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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. III. Methylbenzenes, Methylnaphthalenes, Methylbiphenyls, and a Selection of Poly-Aromatics

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To cite this Article De Vries, G. and Rekker, R. F.(1991) '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', *Journal of Liquid Chromatography & Related Technologies*, 14: 3, 465 – 489

To link to this Article: DOI: 10.1080/01483919108049264

URL: <http://dx.doi.org/10.1080/01483919108049264>

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**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**

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ABSTRACT

Retention data of methylbenzenes, methylnaphthalenes and methylbiphenyls determined on normal-phase silica and alumina columns are submitted to mutual comparison. Binding of all three classes of compounds to the adsorbents seems exclusively located in the π -cloud of their aromatic systems. Conclusive evidence can be obtained from retention experiments on a selection of poly-aromatic hydrocarbons with varying π -patterns.

Additional information to this view is obtainable from UV-spectral literature - data.

A set of pictures visualizes our views on the adsorption of the investigated aromatics both to silica and to alumina.

* to receive all correspondence

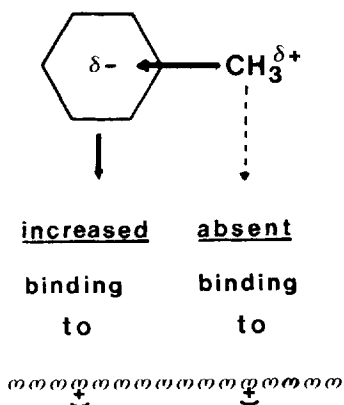


FIGURE 1. Schematization of the binding of alkylbenzenes on silica and alumina, relative to the binding of benzene on these adsorbents; the lower part of the figure picturizes the adsorbent either active with its silanol groups (silica gel) or with its Al^{+} -sites (alumina).

INTRODUCTION

In a previous paper (1) we investigated the chromatographic behaviour of alkyl- and alkylhalogenobenzenes on normal-phase silica and alumina columns. Retentions of methylbenzenes, expressed as $\log K'$ (capacity factor), are regulated by the number of substituting methyl groups and to a lesser extent - although significantly - symmetry conditions in the substitution pattern play a role. Binding of methylbenzenes to silica or alumina is visualized in fig. 1 where the aromatic moiety of the molecule presents itself as the attaching partner to the adsorbent.

The present paper deals with the retentional behaviour of methylbenzenes, methylnaphthalenes, methylbiphenyls and a number of poly-aromatics; special attention will be given to the question as to how far the retentions of the title compounds can be collected under one general denominator. And further,

it would be of great use if we could succeed in designing how the investigated aromatic compounds are attached to the adsorbents.

EXPERIMENTAL

Retention data of methylbenzenes as reported in Table 1 are from earlier studies (2). The remaining compounds in this table (methylnaphthalenes and methylbiphenyls) were measured under conditions strictly comparable with those for the methylbenzenes.

The greater part of the poly-aromatics show up unacceptably long retention times under the given conditions of the experiments, so that the whole series - including benzene, naphthalene and biphenyl - had to be measured on silicagel with slightly increased water-content (1 mg per gram of silicagel) in order to keep the retention times in a fully surveyable range.

Regarding other materials, apparatus and further experimental conditions, reference is made to the first paper in the present series (2).

RESULTS AND DISCUSSION

The equilibrium between adsorption and desorption is of a dynamic nature, i.e., the molecules under consideration find themselves intermittently free in the mobile phase and adsorbed to the adsorbent; the time-ratio between these two situations virtually determines retention and depends on a number of factors such as type of adsorbent, structure of the adsorbent, number and location of its active sites, properties - physical as well as chemical - of the adsorbed molecules and properties of the mobile phase.

METHYLBENZENES, METHYLNAPHTHALENES AND METHYLBIPHENYLS

Log k' versus Number of Methylgroups

Table 1 overviews the experimentally derived log k' -values of thirteen methylbenzenes, seven methylnaphthalenes and thirteen methylbiphenyls.

TABLE 1
Polymethylderivatives of Benzene, Naphthalene and Biphenyl
on Silica and Alumina Columns

