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Retention Studies of Alkyl- and Halogen-Substituted Aromatics on Normal-Phase Silica and Alumina Columns. II. Halogenobenzenes and Halogenobiphenyls

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**RETENTION STUDIES OF ALKYL- AND
HALOGEN-SUBSTITUTED AROMATICS
ON NORMAL-PHASE SILICA AND
ALUMINA COLUMNS
II. HALOGENOBENZENES AND
HALOGENOBIPHENYLS**

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ABSTRACT

Previously reported data on the retention of halogenobenzenes and halogenobiphenyls on normal-phase silica and alumina columns were submitted to regression analysis.

The derived $\log k'$ (capacity factor) values were correlated with structural features; mutual analogies, for instance those between halogenobiphenyls and halogenobenzenes were unraveled. In many cases the applied methods have predictive merits.

INTRODUCTION

In a previously published study (1) we investigated the chromatographic behaviour of alkyl- and alkylhalogenobenzenes

* to receive all correspondence

on normal-phase silica and alumina columns. Retentions, expressed as $\log k'$ (capacity factor), are regulated by the number of substituting groups and to a lesser extent - although significantly - by symmetry conditions.

The present paper deals with the regression analysis of halogenobenzenes and halogenobiphenyls; a number of rules that govern the retention behaviour are proposed.

EXPERIMENTAL

Retention data as reported in the various tables are from earlier studies (2, 3, 4, 5, 6, 7), largely performed by one of the present authors (GdV).

Regarding materials, apparatus and further experimental conditions, reference is made to the first paper in the present series (1).

The consistency of previous data obtained on silica columns was checked by repeating a full range of measurements on a recently construed column. The results indicate that the earlier retention data can be very easily transformed to new ones, and vice versa.

RESULTS AND DISCUSSION

HALOGENOBENZENES

Log k' versus Number of Halogen-atoms

Table 1 overviews the experimentally derived $\log k'$ -values of thirty-four halogenobenzenes.

Careful inspection of these data with in mind a possible correlation of $\log k'$ versus the number of halogen atoms, shows that retention data obtained on an alumina column give incoherent mutual differences. For the moment, it seems sensible to exclude these data from further analysis.

The retentional behaviour of eight out of ten fluorobenzenes on a silica column can be correlated as follows:

$$\log k' = -0.049(\pm 0.041) n_F + 0.148(\pm 0.122) * \quad (\text{eq. 1})$$

$$n = 8 \quad (\text{Nos } 2-9) \quad r = 0.765 \quad s = 0.052 \quad F = 8.47$$

where n_F denotes the total number of fluoro-substituents. The rather unsatisfying equation can be significantly improved by application of a second parameter: $n_{\text{ortho} + \text{para}}$, representing the summated number of ortho-pairs and para-pairs present in each of the fluorobenzenes under consideration (see Table 1 for detailed information).

$$\log k' = -0.166(\pm 0.067) n_F + 0.087(\pm 0.048) n_{\text{ortho} + \text{para}}$$

$$0.305(\pm 0.106) \quad (\text{eq. 2})$$

$$n = 8 \quad r = 0.954 \quad s = 0.027 \quad F = 29.8$$

Numerical parameters, like $n_{\text{ortho} + \text{para}}$, can adequately account for changes in molecular symmetry as was demonstrated in our previous paper (1) for methylbenzenes.

All numerical combinations which make a satisfying distinction between substituent positions in the substitution pattern applied in some data set, can in principle be considered for a try out. In equation 2 the ortho- and para-pair summation proved preferable: the higher its value the more dissymmetry is accentuated. A consequent application of this concept, however, demands for exclusion of pentafluoro- and hexafluorobenzene from the above regression. Differences between observed and estimated $\log k'$ -values of -0.14 and -0.42 , respectively, qualify both compounds as considerable outliers.

Chloro-, bromo- and iodobenzenes can be collected in the following regression equation:

$$\log k' = -0.242(\pm 0.026) n_{\text{hal}} + 0.156(\pm 0.025) n_{\text{ortho}}$$

$$+ 0.024(\pm 0.028) n_{\text{para}} + 0.077(\pm 0.025) D_1$$

$$+ 0.047(\pm 0.012) D_2 + 0.295(\pm 0.051) \quad (\text{eq. 3})$$

$$n = 20 \quad r = 0.984 \quad s = 0.033 \quad F = 105$$

* in brackets the 95% confidence intervals.

TABLE 1
Halogenobenzenes on Silica and Alumina Columns

No substituents	log k' (obs)		1...5					log k' (est)	Δ	A_w
	(SiO ₂)	(Al ₂ O ₃)								
1 benzene	0.375	-0.032								
<u>fluoro-benzenes</u>										
2 mono	0.111	0.000	1	0+0			0.139	-0.028	6.43	
3 1,2-di	0.057	0.025	2	1+0			0.060	-0.003	6.85	
4 1,3-di	-0.022	-0.119	2	0+0			-0.026	0.004	6.85	
5 1,4-di	0.093	0.025	2	0+1			0.060	0.033	6.85	
6 1,2,4-tri	0.000	-0.051	3	1+1			-0.018	0.018	7.27	
7 1,2,3,4-tetra	-0.013	-0.119	4	3+1			-0.011	-0.002	7.69	
8 1,2,3,5-tetra	-0.125	-0.292	4	2+1			-0.097	-0.028	7.69	
9 1,2,4,5-tetra	-0.004	-0.114	4	2+2			-0.011	0.007	7.69	
10 penta	-0.143	-0.143	5	(4+2)			-0.003	-0.140	8.11	
11 hexa	<u>-0.328</u>	-0.328	6	(6+3)			0.092	-0.420	8.53	
<u>chloro-benzenes</u>										
12 mono	0.033	0.061	1	0 0 0 0			0.053	-0.020	7.14	
13 1,2-di	-0.027	0.196	2	1 0 0 0			-0.033	0.006	8.27	
14 1,3-di	-0.187	-0.032	2	0 0 0 0			-0.189	0.002	8.27	
15 1,4-di	-0.149	0.049	2	0 1 0 0			-0.165	0.016	8.27	
16 1,2,3-tri	-0.086	0.276	3	2 0 0 0			-0.119	0.033	9.40	
17 1,2,4-tri	-0.194	0.009	3	1 1 0 0			-0.251	0.057	9.40	
18 1,3,5-tri	-0.432	-0.357	3	0 0 0 0			-0.430	-0.002	9.40	
19 1,2,3,4-tetra	-0.180	0.223	4	3 1 0 0			-0.181	0.001	10.53	
20 1,2,3,5-tetra	-0.387	-0.161	4	2 1 0 0			-0.337	-0.050	10.53	
21 1,2,4,5-tetra	-0.337	-0.125	4	2 2 0 0			-0.313	-0.024	10.53	
22 penta	<u>-0.409</u>	-0.046	5	(4)2			0 0	-0.243	-0.166	11.66
23 hexa	<u>-0.523</u>	-0.046	6	(6)3			0 0	-0.149	-0.374	12.79
<u>bromo-benzenes</u>										
24 mono	0.079	0.243	1	0 0 0 1			0.100	-0.021	7.46	
25 1,2-di	0.072	0.530	2	1 0 0 2			0.062	0.010	8.91	
26 1,3-di	-0.092	0.272	2	0 0 0 2			-0.094	0.002	8.91	
27 1,4-di	-0.060	0.398	2	0 1 0 2			-0.070	0.010	8.91	
28 1,2,4-tri	-0.076	0.509	3	1 1 0 3			-0.109	0.033	10.36	
29 1,3,5-tri	-0.310	0.104	3	0 0 0 3			-0.288	-0.022	10.36	
30 1,2,4,5-tetra	-0.137	0.593	4	2 2 0 4			-0.124	-0.013	11.81	
31 penta	<u>-0.119</u>	1.11	5	(4)2			0 5	-0.008	-0.111	13.26
32 hexa	<u>-0.119</u>	1.49	6	(6)3			0 6	0.133	-0.252	14.71
<u>iodo-benzenes</u>										
33 mono	0.097	0.465	1	0 0 1 0			0.130	-0.033	7.84	
34 1,3-di	-0.027	0.765	2	0 0 2 0			-0.035	0.008	9.67	
35 1,4-di	-0.004	0.988	2	0 1 2 0			-0.012	0.008	9.67	

Notes to Table I:

Column 5: 1 = n_h , 2 = n_o , 3 = n_p , 4 = D_1 and 5 = D_2 ; n_h = total number of halogen-substituents; indices o and p denote ortho and para, respectively (see text for closer information; D_1 and D_2 : dummy-parameters; for chloro-benzenes $D_1 = D_2 = 0$, for bromo-benzenes $D_1 = 0$ and $D_2 = n_h$ and for iodo-benzenes $D_1 = n_h$ and $D_2 = 0$;
Parameters given in brackets are formally correct but fail in a proper description of the compounds in eqns. 2 and 3;
Underlined log k' - values were excluded from the final regression calculation; their heavily deviating estimates are included in the column concerned; this column gives log k' (est) - values either from eqn. 2 or from eqn. 3 (see text).

A_w = molecular surface area, given in \AA^2 .

where n_{hal} indicates the total number of halogen-substituents and n_{ortho} and n_{para} denote the number of ortho- and para-pairs, respectively; the latter parametrization proved superior to the parametrization with $n_{\text{ortho+para}}$ applied for fluorobenzenes (note the substantial differences between the regressor-values of n_{ortho} and n_{para} in eqn. 3). D_1 and D_2 represent so-called dummy-parameters (sometimes denoted as indicator-values): for chlorobenzenes $D_1 = D_2 = 0$, independent of the total number of chloro-substituents, for bromobenzenes $D_1 = 0$ and $D_2 = n_{\text{hal}}$ and for the iodobenzenes $D_1 = n_{\text{hal}}$ and $D_2 = 0$. Although the impact of parameter n_{para} is not more than a fraction of that of n_{ortho} , it seems significant.

