobenzenes (no more than three compounds were available) and bromobiphenyls. Table 5 collects a series of methylbiphenyls. The data were treated in the same way as those of the chloro-derivatives (fig.5) and the final results are presented in Figures 6 and 7. As far as relevant they are accompanied by the corresponding chloro - data.

In brief outline the two graphs in Fig.6 are comparable to a great extent. An exception is presented by 2-bromobiphenyl with a significant Δ-increase when being compared with its 2-chloro analogue.

Figure 7 clearly demonstrates that - on a slightly decreased level - the pattern of methyl-substitution is not essentially different from the pattern observed for the chloro analogues.

When we take into regard the fact that the electronic character of the substituents - halogen versus methyl - is rather different (8), we may draw the conclusion that the shape of the molecule in which it enters confrontation with the eluting hydrocarbon is the most important factor in the reported experiments.

CONCLUSIONS

In a series of three preceding papers we studied the retentional behaviour of alkylbenzenes, halogeno-alkylbenzenes, halogenobenzenes, methylbiphenyls, halogenobiphenyls and chloronaphthalenes on normal phase silica and alumina columns with application of *n*-hexane as the mobile phase (7,8,9).

From extended correlation studies it became clear that the transitory binding of the above denoted compounds during their transport over the stationary phase originates in the electron-density of their π - clouds; and that the striking differences between alkyl- and halogen-substituents are related to their inductive properties: electron - releasing for alkylgroups and electron - withdrawing for halogens.

The present study paid due attention to the hitherto hardly envisaged effect of the mobile phase structure. Both the effects of chainlength - changes and the effect of bulkiness of the applied hydrocarbonaceous mobile phase got attention and we could establish small though significant effects. In the sequence _n_-hexane - _n_-octane - _n_-decane the log k' - increasing effect amounts to approximately 0.013 per CH_2 - unit.

Under the applied experimental conditions the effect of branching (_iso_-octane) and ring - formation is much more pronounced than that of chain-elongation. Grosso - modo we think that spatial features interplaying between mobile phase and solute are the determining factors in the ultimate procedure of de- and adsorption.

REFERENCES

1. Brinkman, U.A.Th., de Kok, A., de Vries, G. and Reijmer, H.G.M., High-speed Liquid and Thin-layer Chromatography of Polychlorinated Biphenyls, J. Chromatogr., 128, 101, 1976.
2. Brinkman, U.A.Th., de Kok, A., Reijmer, H.G.M. and de Vries, G., Analysis of Polychlorinated Naphthalenes by High-performance Liquid and Thin-layer Chromatography, J. Chromatogr., 129, 193, 1976.
3. de Kok, J.J., de Kok, A., Brinkman, U.A. Th. and Kok, R.M., Analysis of Polybrominated Biphenyls, J. Chromatogr., 142, 367, 1977.
4. Brinkman, U.A.Th. and de Vries, G., Relationship between Structure and Retention of Polyhalogenated Aromatics in two Adsorption Chromatograohic Systems, J. Chromatogr., 169, 167, 1979.
5. Brinkman, U.A.Th., de Vries, G. and Seetz, J.W.F.L., High-speed Liquid Chromatography of Polychlorinated Biphenyls and related Compounds, J. Chromatogr., 116, 353, 1976.

6. Brinkman, U.A.Th., Onel, O.N. and de Vries, G., Application of the Electron-capture Detector in Liquid Chromatography, J. Chromatogr., 171, 424, 1979.

7. Rekker, R.F., de Vries, G. and Bijloo, G.J., Retention Studies of Alkyl- and Halogen-substituted Aromatics on Normal - phase Silica and Alumina Columns; I. Alkylbenzenes and Halogenalkylbenzenes, J. Chromatogr., 370, 355, 1986.

8. Rekker, R.F., de Vries, G. and Bijloo, G.J., Retention Studies of Alkyl- and Halogen-substituted Aromatics on Normal - phase Silica and Alumina Columns; II. Halogenobenzenes and Halogenobiphenyls, J. Liq. Chromatogr., 12, 695, 1989.

9. de Vries, G. and Rekker, R.F., Retention Studies of Alkyl- and Halogen-substituted Aromatics on Normal - phase Silica and Alumina Columns; III. Methylbenzenes, methylnaphthalenes, methylbiphenyls and a selection of poly-aromatics, J. Liq. Chromatogr., 14, 465, 1991.

Received: May 1, 1992
Accepted: May 12, 1992