No	Substituents	log k' (Silica)			log k' (Alumina)		
		obs.	est.	Δ	obs.	est.	Δ
<u>Benzenes</u>							
1	unsubst.	0.375	0.377	-0.002	-0.032	-0.004	-0.028
2	1-	0.461	0.462	-0.001	0.093	0.111	-0.018
3	1,2-di	0.585	0.587	-0.002	0.350	0.316	0.034
4	1,3-di	0.548	0.546	0.002	0.233	0.226	0.007
5	1,4-di	0.512	0.506	0.006	0.193	0.226	-0.033
6	1,2,3-tri	0.690	0.692	-0.002	0.591	0.521	0.070
7	1,2,4-tri	0.633	0.631	0.002	0.433	0.432	0.001
8	1,3,5-tri	0.621	0.631	-0.010	0.318	0.342	-0.024
9	1,2,3,4-tetra	0.767	0.756	0.011	0.778	0.727	0.051
10	1,2,3,5-tetra	0.736	0.736	0.000	0.643	0.637	0.006
11	1,2,4,5-tetra	0.716	0.716	0.000	0.625	0.637	-0.012
12	penta	0.820	0.821	-0.001	0.929	0.932	-0.003
13	hexa	0.881	0.885	-0.004	1.176	1.227	-0.051
<u>Naphthalenes</u>							
14	unsubst.	0.582	(0.582)		1.43	(1.43)	
15	1-	0.650	0.667	-0.017	1.61	1.55	0.06
16	2-	0.659	0.667	-0.008	1.62	1.55	0.07
17	1,2-di	0.754	0.792	-0.038	1.90	1.75	0.15
18	1,4-di	0.676	0.712	-0.036	1.77	1.66	0.11
19	1,5-di	0.695	0.752	-0.057	1.81	1.66	0.15
20	2,3-di	0.777	0.792	-0.015	1.94	1.75	0.19
<u>Biphenyls</u>							
21	unsubst.	0.97	(0.97)		1.54	(1.54)	
22	2-	1.08	1.05	0.03	0.78	1.66	-0.88
23	4-	1.08	1.05	0.03	1.96	1.66	0.30
24	2,2'-di	1.15	1.14	0.01	0.48	1.77	-1.29
25	3,3'-di	1.15	1.14	0.01	2.52	1.77	0.75
26	4,4'-di	1.15	1.14	0.01	2.37	1.77	0.60
27	3,5-di	1.11	1.14	-0.03	1.73	1.77	-0.04
28	2,3,2',3'-tetra	1.34	1.39	-0.05	0.74	2.18	-1.44
29	2,4,2',4'-tetra	1.32	1.31	0.01	0.45	2.00	-1.55
30	2,5,2',5'-tetra	1.23	1.23	0.00	0.146	2.00	-1.85
31	3,4,3',4'-tetra	1.38	1.39	-0.01	2.76	2.18	0.58
32	2,4,5,2',4',5'- hexa	1.43	1.48	-0.05	0.26	2.42	-2.16
33	2,4,6,2',4',6'- hexa	1.28	1.48	-0.20	-0.10	2.23	-2.33

Notes: Bracketed values are used as references (see text);
Estimated log k' - values are from eqn. 2 (silica) and
eqn. 8 (alumina), respectively.

Log k' - values (log capacity factors) are obtained from retention times using the equation

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

where t_R is the retention time of the compound considered and t_0 the retention time of the unretained mobile phase.

Results on a Silicagel Column

In one of our earlier publications (2) we found that methylbenzene retention on silica is largely regulated by the number of substituting methylgroups (n_{CH_3}) as is clearly visualized by the solid line in fig. 2.

To a lesser extent symmetry conditions play a role: the original correlation coefficient $r = 0.985$ (of acceptable quality) could be significantly improved to 0.9994 (1) by the introduction of ($n_{\text{ortho}} - n_{\text{para}}$) as a second parameter; with n_{ortho} and n_{para} denoting the number of CH_3 -groups participating in ortho and para-substitution, respectively. In their way these differences between ortho and para substitution-numbers* seem to represent quite properly the differences in symmetry conditions between the several substitution patterns (eqn 1)**.

$$\log k' = 0.085(\pm 0.002) n_{\text{CH}_3} + 0.020(\pm 0.003) (n_{\text{ortho}} - n_{\text{para}}) + 0.377(\pm 0.007) \quad (\text{eq. 1})$$

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

The data-plots for methyl-naphthalenes and methylbiphenyls, respectively, represented in fig. 2 reveal a rather close parallelism with the methylbenzenes. Although some pronounced differ-

* Two examples may illustrate how these differences are estimated: 1,2,3,4-tetramethylbenzene: $n_{\text{ortho}} - n_{\text{para}} = 4 - 2 = 2$; hexamethylbenzene: $6 - 6 = 0$.

** The successful application of the methyl-group dipole moment values instead of ($n_{\text{ortho}} - n_{\text{para}}$) (2) is worth mentioning in this connection (correlation coefficient: 0.997).

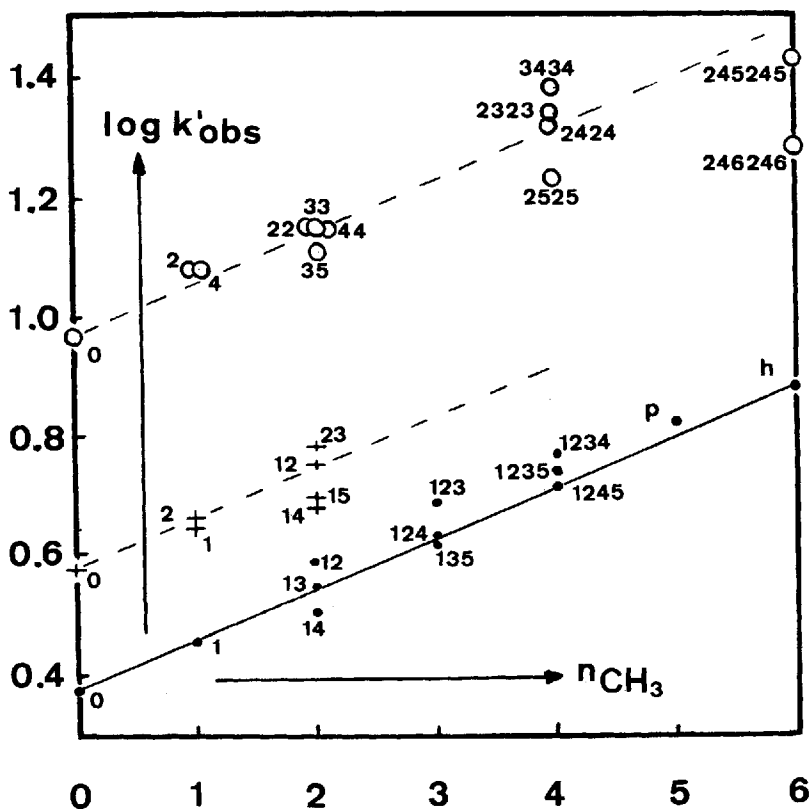


FIGURE 2. Plot of observed $\log k'$ for methylaromatics versus the number of methylgroups. Column: silica gel.