Here too, penta- and hexahalogen-substituted benzenes have to be omitted from the regression-equation. Differences between observed and estimated $\log k'$ -values varying from -0.11 to -0.25 show that they are unacceptable outliers, probably for the same reasons as for pentafluoro- and hexafluorobenzene (see the concluding paragraphs of next section).

The intercept values of eqns. 2 and 3, with an average of 0.300, represent the estimated $\log k'$ -value for benzene on a silica column. The observed value for benzene is 0.375, however, and this difference should be related to a principle change in the electronic behaviour of the phenyl ring: it operates as an electron-sink in case the ring is attached to H or to an alkyl-group but as an electron-supplier if attached to halogen.

In view of the good quality of eqn. 3 the application of a separate n_{ortho} and n_{para} parametrization instead of the combined $n_{\text{ortho+para}}$ parameter-set would virtually be recommendable for eqn. 2. With an extra parameter added to the pair already used in eqn. 2, however, a fully unacceptable ratio between the number of data points and the system's degree of freedom would occur.

A sample of 1,3,5-trifluorobenzene we had since recently at our disposal, enabled us to perform some check on the predictive merits of eqn. 2: the observed $\log k'$ -value (-0.205) for this

compound was in an acceptable accordance with its estimate from eqn. 2: $\log k' = -0.193$, the more so as we had to use a freshly prepared column including a full calibration procedure.

Comparison of eqns. 2 and 3 with the corresponding equation derived for methylbenzene retentions (1) reveals some interesting details:

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

$$n = 13 \quad r = 0.999 \quad s = 0.006 \quad F = 4390$$

Note: The intercept of this equation has the correct $\log k'$ - value as observed for benzene: the phenyl ring operates as an electron-sink both for H and for methyl groups. The second parameter had to be applied in order to obtain optimal correlation: the correlation coefficient increased from 0.985 to 0.999.

Differences between methyl- and halogen-substitution will be discussed in the next section.

Halogenobenzene versus Methylbenzene Retention

The adsorption of benzene on silica seems to involve hydrogen bonding between the π -cloud of the benzene-nucleus and surface silanol groups of the adsorbent, an idea raised by Puranik and Kumar (8), which finds regular application; see, for instance, Snyder (9, 10), Knözinger (11) and Pchle (12). The principle of benzene adsorption to an alumina surface will only differ from this pattern in as far as the Al^+ -sites take over the role of the silica -OH groups with a binding of the ionic type.

For each methyl group introduced in the benzene-nucleus we observe a constant positive impact on the adsorption: $\Delta \log k' = 0.085$. The effect of the methyl group is electronic in nature and has to be connected with its negative Hammett σ -value. This value reflects the resonance contribution of the electronic effect, the inductive part of this effect being equal to zero for all alkyl groups (13).

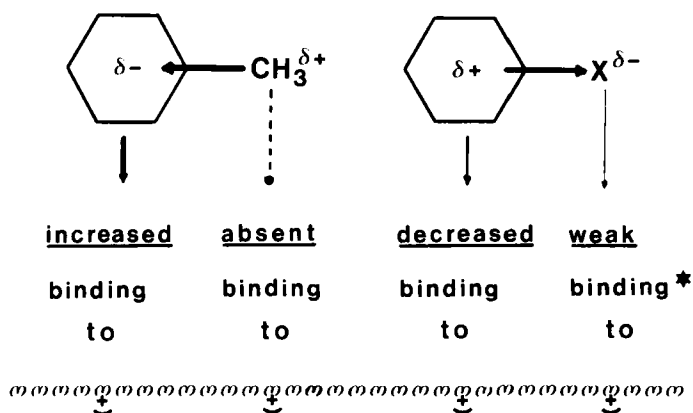


FIGURE 1. Schematized binding-differences between alkylbenzenes and halogenobenzenes on silica and alumina, relative to the binding of benzene on these adsorbents. X denotes halogen; the lower part of the figure pictures the adsorbent either active with its silanol-OH groups or with its Al⁺-sites; ★: some increased binding may arise from polarizability effects.

The negative sign of σ denotes that the effect is directed away from the CH₃ towards the phenyl group. A clear visualization is given in fig. 1. In this figure binding differences between alkylbenzenes and halogenobenzenes become clear from the signs of their Hammett σ -constants. As distinct from methyl (and other alkyl groups) halogens have positive Hammett σ -constants, i.e., their total electronic effects (summed inductive and resonance effects) are directed towards the halogen-atom away from the phenyl group and this will result in a move of a δ^- charge into the direction of the halogenatom and hence the indication δ^+ for the phenyl group in fig. 1. As a consequence the π -field is relatively weakened and the hydrogen-bonding power is correspondingly decreased. In its turn the halogen-atom with its δ^- charge will attain a weak binding power to Si-OH sites on the silica.

The typical effects observed when changing the halogen - substituent along the sequence F...Cl...Br...I puts F apart from the others (compare eqn. 2 with eqn. 3). It necessitates the usage of a dummy parametrization for Cl, Br and I in order to obtain an acceptable regression equation. In our opinion this would suggest a joint operation of an electronic parameter (Hammett σ) and a second one which is connected with size. In other words: the effect of halogen on the binding effect could depend on halogen polarizability, a property of which we know that it is small for F and increases in the order F...Cl...Br...I.

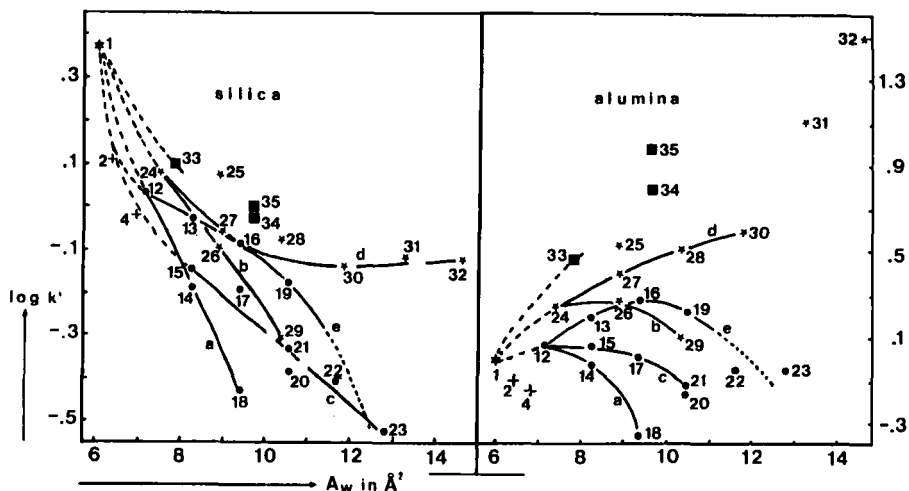
In the next section we will present an evident relationship between retention and the size of the molecule; and more discussions about this subject will be held in a forthcoming paper.

In the previous section we reported on the deviating behaviour of penta- and hexahalogenobenzenes. One of the reasons for these compounds of not being accepted in eqns. 2 and 3 should have due connection with the fact that both penta- and hexahalogenobenzenes, although parametrized correctly according to the scheme outlined in Table 1, are actually regaining symmetry on completion of their substitution pattern.

Other factors are certainly playing a role of their own; and it would seem not unrealistic to keep the dualistic electronic behaviour of halogen (a combined negative inductive and positive mesomeric effect) responsible for the striking difference between halogenobenzenes and methylbenzenes (the latter subject to an exclusive positive mesomeric effect from the CH_3 groups). These problems demand for future reflection.

Halogenobenzene and Methyl-monohalogenobenzene Retentions correlated with Bondi's Molecular Surface Area A_w

Figure 2 shows plots of $\log k'$ - values for halogenobenzenes versus molecular surface areas A_w . These values, expressed in $\overset{\bullet}{A}^2$, are composed from Bondi's original Tables (14). In making our choice we based ourselves on the perhaps questionable



latin crosses: fluorobenzenes, filled circles: chlorobenzenes, asterisks: bromobenzenes, squares:iodobenzenes, heavy asteriks: benzene (1); numbering of compounds: see Table 1.

line a connects: monoCl (12) - 1,3-diCl (14) - 1,3,5-triCl (18);

line b connects: monoBr (24) - 1,3-diBr (26) - 1,3,5-triBr (29);

line c connects: 1,4-diCl (15) - 1,2,4,5-tetraCl (21) - hexaCl (23);

line d connects: 1,4-diBr (27) - 1,2,4,5-tetraBr (30) - hexaBr (32);

line e connects: monoCl (12) - 1,2-diCl (13) - 1,2,3-triCl (16) - 1,2,3,4-tetraCl (19).

FIGURE 2. Plots of $\log k'$ - values of halogenobenzenes versus molecular surface area A_w obtained from Bondi-parameters.

but nevertheless reasonable assumption that these A_w - values match fairly correctly the surface of the molecules as they expose themselves to the adsorbent.

Instead of molecular surface area A_w , one might use as well van der Waals volume V_w and correlations obtained with the latter parameter do not differ substantially from those with A_w .

The curve-sets represented in fig. 2 allow an evident extrapolation to the unsubstituted benzene molecule; another point

of interest is that the alumina curve-set, when observed in the direction of the $\log k'$ - axis, has a more concavely shaped appearance than the silica curve-set. The reason is that the location of $\log k'$ for benzene in the graphs strongly predetermines the final curvatures.