• methylbenzenes; + methylnaphthalenes; ○ methylbiphenyls; ○ denotes unsubstituted parent compounds (either benzene, naphthalene or biphenyl); the other numbers are simplified substitution codes corresponding with column 2 from Table 1.

p = pentamethyl; h = hexamethyl.

ences certainly occur, especially in the biphenyl-series, the two broken lines seem not too unrealistic. At least they invite us to some further considerations with regard to equation 1.

Its intercept is practically equal to the observed $\log k'$ -value of benzene ($=0.375$). If the retention increasing effect of a CH_3 -group really has a constant value of 0.085, i.e., is not depending on the nature of the aromatic parent structure to which it has been attached; and if further the magnitude of the additional ($n_{\text{ortho}} - n_{\text{para}}$) parameter is sufficiently consistent, we are allowed to transform eqn. 1 into eqn. 2:

$$\log k'_{\text{PMeAr}} = 0.085 n_{\text{CH}_3} + 0.020 (n_{\text{ortho}} - n_{\text{para}}) + P \quad (\text{eq.2})$$

with $\log k'_{\text{PMeAr}}$ representing the retention value of any of the 33 compounds from Table 1 and the intercept P denoting the $\log k'$ -value of the proper parent structure: benzene, naphthalene or biphenyl.

Verification of eqn. 2 could most convincingly be achieved by drawing up following three regression equations:

$$\begin{aligned} \log k'_{\text{PMeBz}}^{\text{obs}} &= 1.000(\pm 0.015) \log k'_{\text{PMeBz}}(\text{eq. 2}) + \\ & \quad 0.000(\pm 0.022) \quad (\text{eq.3}) \\ n &= 13 \quad r = 0.9994 \quad s = 0.005 \quad F = 9490 \end{aligned}$$

$$\begin{aligned} \log k'_{\text{PMeN}}^{\text{obs}} &= 0.833(\pm 0.229) \log k'_{\text{PMeN}}(\text{eq. 2}) + \\ & \quad 0.094(\pm 0.164) \quad (\text{eq.4}) \\ n &= 7 \quad r = 0.972 \quad s = 0.017 \quad F = 87.0 \end{aligned}$$

$$\begin{aligned} \log k'_{\text{PMeB}}^{\text{obs}} &= 0.880(\pm 0.085) \log k'_{\text{PMeB}}(\text{eq. 2}) + \\ & \quad 0.141(\pm 0.105) \quad (\text{eq.5}) \\ n &= 12 \quad r = 0.991 \quad s = 0.020 \quad F = 524 \end{aligned}$$

where the indices PMeBz, PMeN and PMeB denote polymethylbenzene, polymethylnaphthalene and polymethylbiphenyl, respectively, and the right-hand member $\log k'$ -values were obtained from eq. 2. Being a severe outlier, 2,4,6,2',4',6'-hexamethylbiphenyl was omitted from regression equation 5; its residual amounts to

0.16 and equals the eight-fold standard error of estimate. The typical rather exclusive behaviour of the compound will come up for discussion in one of the next sections.

The good qualities of equations 3, 4 and 5 justify the incorporation of the three data-sets into one equation:

$$\log k'_{\text{PMeAr}}^{\text{obs}} = 0.995(\pm 0.025) \log k'_{\text{PMeAr}}(\text{eq. 2}) - 0.001(\pm 0.022) \quad (\text{eq.6})$$

n = 32 r = 0.998 s = 0.020 F = 6610

A graphic representation of this fully satisfying equation is given in fig. 3.

Even the data-set of methylnaphthalenes is insertable in this total equation: none of the seven compounds virtually behaves as an outlier. Close inspection of the methylnaphthalene residuals, however, reveals that an improved fit in eqn. 6 is attainable by introducing for each CH_3 -group neighbouring one of the ring joints a correction of -0.20 , i.e., a value equal to the one necessary for expressing para- CH_3 occurrence. A lack of suitably substituted methylnaphthalenes prevented us from working out a more detailed approach, so that we have to confine ourselves to reporting that the correlation coefficient obtained for eqn. 6 shows an increase from 0.9978 to 0.9986 after the introduction of the above indicated correction.

Results on an Alumina Column

A similar treatment as described in the previous section for methylbenzenes on silicagel was elaborated for the experiments on alumina. Here too, the parameter of first choice is the parameter η_{CH_3} as is visualized in fig. 4 by the solid line. Its correlation coefficient ($r = 0.969$, see ref.2) is slightly inferior to that obtained on silicagel ($r = 0.985$) but it underwent a significant improvement to $r = 0.995$ after the introduction of a second parameter, which has due connection with symmetry conditions in the substitution pattern;

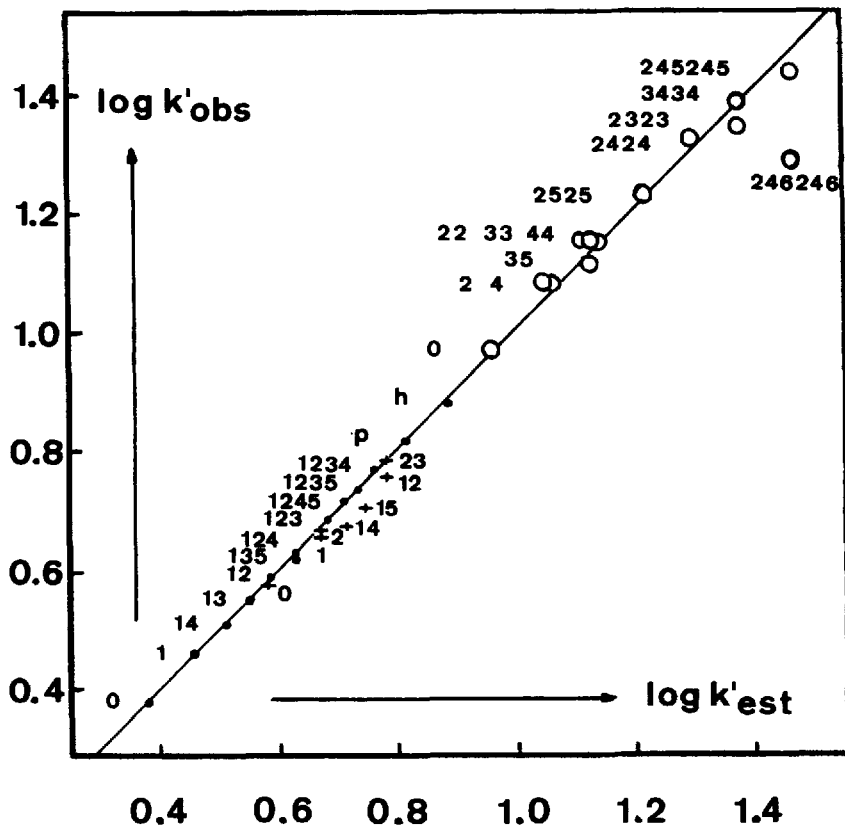


FIGURE 3. Plot of observed $\log k'$ versus estimated $\log k'$ -values obtained from eqn.6. Column: silica gel.
 • methylbenzenes; + methylnaphthalenes; ○ methylbiphenyls; 0 denotes unsubstituted parent compounds (either benzene, naphthalene or biphenyl); the other numbers are simplified substitution codes corresponding with column 2 from Table 1.
 p = pentamethyl; h = hexamethyl.

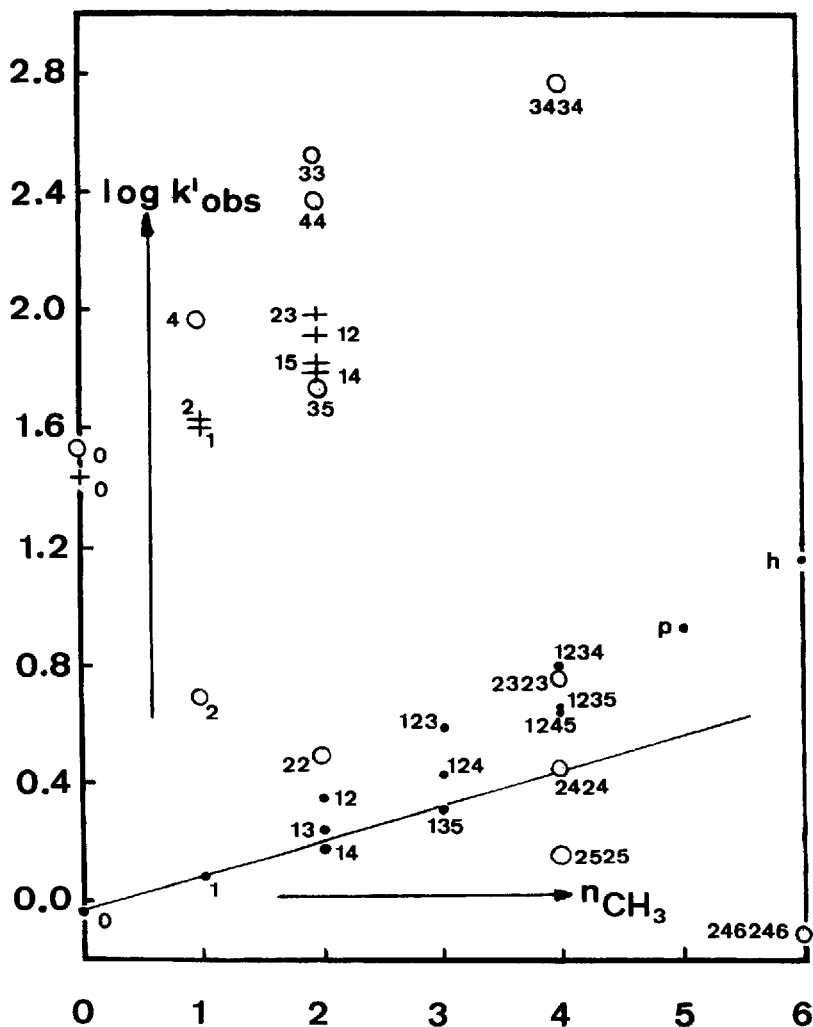


FIGURE 4. Plot of observed $\log k'$ for methylaromatics versus the number of methyl groups. Column: alumina.
 ● methylbenzenes; + methylnaphthalenes; ○ methylbiphenyls; ○ denotes unsubstituted parent compounds (either benzene, naphthalene or biphenyl); the other numbers are simplified substitution codes corresponding with column 2 from Table 1.
 p = pentamethyl; h = hexamethyl.