An acceptable construction of $\log k' / A_w$ regression equations for silicagel-retention was unsuccessful. The alumina data, however, allow some interesting correlations.

It appeared worth while to apply the ideas developed above to a series of compounds taken from Table 1 and to include a number of related derivatives in which one or more halogens were replaced by methyl groups. The collected data (see Table 2) gives an opportunity to compose five series of compounds: mono-, ortho-, meta-, para- and 1,2,4-trisubstituted derivatives with halogen and/ or methylsubstitution. Simple correlations of $\log k'$ with the appropriate molecular surface area A_w calculated from Bondi-values could be attained. Although the qualities of the regression equations are not as good as we usually find, they allow the conclusion that the slopes of the four regression lines (ortho- and para-disubstituted compounds were combined in one regression) are almost identical: mean slope-value = 0.560 (st. dev. = 0.042).

mono-substitution

$$\log k' = 0.591(\pm 0.774) A_w - 4.199(\pm 5.785) \quad (\text{eq. 5})$$

$$n = 4 \quad r = 0.918 \quad s = 0.089 \quad F = 10.8$$

Note: with no more than four data points the data matrix is too poorly filled for proper judgement of the equation with regard to significance (its confidence intervals are unexpectedly high). Compared with the results from the eqns. 6, 7 and 8, however, and giving due consideration to the four line-slopes, the equation seems acceptable and useful.

ortho- and para-disubstitution (combined)

$$\log k' = 0.578(\pm 0.194) A_w - 4.756(\pm 0.769) \quad (\text{eq. 6})$$

$$n = 12 \quad r = 0.903 \quad s = 0.113 \quad F = 44.2$$

TABLE 2
Relationship between Molecular Surface Area and Retention
determined for Halogenobenzenes and Methyl-monohalogenobenzenes
on Alumina Columns

No	compound	log k' (obs)	A _w	D ₁	D ₂	log k' (est)	Δ
1	Cl-benzene	0.061	7.14	0	0	0.043	0.018
2	Me-benzene	0.093	7.45	0	0	0.204	-0.111
3	Br-benzene	0.243	7.46	0	0	0.209	0.034
4	I-benzene	0.465	7.84	0	0	0.406	0.059
5	1,2-diCl-benzene	0.196	8.27	1	0	<u>-0.010</u>	0.206
6	1,3-diCl-benzene	-0.032	8.27	1	0	<u>-0.010</u>	-0.022
7	1,4-diCl-benzene	0.049	8.27	1	0	<u>-0.010</u>	0.059
8	1,2-diMe-benzene	0.350	8.89	1	0	0.311	0.039
9	1,3-diMe-benzene	0.233	8.89	1	0	0.311	-0.078
10	1,4-diMe-benzene	0.193	8.89	1	0	0.311	-0.118
11	1,2-diBr-benzene	0.530	8.91	1	0	<u>0.322</u>	0.208
12	1,3-diBr-benzene	0.272	8.91	1	0	<u>0.322</u>	-0.050
13	1,4-diBr-benzene	0.398	8.91	1	0	0.322	0.076
14	1,3-diI-benzene	0.785	9.67	1	0	0.715	0.070
15	1,4-diI-benzene	0.987	9.67	1	0	<u>0.715</u>	0.272
16	2-Cl-Mebenzene	0.143	8.58	1	0	<u>0.151</u>	-0.008
17	3-Cl-Mebenzene	0.143	8.58	1	0	0.151	-0.008
18	4-Cl-Mebenzene	0.176	8.58	1	0	0.151	0.025
19	2-Br-Mebenzene	0.307	8.90	1	0	0.317	-0.010
20	3-Br-Mebenzene	0.297	8.90	1	0	0.317	-0.020
21	4-Br-Mebenzene	0.332	8.90	1	0	0.317	0.015
22	2-I-Mebenzene	0.542	9.28	1	0	0.513	0.029
23	3-I-Mebenzene	0.516	9.28	1	0	0.513	0.003
24	1,2,4-triCl-benzene	0.009	9.40	0	1	-0.032	0.041
25	1,2,3-triCl-benzene	0.276	9.40	0	1	<u>-0.032</u>	0.308
26	1,3,5-triCl-benzene	-0.357	9.40	0	1	<u>-0.032</u>	-0.325
27	1,2,3-triMe-benzene	0.591	10.33	0	1	<u>0.449</u>	0.142
28	1,2,4-triMe-benzene	0.433	10.33	0	1	0.449	-0.016
29	1,3,5-triMe-benzene	0.318	10.33	0	1	0.449	-0.131
30	1,2,4-triBr-benzene	0.509	10.36	0	1	0.465	0.044
31	1,3,5-triBr-benzene	0.104	10.36	0	1	<u>0.465</u>	-0.361
32	2,3-diMe-Clbenzene	0.380	10.02	0	1	<u>0.289</u>	0.091
33	2,4-diMe-Clbenzene	0.283	10.02	0	1	0.289	-0.006
34	2,6-diMe-Clbenzene	0.250	10.02	0	1	0.289	-0.039
35	3,4-diMe-Clbenzene	0.384	10.02	0	1	0.289	0.095
36	2,5-diMe-Clbenzene	0.201	10.02	0	1	0.289	-0.088
37	2,4-diMe-Brbenzene	0.436	10.34	0	1	0.455	-0.019
38	3,5-diMe-Brbenzene	0.346	10.34	0	1	0.455	-0.109
39	3,4-diMe-Brbenzene	0.526	10.34	0	1	0.455	0.072
40	2,3-diMe-Brbenzene	0.538	10.34	0	1	0.455	0.084
41	2,6-diMe-Brbenzene	0.410	10.34	0	1	0.455	-0.045
42	2,5-diMe-Brbenzene	0.350	10.34	0	1	0.455	-0.105
43	2,4-diMe-Ibenzene	0.639	10.72	0	1	0.651	-0.012

Note: underlined log k' (est) - values are outliers

meta-substitution

$$\log k' = 0.578(\pm 0.095) A_w - 4.848(\pm 0.844) \quad (\text{eq. 7})$$

$$n = 7 \quad r = 0.990 \quad s = 0.041 \quad F = 247$$

1,2,4-trisubstitution

$$\log k' = 0.495(\pm 0.134) A_w - 4.660(\pm 1.366) \quad (\text{eq. 8})$$

$$n = 9 \quad r = 0.957 \quad s = 0.059 \quad F = 76.2$$

The application of a suitable dummy-parametrization enabled us to combine the above four regression equations into a set of 37 retention data:

$$\log k' = 0.518(\pm 0.077) A_w - 0.638(\pm 0.134) D_1$$

$$- 1.246(\pm 0.226) D_2 - 3.653(\pm 0.581) \quad (\text{eq. 9})$$

$$n = 37 \quad r = 0.927 \quad s = 0.072 \quad F = 71.3$$

where the dummy-parametrization denotes $D_1 = D_2 = 0$ for mono-substitution, $D_1 = 1$ and $D_2 = 0$ for di-substitution, $D_1 = 0$ and $D_2 = 1$ for tri-substitution. Figure 3 represents a graphical overview of the four eqns. 5, 6, 7 and 8. Equation 9 accounts for 86% of the total variances. We suppose that the lacking 14% are mainly connected with electronic differences among the various substituents. The regressor value of D_2 (= 1.246) allows the construction of a sequence for increasing substitution with intervals of $1.246 / 2 = 0.623$ (in acceptable agreement with 0.638).

0.000	..	0.638	..	1.246	..	1.869	..	2.492	..	3.116
mono		di		tri		tetra		penta		hexa

If the suggested pattern is correct, eqn. 9 should have predictive merits in calculating $\log k'$ - values for a number of tetra-, penta- and hexa-substituted derivatives. Predicted and observed values are compared in Table 3; and our conclusion is that out of the total of 65 compounds from Tables 2 and 3 as many as 51 (or 78%) fit in an acceptable way in eqn. 9 provided that the proper adjustments are made in this equation. With regard to the outliers, we observe bad predictions for: a) symmetrical halogen-substitution, b) ortho-halogen substitution, especially in compounds with a too frequently repeated vicinal

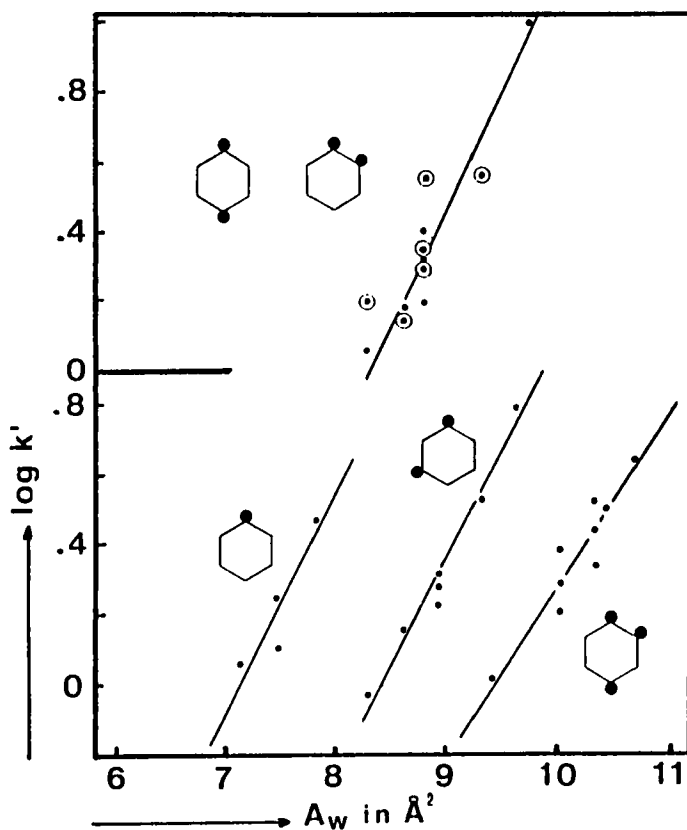


FIGURE 3. Log k' versus molecular surface area A_w for halogeno-, methyl- and methyl-halogenobenzenes; encircled points belong to 1,4-disubstituted derivatives; column: Al_2O_3 .

substitution pattern (Nos. 25, 44, 56, 61). Methyl-substituents tend to a more normal behaviour: the number of outliers is positively lower.

POLYCHLOROBIPHENYLS (PCBs)

Tables 4, 5, 6 and 7 collect log k' - values of 65 polychlorobiphenyls (PCBs) determined on a silica column. Striking parallelisms between PCB retention data and the data obtained for

TABLE 3
Log k' Predictions for Higher Substituted Molecules

No	compound	log k' (obs)	A_w	log k' (est)	Δ
<u>tetra-substitution</u>					
44	1,2,3,4-tetraCl-benzene	0.223	10.53	<u>-0.067</u>	0.290
45	1,2,3,5-tetraCl-benzene	-0.161	10.53	<u>-0.067</u>	-0.094
46	1,2,4,5-tetraCl-benzene	-0.125	10.53	<u>-0.067</u>	-0.058
47	1,2,4,5-tetraBr-benzene	0.593	11.81	0.596	-0.003
48	1,2,3,4-tetraMe-benzene	0.778	11.77	<u>0.575</u>	0.203
49	1,2,3,5-tetraMe-benzene	0.643	11.77	<u>0.575</u>	0.068
50	1,2,4,5-tetraMe-benzene	0.625	11.77	0.575	0.050
51	2,4,6-triMe-Brbenzene	0.528	11.78	0.580	-0.052
52	2,3,6-triMe-Brbenzene	0.598	11.78	0.580	-0.018
53	2,5-diMe-1,4-diBrbenzene	0.446	11.79	0.585	-0.139
54	2,5-diMe-1,4-diClbenzene	0.143	11.15	0.254	-0.111
<u>penta-substitution</u>					
55	pentaCl-benzene	-0.046	11.66	-0.105	0.059
56	pentaBr-benzene	1.11	13.26	<u>0.724</u>	0.39
57	pentaMe-benzene	0.929	13.21	<u>0.698</u>	0.231
58	2,3,4,6-tetraMe-Brbenzene	0.825	13.22	<u>0.703</u>	0.122
59	2,3,5,6-tetraMe-Brbenzene	0.782	13.22	0.703	0.079
<u>hexa-substitution</u>					
60	hexaCl-benzene	-0.046	12.79	-0.143	0.097
61	hexaBr-benzene	1.49	14.71	<u>0.852</u>	0.64
62	hexaMe-benzene	1.18	14.65	<u>0.821</u>	0.36
63	2,3,4,5,6-pentaMe-Brbenzene	1.09	14.66	<u>0.826</u>	0.26
64	2,4,5,6-tetraMe-1,3-diBrbenz.	0.862	14.67	<u>0.831</u>	0.031
65	3,5,6-triMe-1,2,4-triBrbenz.	0.467	14.68	<u>0.836</u>	-0.369
<u>Note:</u> underlined log k' (est)- values are outliers					

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structurally related chlorobenzenes are easily noticed. Due comparisons were performed following three different approaches.

1. Quite an interesting comparison of PCBs and polychlorobenzenes (PCBzs) on the basis of their molecular surface area is possible with the help of figure 4.

A marked parallelism between the two series of compounds is visualized by the four boundary lines in the data plot: the straight top line assembling the four ortho-chlorosubstituted biphenyls runs parallel with the one which includes chlorobenzene, 1,2-dichlorobenzene, 1,2,3-trichlorobenzene and 1,2,3,4-tetrachlorobenzene; the slopes of the two boundary lines amount

TABLE 4
 Chromatographic Data of PCB's on a SiO₂-column
 (in one of the rings no more than one Cl-substituent present)
 Evaluation by Approach 2

No	Substitution pattern	log k' (obs)	$\frac{1}{2} \sum \log k'$	n _o	n _m	n _p	log k' (est)
1	unsubstituted	0.967	0.375	0	0	0	0.993
2	2	0.804	0.204	1	0	0	0.818
3	3	0.663	0.204	0	1	0	0.715
4	4	0.702	0.204	0	0	1	0.707
5	2,3	0.720	0.174	1	1	0	0.718
6	2,4	0.578	0.094	1	0	1	0.609
7	2,5	0.553	0.113	1	1	0	0.642
8	2,6	0.734	0.094	2	0	0	0.721
9	3,4	0.602	0.174	0	1	1	0.607
10	3,5	0.411	0.094	0	2	0	0.515
11	2,3,4	0.629	0.145	1	1	1	0.611
12	2,3,6	0.634	0.091	2	1	0	0.655
13	2,4,5	0.453	0.091	1	1	1	0.543
14	2,4,6	0.453	-0.029	2	0	1	0.495
15	2,3,4,5	0.432	0.098	1	2	1	0.490
16	2,3,5,6	0.466	0.019	2	2	0	0.502
17	2,3,4,5,6	0.381	-0.017	2	2	1	0.386
18	2	0.741	0.033	2	0	0	0.644
19	2,3	0.638	0.003	2	1	0	0.544
20	2,4	0.553	-0.077	2	0	1	0.435
21	2,5	0.503	-0.058	2	1	0	0.467
22	3,4	0.432	0.003	1	1	1	0.433
23	3	0.426	0.033	0	2	0	0.438
24	2,5	0.332	-0.058	1	2	0	0.364
25	2,4,6	0.230	-0.200	2	1	1	0.218
26	2	0.520	0.033	1	0	1	0.533
27	4	0.459	0.033	0	0	2	0.421
28	2,4	0.295	-0.110	1	0	2	0.292
29	2,5	0.314	-0.058	1	1	1	0.356
30	2,4,6	0.190	-0.200	2	0	2	0.210

Notes: n_o = number of ortho-Cl, n_m = number of meta-Cl, n_p = number of para-Cl substituents, respectively;
 log k' (est) - values were obtained from eqn. 11.

TABLE 5

Chromatographic Data of PCB's on a SiO_2 - column
(in one of the rings no more than one Cl-substituent present)
Evaluation by Approach 3

No	$\log k'$ (I) (est)		$\log k'$ (II) (est)		$\log k'$ (III) (pred)
1	0.854 (A)		0.876 (A)		
2	0.796 (A)	0.809 (B)	0.814 (A)	0.762 (B)	
3	0.642 (A)		0.646 (A)		0.57 (P)
4	0.679 (A)		0.686 (A)		0.61 (E)
5	0.739 (A)	0.696 (C)	0.752 (A)	0.676 (C)	
6	0.635 (A)	0.597 (M)	0.639 (A)	0.516 (M)	
7	0.635 (A)	0.513 (G)	0.639 (A)	0.561 (G)	
8	0.739 (A)		0.752 (A)		0.69 (R)
9	0.635 (A)		0.639 (A)		0.56 (F)
10	0.411 (A)		0.389 (A)		
11	0.649 (A)	0.591 (D)	0.653 (A)	0.594 (D)	
12	0.649 (A)	0.599 (H)	0.653 (A)	0.617 (H)	
13	0.498 (A)	0.439 (J)	0.488 (A)	0.437 (J)	
14	0.449 (A)	0.470 (L)	0.436 (A)	0.379 (L)	
15	0.428 (A)	0.413 (K)	0.413 (A)	0.407 (K)	
16	0.428 (A)		0.413 (A)		0.39 (O)
17	0.318 (A)		0.294 (A)		0.35 (N)
18	0.724 (B)		0.699 (B)		
19	0.641 (B)	0.626 (C)	0.637 (B)	0.613 (C)	
20	0.488 (B)	0.502 (M)	0.524 (B)	0.453 (M)	
21	0.488 (B)	0.463 (G)	0.524 (B)	0.498 (G)	
22	0.488 (B)		0.524 (B)		0.50 (F)
23					0.34 (P)
24	0.328 (G)		0.330 (G)		0.33 (P)
25	0.166 (L)		0.149 (L)		0.13 (P)
26	0.552 (B)		0.570 (B)		0.55 (E)
27					0.42 (E)
28	0.307 (M)		0.325 (M)		0.37 (E)
29	0.360 (G)		0.370 (G)		0.36 (E)
30	0.219 (L)		0.189 (L)		0.17 (E)

Notes: $\log k'$ (est,I) - values were obtained by applying the appropriate regression equation from the collection given in Table 8;

$\log k'$ (est,II) - values were obtained from eqn. 12;

$\log k'$ (pred,III) - values were obtained from eqn. 12 by applying "moiety-values" calculated from eqn. 13;

Capitals in round brackets denote the applied p-value from the collection given in fig. 7.