the extended regression equation (derived in ref. 2) is represented by eqn. 7:

$$\log k' = 0.115(\pm 0.032) n_{\text{CH}_3} + 0.090(\pm 0.028) n_{\text{o-o}} - 0.004(\pm 0.063) \quad (\text{eq. 7})$$

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

where $n_{\text{o-o}}$ denotes the number of ortho-pairs in the structures under consideration. Note, that the application of $n_{\text{o-o}}$ in eqn. 7 differs from the preferred parametrization selected for eqn. 1. Using the parametrization ($n_{\text{ortho}} - n_{\text{para}}$) instead of $n_{\text{o-o}}$ in eqn. 7 would result in an unacceptable decrease of its quality (see ref. 2).

The intercept of eqn. 7 is practically not different from the $\log k'$ -value of benzene observed on alumina ($= -0.032$), so that we felt qualified to apply an equivalent arguing as given in the previous section for eqn. 1 and to transform eqn. 7 into eqn. 8:

$$\log k'_{\text{PMeAr}} = 0.115 n_{\text{CH}_3} + 0.090 n_{\text{o-o}} + P \quad (\text{eq. 8})$$

Following equations were derived for eqn. 8 in a stepwise verification procedure:

$$\log k'_{\text{PMeBz}}^{\text{obs}} = 1.000(\pm 0.066) \log k'_{\text{PMeBz}} (\text{eqn. 8}) + 0.000(\pm 0.040) \quad (\text{eq. 9})$$

$n = 13 \quad r = 0.995 \quad s = 0.036 \quad F = 1090$

$$\log k'_{\text{PMeAr}}^{\text{obs}} = 0.990(\pm 0.034) \log k'_{\text{PMeAr}} (\text{eqn. 8}) + 0.004(\pm 0.030) \quad (\text{eq. 10})$$

$n = 16 \quad r = 0.998 \quad s = 0.033 \quad F = 3930$

where the indices PMeBz and PMeAr denote polymethylbenzenes and polymethylaromatics, respectively, and the right-hand member $\log k'$ -values were obtained from eqn. 8. Equation 10 is visualized by the solid line in fig. 5 and it includes 13 methylbenzenes and the trio naphthalene, biphenyl and 3,5-dimethylbiphenyl. Contrary to eqn. 6 derived in the previous section for