TABLE 6
 Chromatographic Data of PCB's on a SiO₂-column
 (in both rings two or more Cl-substituents present)
 Evaluation by Approach 2

No	Substitution pattern	log k' (obs)	$\frac{1}{2} \sum \log k'$	n _o	n _m	n _p	log k' (est)	
31	2,3	2,3'	0.542	-0.027	2	2	0	0.444
32	2,4,5	2,3'	0.305	-0.149	2	2	1	0.268
33	2,3	2,4'	0.373	-0.107	2	1	1	0.335
34	2,4	2,4'	0.212	-0.187	2	0	2	0.226
35	2,3	2,5'	0.426	0.088	2	2	0	0.589
36	2,4	2,5'	0.276	-0.168	2	1	1	0.258
37	2,5	2,5'	0.305	-0.149	2	2	0	0.291
38	2,3,4	2,5'	0.323	-0.118	2	2	1	0.259
39	2,3,6	2,5'	0.357	-0.172	3	2	0	0.303
40	2,4,5	2,5'	0.182	-0.172	2	2	1	0.191
41	2,3,4,5	2,5'	0.163	-0.165	2	3	1	0.138
42	2,3,5,6	2,5'	0.176	-0.243	3	3	0	0.151
43	2,3,4,5,6	2,5'	0.063	-0.279	3	3	1	0.035
44	2,6	2,6'	0.573	-0.187	4	0	0	0.449
45	2,4	3,4'	0.234	-0.107	1	1	2	0.224
46	2,5	3,4'	0.266	-0.088	1	2	1	0.256
47	3,4	3,4'	0.371	-0.027	0	2	2	0.221
48	3,5	3,5'	-0.027	-0.187	0	4	0	0.037
49	2,3,4	2,3,4'	0.322	-0.086	2	2	2	0.229
50	2,3,4,5	2,3,4'	0.176	-0.133	2	3	2	0.108
51	2,3,6	2,3,6'	0.349	-0.194	4	2	0	0.316
52	2,3,4,5	2,3,6'	0.212	-0.187	3	3	1	0.151
53	2,3,4	2,4,5'	0.200	-0.140	2	2	2	0.161
54	2,3,6	2,4,5'	0.223	-0.194	3	2	1	0.204
55	2,4,5	2,4,5'	0.063	-0.194	2	2	2	0.093
56	2,3,4,5	2,4,5'	-0.008	-0.187	2	3	2	0.040
57	2,4,5	2,4,6'	-0.027	-0.313	3	1	2	0.046
58	2,4,6	2,4,6'	-0.115	-0.432	4	0	2	-0.001
59	2,3,4,5	2,4,6'	-0.167	-0.306	3	2	2	-0.007
60	3,4,5	3,4,5'	0.176	-0.086	0	4	2	0.023
61	2,3,4,5	3,4,5'	-0.008	-0.133	1	4	2	0.005
62	2,3,4,5	2,3,4,5'	-0.027	-0.180	2	4	2	-0.014
63	2,3,4,5,6	2,3,4,5'	-0.140	-0.295	3	4	2	-0.117
64	2,3,5,6	2,3,5,6'	-0.008	-0.337	4	4	0	0.012
65	2,3,4,5,6	2,3,4,5,6'	-0.332	-0.409	4	4	2	-0.220

Notes: n_o = number of ortho-Cl, n_m = number of meta-Cl, n_p = number of para-Cl substituents, respectively;
 log k' (est) - values were obtained from eqn. 11.

TABLE 7

Chromatographic Data of PCB's on a SiO_2 - column
(in both rings two or more Cl-substituents present)
Evaluation by Approach 3

No	$\log k'$ (I) (est)		$\log k'$ (II) (est)		$\log k'$ (III) (pred)
31	0.557 (C)		0.551 (C)		
32	0.264 (C)	0.314 (J)	0.288 (C)	0.312 (J)	
33	0.431 (C)	0.408 (M)	0.438 (C)	0.391 (M)	
34	0.236 (M)		0.278 (M)		
35	0.431 (C)	0.413 (G)	0.438 (C)	0.436 (G)	
36	0.322 (G)	0.236 (M)	0.323 (G)	0.278 (M)	
37	0.322 (G)		0.323 (G)		
38	0.356 (D)	0.334 (G)	0.356 (D)	0.338 (G)	
39	0.333 (G)	0.378 (H)	0.338 (G)	0.380 (H)	
40	0.202 (G)	0.199 (J)	0.173 (G)	0.199 (J)	
41	0.142 (G)	0.180 (K)	0.098 (G)	0.169 (K)	
42	0.142 (G)		0.131 (G)		0.15 (O)
43	0.046 (G)		-0.022 (G)		0.11 (N)
44					0.52 (R)
45	0.236 (M)		0.278 (M)		0.32 (F)
46	0.322 (G)		0.323 (G)		0.32 (F)
47					0.22 (F)
48					-0.11 (Q)
49	0.371 (D)		0.371 (D)		
50	0.133 (D)	0.194 (K)	0.131 (D)	0.184 (K)	
51	0.392 (H)		0.394 (H)		
52	0.194 (K)	0.168 (H)	0.184 (K)	0.154 (H)	
53	0.208 (D)	0.214 (J)	0.207 (D)	0.214 (J)	
54	0.238 (H)	0.214 (J)	0.230 (H)	0.214 (J)	
55	0.048 (J)		0.049 (J)		
56	0.034 (K)	-0.028 (J)	0.019 (K)	-0.003 (J)	
57	-0.004 (J)	-0.041 (L)	-0.003 (J)	-0.008 (L)	
58	-0.110 (L)		-0.061 (L)		
59	-0.018 (K)	-0.140 (L)	-0.032 (K)	-0.084 (L)	
60					-0.04 (S)
61	-0.018 (K)		-0.033 (K)		-0.04 (S)
62	-0.040 (K)		-0.056 (K)		
63	-0.160 (K)		-0.175 (K)		-0.11 (N)
64					-0.07 (O)
65					-0.23 (N)

Notes: $\log k'$ (est,I) - values were obtained by applying the appropriate regression equation from the collection given in Table 8;
 $\log k'$ (est,II) - values were obtained from eqn. 12;
 $\log k'$ (pred,III) - values were obtained from eqn. 12 by applying "moiety-values" calculated from eqn. 13;
 Capitals in round brackets denote the applied p-value from the collection given in fig. 7.

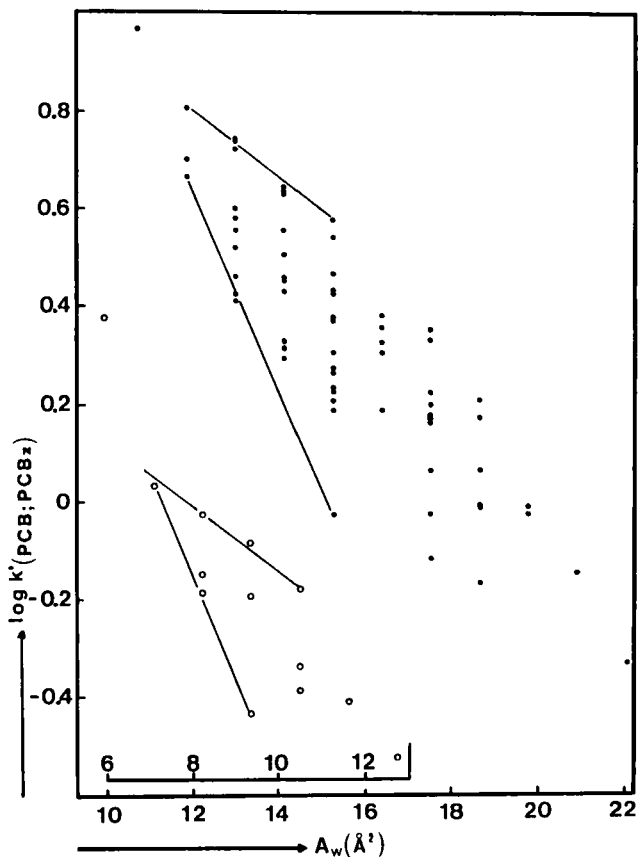


FIGURE 4. Log K' versus molecular surface area A_w for polychlorobiphenyls (●) and polychlorobenzenes^w (○) on silica; Four boundary lines include from top to bottom: 2-ClBP, 2,2'-diClBP, 2,6-diClBP and 2,6,2',6'-tetraClBP; 3-ClBP, 3,3'-diClBP, 3,5-diClBP and 3,5,3',5'-tetraClBP; Cl-benz., 1,2-diClbenz., 1,2,3-triClbenz. and 1,2,3,4-tetraClbenz.; Cl-benz., 1,3-diClbenz. and 1,3,5-triClbenz.; Data were taken from Tables 1, 4 and 6.

to -0.069 and -0.062, respectively. The two other boundaries assemble the four meta-chlorosubstituted biphenyls, on the one hand, and chlorobenzene, 1,3-dichlorobenzene and 1,3,5-trichlorobenzene, on the other hand; their slopes amount to -0.202 and -0.206, respectively.

A number of other similarities are demonstrable; just two of them may be mentioned: biphenyl can be connected non-problematically with the meta-biphenyl boundary line and the same is true for benzene with respect to the meta-benzene boundary line; a noteworthy relationship among the data points can be observed when a Cl-atom in a chlorobenzene is replaced by a phenyl group: retentions are then (without exceptions) increased by a proportional amount (see Approach 3).

The data-cluster of the PCBs ($\log k'$ versus an appropriate set of A_w -values) can be correlated with a correlation coefficient $r = 0.873$, which is not at all unsatisfying; introduction of an adequate additional *o-m-p* parametrization, however, gives no substantial improvement ($r = 0.889$) of the quality of the data-fit.