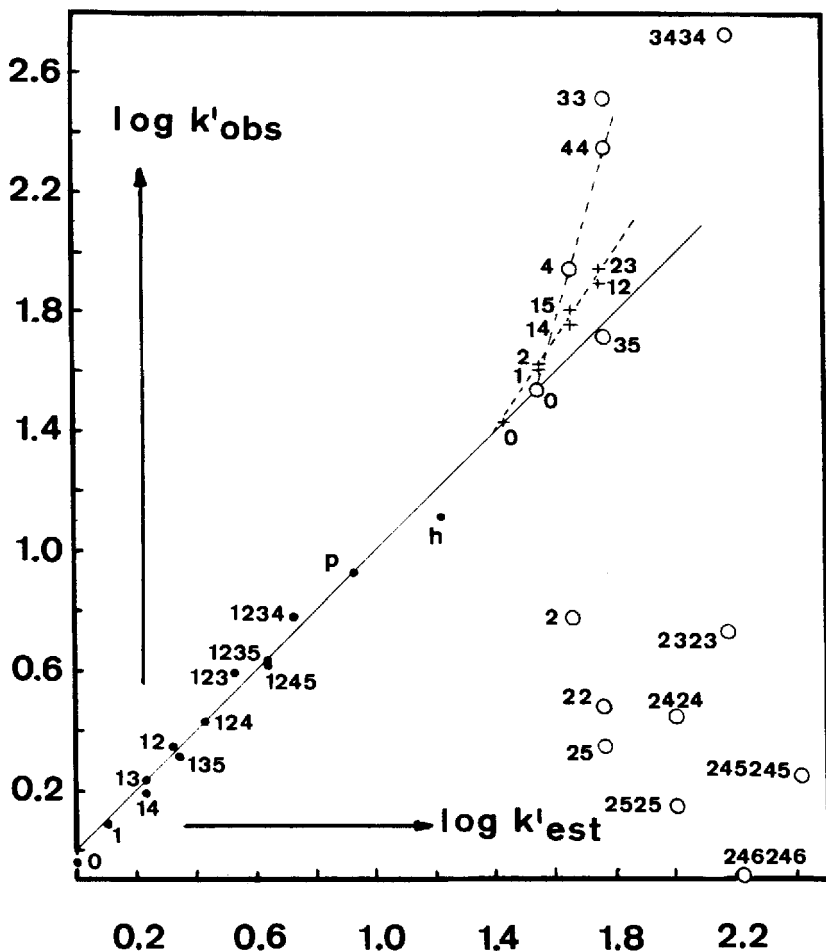


FIGURE 5. Plot of observed $\log k'$ versus estimated $\log k'$ -values obtained from eqn. 10. Column: alumina.
 • methylbenzenes; + methylnaphthalenes; ○ methylbiphenyls; ○ denotes unsubstituted parent compounds (either benzene, naphthalene or biphenyl); the other numbers are simplified substitution codes corresponding with column 2 from Table 1.
 p = pentamethyl; h = hexamethyl.
 The solid line connects the methylbenzene-series, naphthalene, biphenyl and its 3,5-dimethyl-derivative; the two broken lines connect the seven naphthalenes, and biphenyl, 4-methylbiphenyl and 4,4'-dimethylbiphenyl, respectively.

silicagel, it opposes the incorporation of the remaining compounds from Table 1, especially the ortho-substituted biphenyls. The latter compounds would seriously deteriorate the quality of our equation.

It is possible, however, to incorporate all seven methyl-naphthalenes in a separate regression:

$$\log k'_{\text{PMeN}}^{\text{obs}} = 1.536(\pm 0.167) \log k'_{\text{PMeN}} \text{ (eqn. 8)} - 0.736(\pm 0.270) \text{ (eq. 11)}$$

$$n = 7 \quad r = 0.996 \quad s = 0.019 \quad F = 567$$

Although satisfying in itself, this equation can in no way be combined with eqn. 10, on account of its deviating slope, which is approximately 50% higher than that of eqn. 10. Some additional commenting will be given in one of the next sections.

Visualization of some Attachment Patterns

In order to obtain some notion with respect to the positioning of the studied molecules on the applied adsorbents, we construed figs. 6-9 paying due attention to the differences between silicagel and alumina. Because the solvent strength of hexane is practically zero, any competition of hexane molecules in the adsorption mechanism can be excluded and the same will be true for interactions between the solvent and the solutes at issue. Accordingly, the figures show only the way in which we think that the exemplified solute molecules are localized.

In the drawing of the solute molecules we followed the suggestions given by Gould (3).

With regard to the adsorbents: a. the silicagel structure is derived from a figure presented by Halpaap (4); the silanol groups can freely rotate around their axes perpendicular to the silicon atoms and they are able to participate in hydrogen-bonding with the aromatic π -system of the solute.* Besides, partial non-

* De Boer and Vleeskens (5) did not realize these facts. In this respect we wish to refer to the overview given by Knüszinger(6) on these topics.

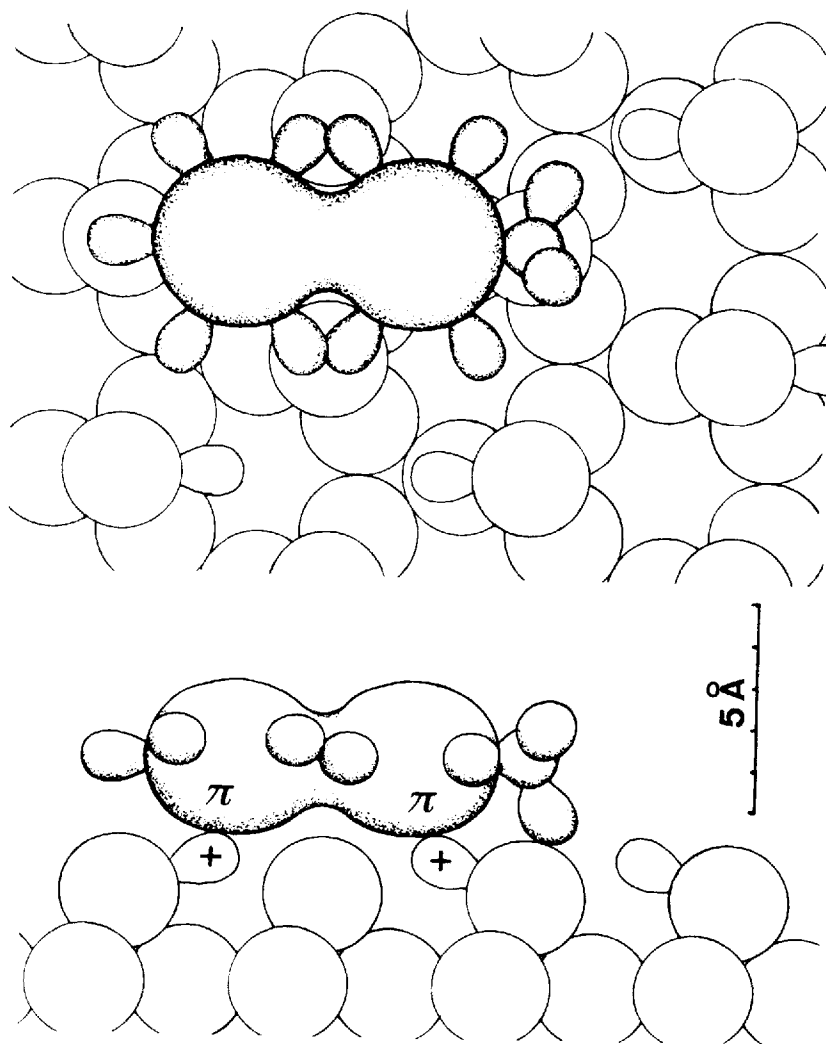


FIGURE 6. Proposed position of a molecule of 4-methylbiphenyl adsorbed on a crystalline silicagel structure; only the oxygen atoms and a restricted number of silanol groups are sketched. Upper part: top view; lower part: side-view.