2. In a second approach a given PCB is compared with its two "disconnected" moieties in which H-atoms are attached to the vacant positions. Figure 5 shows the graph of $\log k'(\text{PCB})$ - data versus the halved retention-summation of the appropriate chlorobenzenes. Equation 10 gives the correlation of the sixty five data-points:

$$\log k'(\text{PCB}) = 1.437(\pm 0.184) \left(\frac{1}{2} \sum \log k'(\text{PCB}_2) \right) + 0.440(\pm 0.034) \quad (\text{eq. 10})$$

$$n = 65 \quad r = 0.887 \quad s = 0.121 \quad F = 233$$

A significant improvement of this equation can be achieved by the introduction of a set of three numeric parameters (η_o , η_m and η_p) to adequately account for the substitution pattern in the PCBs:

$$\log k'(\text{PCB}) = 1.259(\pm 0.222) \left(\frac{1}{2} \sum \log k'(\text{PCB}_2) \right)$$

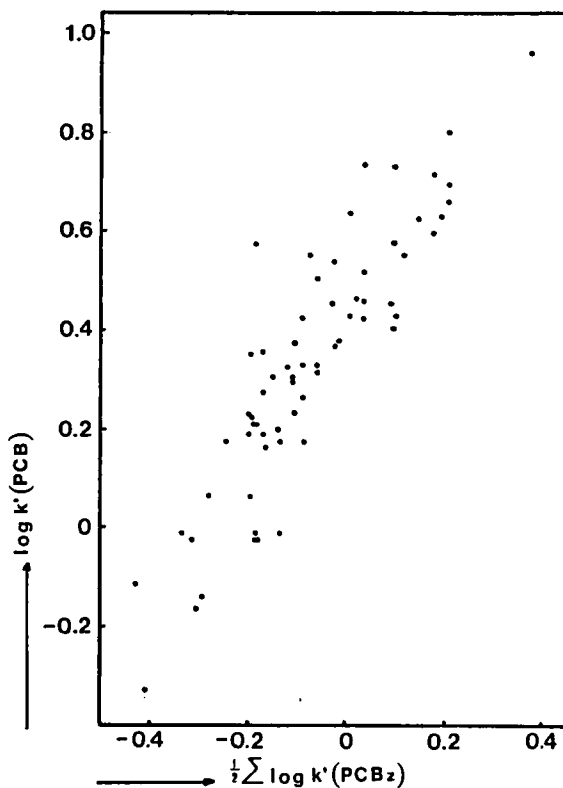


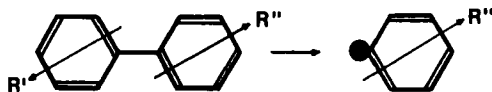
FIGURE 5. Plot of $\log k'$ for polychlorobiphenyls versus $\frac{1}{2} \sum \log k'$ of the composing chlorobenzenes.

$$\begin{aligned}
 &+ 0.041(\pm 0.026) n_o - 0.062(\pm 0.016) n_m \\
 &- 0.071(\pm 0.026) n_p + 0.521(\pm 0.062) \quad (\text{eq. 11})
 \end{aligned}$$

$$n = 65 \quad r = 0.965 \quad s = 0.068 \quad F = 220$$

Latter equation accounts for as much as 93% of the variances; Tables 4 and 6 enable the comparison of estimated and observed $\log k'(\text{PCB})$ - values and in addition they give information about the applied $n_o - n_m - n_p$ parametrization.

3. A final approach compares a PCB with a chlorobenzene derivative in which a chlorine-atom has taken over the role of one PCB-moiety:



with R' representing a fixed chloro-substitution pattern and R'' denoting a varying chloro-substitution. Figure 6 visualizes a number of marked parallels and Table 8 collects details of the regression analysis performed on the 12 data sets represented in the figure.

The line-pattern in figure 6 shows a significant parallelism; the average slope amounts to 1.17 with a standard deviation of 0.22. This made us decide to incorporate all PCBs from above Tables in one regression equation applying a proper dummy-parametrization ($\underline{D} = 1$ to indicate presence and $\underline{D} = 0$ to indicate absence of a specified chlorobenzene moiety). The result is following highly significant regression equation:

$$\log k'(\text{PCB}) = 1.048(\pm 0.074) \log k'(\text{PCBz}) - \sum p \underline{D} + 0.842(\pm 0.028) \quad (\text{eq. 12})$$

TABLE 8
Regression Equations $\log k'(\text{PCB})$ versus $\log k'(\text{PCBz})$

basic moiety	$\log k'(\text{PCB}) = a \log k'(\text{PCBz}) + b$					
	a	b	n	r	s	F
A	0.963(+.160)	0.822(+.044)	17	0.957	0.047	165
B	1.411(+.483)	0.762(+.069)	7	0.958	0.042	56.3
C	1.168(+.359)	0.657(+.065)	6	0.976	0.039	81.7
D	1.036(+.415)	0.557(+.110)	5	0.977	0.044	63.2
E	1.248(+.863)	0.618(+.176)	6	0.895	0.092	16.1
F	1.366(+1.65)	0.556(+.250)	5	0.835	0.093	6.91
G	0.840(+.134)	0.485(+.035)	14	0.969	0.034	187
H	0.976(+.405)	0.567(+.107)	5	0.976	0.043	58.9
J	1.057(+.104)	0.405(+.027)	8	0.995	0.017	614
K	1.025(+.129)	0.379(+.041)	8	0.992	0.025	377
L	1.381(+.285)	0.425(+.081)	6	0.989	0.039	181
M	1.591(+.415)	0.544(+.060)	7	0.975	0.036	97.2

Note: In brackets the 95% confidence intervals

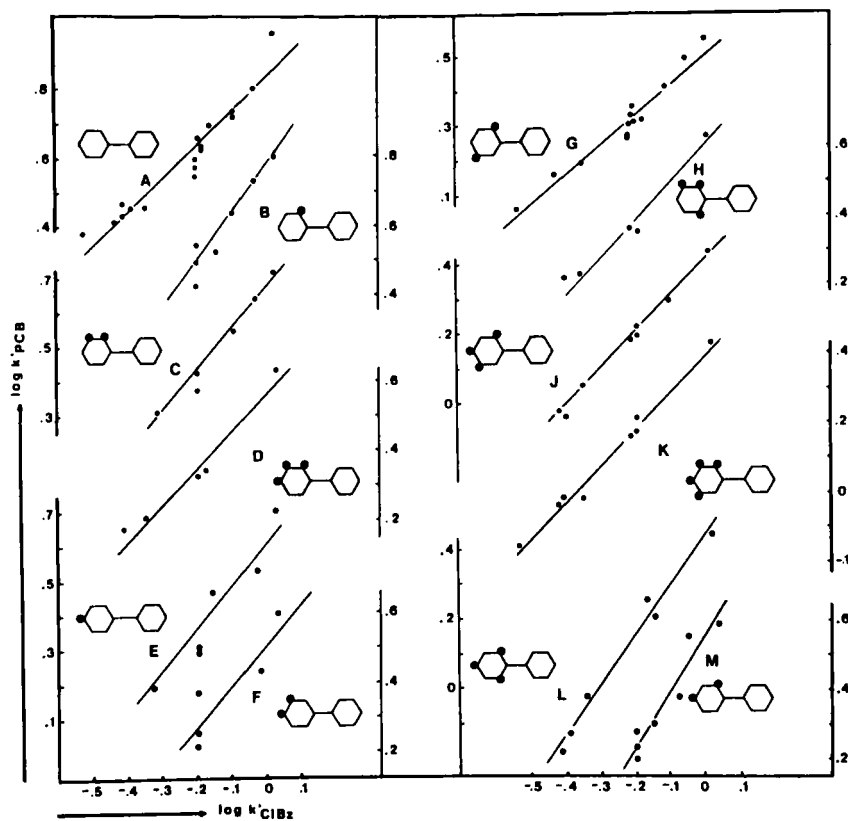


FIGURE 6. Plots of $\log k'(\text{PCB})$ versus $\log k'(\text{Cl-benzenes})$ after replacement of left-hand ring moiety by Cl. Left-hand moieties have fixed substitution patterns as indicated. Right-hand moieties have varying substitution pattern.

where $\sum p_{\underline{D}}$ denotes the summation of ten dummy-terms, belonging to the moieties A, B, C, D, G, H, J, K, L, M, respectively, with p-values as tabulated below:

$$p(A) = 0.000$$

$$p(B) = 0.114(\pm 0.045)$$

$$p(C) = 0.201(\pm 0.045)$$

$$p(D) = 0.282(\pm 0.048)$$

$$p(G) = 0.316(\pm 0.042)$$

$$p(H) = 0.259(\pm 0.048)$$

$$p(J) = 0.439(\pm 0.040)$$

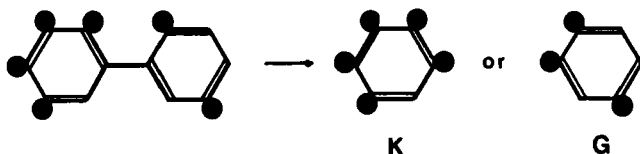
$$p(K) = 0.469(\pm 0.040)$$

$$p(L) = 0.497(\pm 0.044)$$

$$p(M) = 0.360(\pm 0.043)$$

$$n = 83 \quad r = 0.982 \quad s = 0.050 \quad F = 207$$

One should keep in mind that the number of data-points in eqn. 12 exceeds the number of examined PCBs with eighteen. This because classification is allowed in two ways along the above indicated lines; for instance:



An overview of all classifications as applied in equation 12 is given in figure 7, together with all proper contributions of the PCB-moieties to retention.

The relation between the regressor values of the dummy-parameter \underline{D} and the $\log k'$ -values of the appropriate chlorobenzene-moieties is a quadratic function, expressed by equation 13:

$$p = 1.561(\pm 0.452) \log k' + 1.282(\pm 1.070) (\log k')^2 - 0.062(\pm 0.041) \quad (\text{eq. 13})$$

$$n = 10 \quad r = 0.987 \quad s = 0.029 \quad F = 146$$

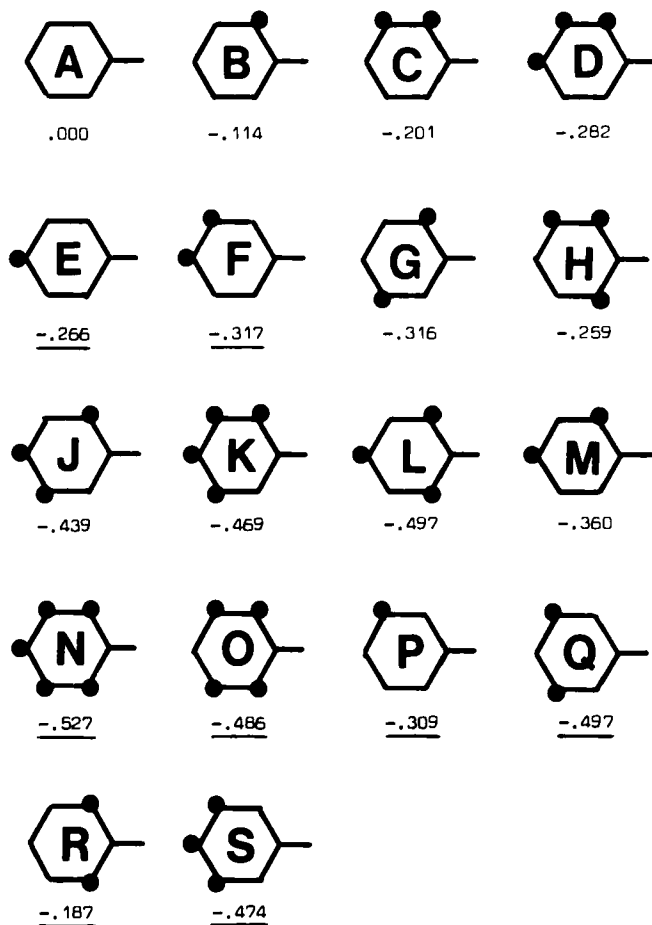


FIGURE 7. Overview of PCB moieties and their contributions to retention (p -values); not-underlined values are from eqn. 12 and underlined values are from eqn. 13.

The equation is of good quality and enables the evaluation of a number missing p -values. They are incorporated in the overview of figure 7 and denoted by E, F, N, O, P, Q, R, S, respectively.

Special attention is focussed to the last column of Tables 5 and 7 which collect the $\log k'$ -predictions obtained by proper usage of these additionally calculated p (moiety) - values.

The regressor-value of $\log k'$ in equation 12 ($=1.048 \pm 0.074$) does not differ significantly from unity and this justifies the conclusion that the retention shift (expressed by $\Delta \log k'$) evoked by replacing a chlorine-atom from a PCBz by a chlorine-substituted phenyl group can be connected with a p -value as given in figure 7 by a simple linear relationship:

$$\begin{aligned} \log k' &= \log k'(\text{PCB}) - \log k'(\text{PCBz}) \\ &= p + 0.842 \end{aligned} \quad (\text{eq. 14})$$

A highly satisfying proof of the validity of the presumption expressed by equation 14 was performed as follows: forty seven data belonging to eight classifications D, E, F, J, K, L, M, N (for details see Table 9) are collected from Tables 1, 4 and 6 and fitted by means of following equation:

TABLE 9

Retention-shifts evoked by replacing a Chlorine-atom in a PCBz by a Chlorine-substituted Phenyl group

basic moiety	$\log k'$	stand. dev.	p -values from Figure 7
D	0.515 (5)	0.039	-0.282
E	0.572 (6)	0.073	-0.266
F	0.529 (5)	0.083	-0.317
J	0.396 (6)	0.020	-0.439
K	0.361 (8)	0.058	-0.469
L	0.340 (6)	0.076	-0.497
M	0.481 (7)	0.062	-0.360
N	0.266 (4)	0.064	-0.527
S	0.482 (2)		-0.474

$\log k'$ - values are based on data from Tables 1, 4 and 6; In brackets: number of cases considered.

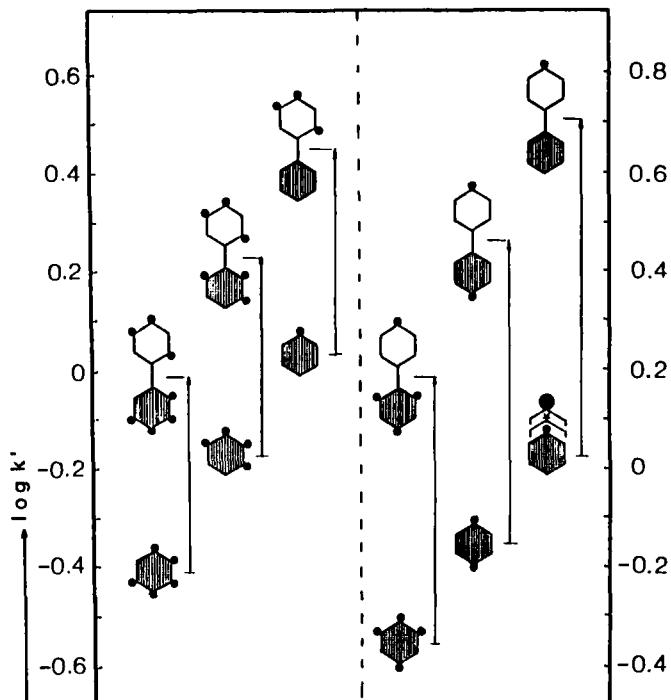


FIGURE 8. Visualization of some retention-shifts evoked by replacing a Cl-atom in a PCBz by a Cl-substituted phenylgroup; small dots: Cl, asterisk: Br, fat dot: I; Br- and I-benzene are added to visualize the relatively small mutual differences between the halogenobenzenes as contrasted with the introduction of the much heavier phenyl-moieties.

$$\log k' = 1.040(\pm 0.080) p + 0.843(\pm 0.033) \quad (\text{eq. 15})$$

$$n = 8 \quad r = 0.982 \quad s = 0.022 \quad F = 167$$

Figure 8 gives a clear visualization of six of these retention shifts (belonging to classifications J and E, respectively). The close parallelism of the shifts is obvious: an estimate of a peak location for PCBs is possible from an appropriately chosen PCBz.

The effectiveness of the correlation procedure on the basis of equation 12 is further illustrated by figure 9 and by equa-

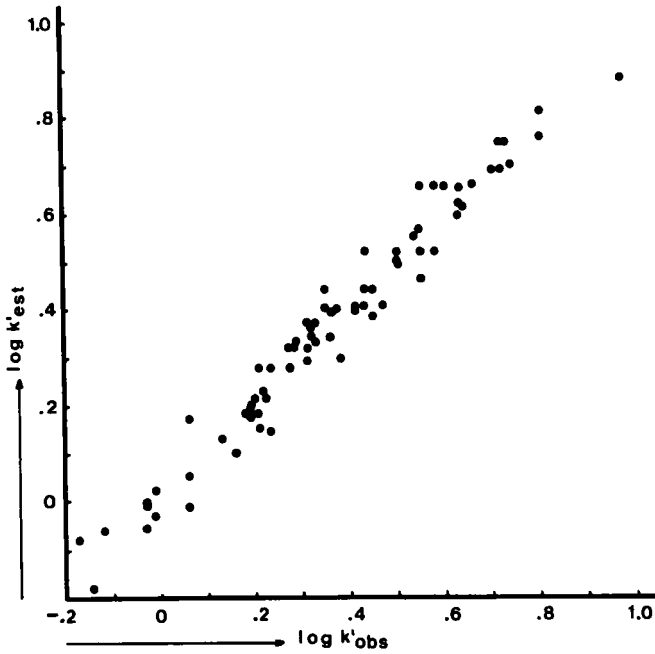


FIGURE 9. Plot of $\log k'(\text{est})$ versus $\log k'(\text{obs})$ for a series of PCBs; see equation 16.

tion 16; they denote the good agreement between observed and estimated $\log k'$ - values for PCBs.

$$\log k'_{\text{est}} = 0.979(\pm 0.046) \log k'_{\text{obs}} + 0.005(\pm 0.025) \quad (\text{eq. 16})$$

$$n = 84 \quad r = 0.978 \quad s = 0.052 \quad F = 1760$$

Rules that govern the retentional behaviour of PCBs on an alumina column (data are included in Table 10) are apparently less transparent than those for silica-retentions as we did not succeed in finding acceptable correlations (7).

It will be clear that the methods of comparison discussed above, each for themselves offer possibilities to make prudent retention-predictions for hitherto not measured PCBs.