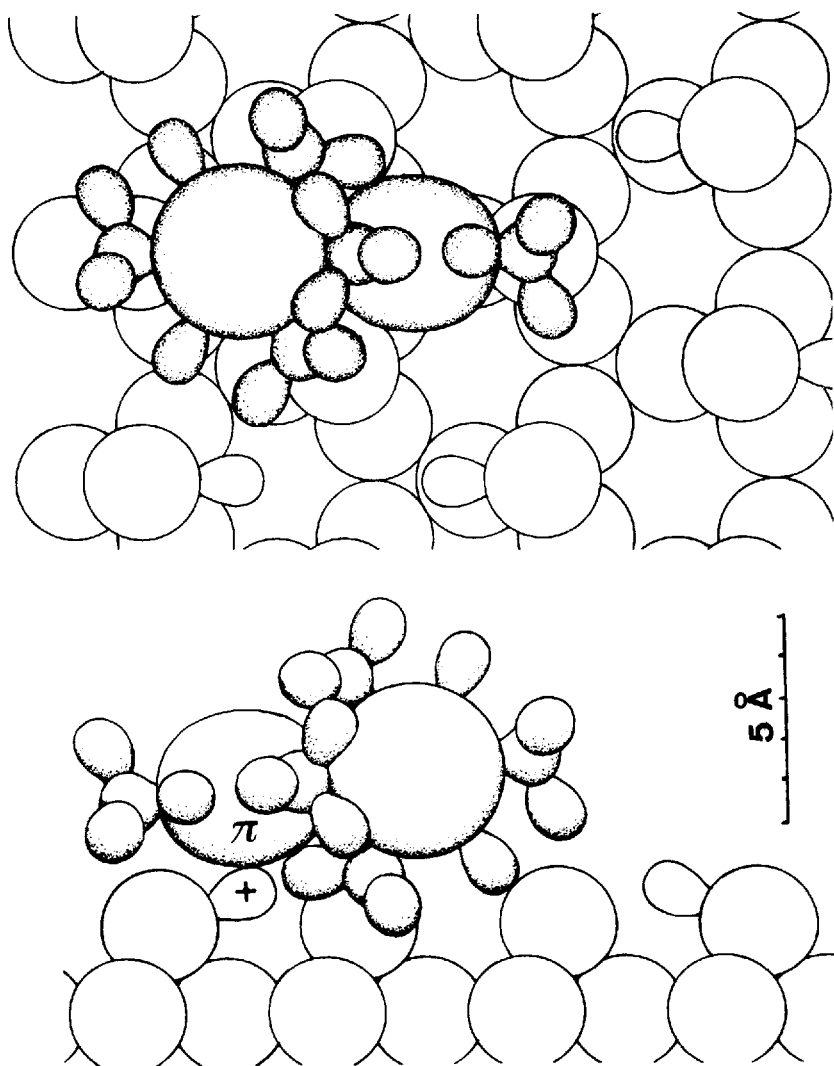


FIGURE 7. Proposed position of a molecule of 2,4,6,2',4',6'-hexamethylbiphenyl on a crystalline silicagel structure: only the oxygen atoms and a restricted number of silanol groups are sketched. Upper part: top-view; lower part: side-view.