TABLE 10

Chromatographic Data of Polybromo-biphenyls (PBBs) and Polychloro-biphenyls (PCBs) on Silica and Alumina Columns

No	substitution	log k' (obs)		log k' (est) - silica			
		silica	alumina	eq. 17	Δ	eq. 18	Δ
1	(biphenyl)	0.967	1.54	0.957	-0.010	0.997	0.030
2	2	0.838 (0.804)	1.01 (0.90)	0.829	-0.009	0.826	-0.012
3	3	0.687 (0.663)	1.47 (1.40)	0.719	0.032	0.699	0.012
4	4	0.717 (0.702)	1.73 (1.54)	0.749	0.032	0.732	0.015
5	2,2'	0.824 (0.741)	1.09 (0.81)	0.780	-0.044	0.767	-0.057
6	2,5	0.620 (0.553)	0.97 (0.70)	0.633	0.013	0.614	-0.006
7	4,4'	0.520 (0.459)	1.98 (1.72)	0.559	0.039	0.551	0.031
8	2,4,6	0.558 (0.453)	nm (nm)	0.554	-0.004	0.546	-0.012
9	2,5,2'	0.629 (0.503)	1.10 (0.69)	0.593	-0.036	0.579	-0.050
10	2,5,3'	0.439 (0.332)	1.07 (0.72)	0.459	0.020	0.478	0.039
11	2,5,4'	0.425 (0.314)	1.16 (0.74)	0.445	0.020	0.469	0.044
12	2,4,2',5'	0.433 (0.276)	nm (nm)	0.415	-0.018	0.451	0.018
13	2,5,2',5'	0.465 (0.305)	1.14 (0.60)	0.438	-0.027	0.465	0.000
14	3,5,3',5'	0.188 (-0.027)	1.23 (0.91)	0.178	-0.010	<u>0.359</u>	0.171
15	2,4,5,2',4',5'	0.322 (0.063)	1.16 (0.41)	<u>0.248</u>	-0.074	0.377	0.055
16	3,4,5,3',4',5'	0.484 (0.176)	1.6 (1.53)	<u>0.337</u>	-0.147	0.411	-0.073
17	2,3,5,6,2',3',5',6'	0.373 (-0.008)	nm (nm)	<u>0.193</u>	-0.180	0.363	-0.010
18	nona	0.373 (-0.140)	nm (nm)	<u>0.090</u>	-0.283	0.349	-0.024
19	deca	0.348 (-0.332)	1.76 (0.15)	<u>-0.061</u>	-0.409	0.358	0.010

Notes: nm = not measured; underlined values are outliers; non-bracketed values belong to PBBs and bracketed values belong to PCBs;

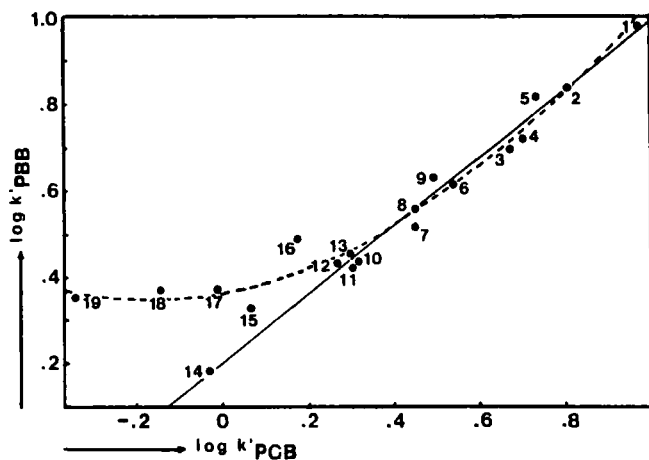


FIGURE 10. Log k' (polybromobiphenyls) versus log k' (polychlorobiphenyls); column: silica; straight line: eqn. 17; curved broken line: eqn. 18.

POLYBROMOBIPHENYLS (PBBs)

Table 10 collects the log k' - values of a series of nineteen polybromobiphenyls (PBBs). Measurements were performed both on silica and alumina columns.

Retention data of PBBs on silica show a good deal of parallelism with the data obtained for structurally related PCBs. This can be concluded from eqn. 17 which relates log k' data for 14 PBBs and PCBs:

$$\log k'(\text{PBB}) = 0.784(\pm 0.064) \log k'(\text{PCB}) + 0.199(\pm 0.036)$$

$$n = 14 \quad r = 0.992 \quad s = 0.026 \quad F = 707 \quad (\text{eq. 17})$$

The equation excludes nos 15-19 of Table 10 as significantly non-fitting compounds. The straight line (eqn. 17) drawn in fig. 10 clearly visualizes the actual situation and suggests a quadratic relation between the complete sets of data with the exclusion, however, of the 3,5,3',5'-tetrasubstituted derivative which did fit the straight line. This quadratic relation is

TABLE 11
Comparison of Polybromobenzenes and Polychlorobenzenes
on Silica Columns

No	substituent	log k'					
		(PBBz) obs	(PCBz) obs	(PBBz) est'	Δ	(PBBz) est''	Δ
1	none	0.375	0.375	0.382	0.007	0.387	0.012
2	mono-	0.079	0.033	0.096	0.017	0.064	-0.015
3	1,2-	0.072	-0.027	0.045	-0.027	0.023	-0.049
4	1,3-	-0.092	-0.187	-0.089	0.003	-0.063	0.029
5	1,4-	-0.060	-0.149	-0.057	0.003	-0.046	0.014
6	1,2,4-	-0.076	-0.194	-0.095	-0.019	-0.066	0.010
7	1,3,5-	-0.310	-0.432	-0.294	0.016	<u>-0.131</u>	0.179
8	1,2,4,5-	-0.137	-0.337	<u>-0.215</u>	-0.078	-0.113	0.024
9	penta-	-0.119	-0.409	<u>-0.275</u>	-0.156	-0.128	-0.009
10	hexa-	-0.119	-0.523	<u>-0.371</u>	-0.252	-0.136	-0.017

Notes: underlined values are outliers;
est': from eqn. 19; est'': from eqn. 20;

given by the curved broken line in fig. 10 and can be expressed by the following equation:

$$\log k'(PBB) = 0.182(\pm 0.113) \log k'(PCB) + 0.489(\pm 0.148) (\log k'(PCB))^2 + 0.364(\pm 0.029) \quad (\text{eq. 18})$$

n = 18 r = 0.980 s = 0.038 F = 198

A similar link seems apparent when we compare corresponding bromobenzene and chlorobenzene data (Table 11).

Seven data points out of the total set of ten have an ideal relation as visualized by the straight line in fig. 11 and by following equation:

$$\log k'(PEBz) = 0.839(\pm 0.076) \log k'(PCBz) + 0.068(\pm 0.019)$$

n = 7 r = 0.997 s = 0.018 F = 796 (eq. 19)

Here too, it is possible to include a series of nine pairs in an acceptable quadratic relation, again, however, with the exclusion of the 1,3,5-trihalogen-substituted pair:

$$\log k'(PBBz) = 0.676(\pm 0.103) \log k'(PCBz) + 0.649(\pm 0.295) (\log k'(PCBz))^2 + 0.041(\pm 0.033) \quad (\text{eq. 20})$$

n = 9 r = 0.987 s = 0.030 F = 133

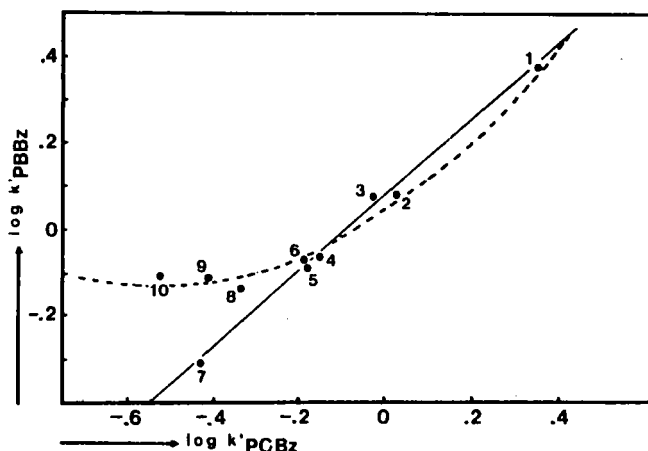


FIGURE 11. $\log k'$ (polybromobenzenes) versus $\log k'$ (polychlorobenzenes); column: silica; straight line: eqn. 19; curved broken line: eqn. 20.

Equation 20 is given as a broken curved line in fig. 11. Why the meta-derivatives show such abnormal behaviour in both series is at present an open question.

An ample search for relationships between retention and structural features in a series of polychloronaphthalenes as done for PCBs did not yield more substantial conclusions than those previously drawn by Brinkman and de Vries (5).

CONCLUSION

Retention of halogenobenzenes in the systems silica-hexane and alumina-hexane is regulated by the number of halogens and by additional factors which can perhaps best be described by polarizability. The mode of interaction is more complicated than that of previously investigated alkylbenzenes (1). The effect of fluoro-substitution is not fully in line with the other halogens.

Differences between methyl- and halogen-substitution can be explained by a concept in which binding is mainly originat-

ing in the phenyl group and is strongly depending on the impact of its π -cloud.

A number of good correlations - most of them with predictive merits - are derived for halogenobenzenes and a number of structurally related methyl-halogenobenzenes.

The retentions of polychlorobiphenyls (PCBs) are studied under analogous conditions and a number of interesting relationships between their $\log k'$ - values and those of correspondingly substituted chlorobenzenes (PCBzs) can be proposed.

In this study into possible relationships between retention and structural features three different approaches were applied: 1) a simple visual comparison of PCB and PCBz data by means of a graphical data-presentation; 2) a correlation of PCB retentions with molecular surface area (Bondi); 3) a correlation of PCB retentions with appropriately chosen PCBz data.

Polybromobiphenyl retentions are in good agreement with linear or quadratic polychlorobiphenyl retentions. The final curve shape depends on the chosen substitution pattern in which a too frequently occurring vicinal substitution requires a quadratic curve. Same characteristics can be established for polybromobenzenes versus polychlorobenzenes.

A number of details concerning the adsorption phenomena of the discussed compounds will be one of the subjects of a forthcoming paper.

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