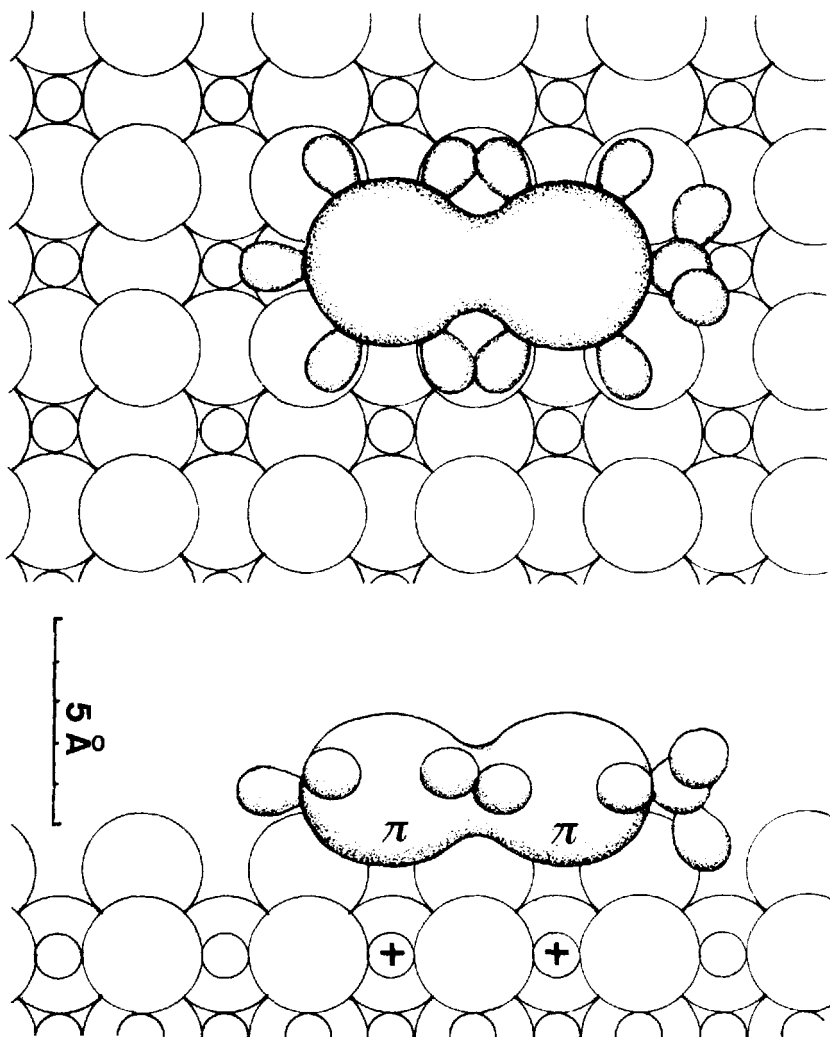


FIGURE 8: Proposed position of a molecule of 4-methylbiphenyl adsorbed on γ -alumina. Upper part: top-view; lower part: side-view.

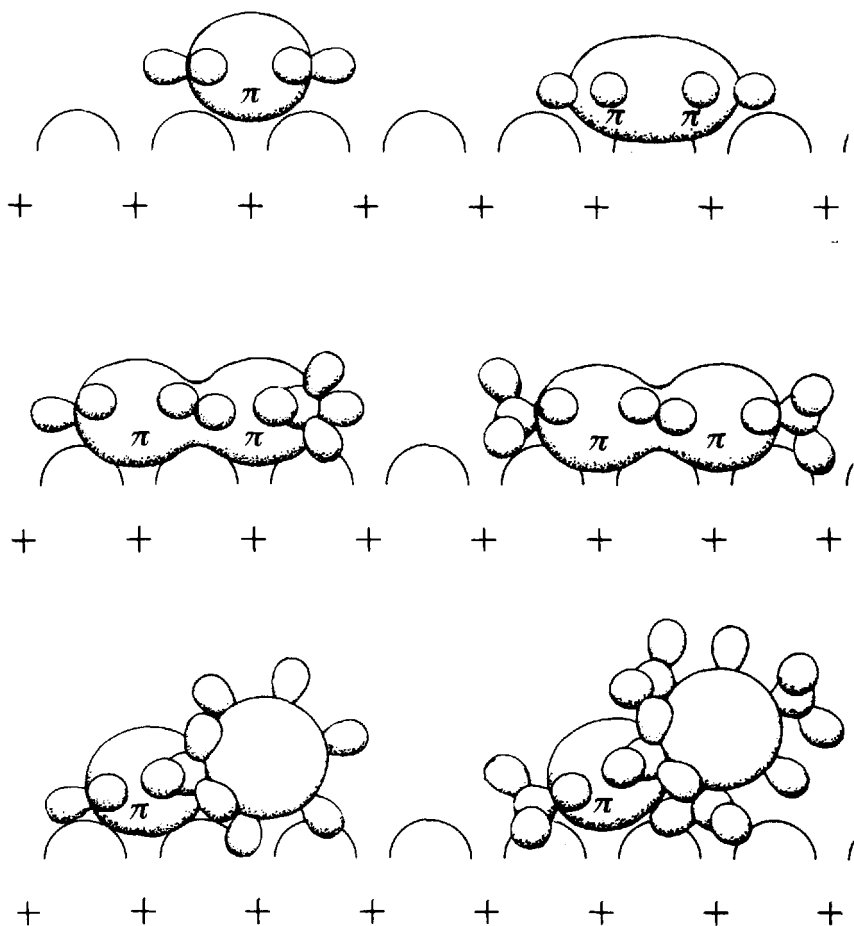


FIGURE 9. Tentatively proposed localization of adsorbed molecules of benzene, naphthalene, 3- (or 3,5-) methylbiphenyl, 4,4'-dimethylbiphenyl, 2- (or 2,2'-) methylbiphenyl and 2,4,6,2',4',6'-hexamethylbiphenyl on a γ -alumina surface. All sketches are given in side-view.

crystallinity and curvature of pore walls add to a whole range of distances between the hydroxyl groups present on the surface of the silicagel. This implies that hydrogen bonds between the centres of both moieties of the aromatic biphenyl derivatives and silanol groups are easily achieved. The existence of such dual site adsorption leads to the conclusion that adsorption, and in turn retention, is fully controlled by the properties of the adsorbate molecules in the dynamic process of ad- and desorption on the column.

b. in depicting the localization on alumina (γ - Al_2O_3 , a spinel structure with cation defects) we made use of a figure given by Peri (7). For practical reasons, however, we chose for an alternative section through the crystal lattice.

In essence, the situation on alumina is not different from that on silicagel as far as the methylbenzenes and methyl-naphthalenes are concerned. Although the circulating dry hexane does not remove all free hydroxyl groups from the surface, it is stated (8), however, that aprotic sites originating from aluminum ions in a "reduced state" are much stronger than H-bonds (see also Snyder (9)). This will result in an increased polarization of the adsorbed molecules, as will be discussed in a forthcoming paper.

Low retentions, comparable with those of methyl benzenes, are observed for ortho-substituted methylbiphenyls: note the scattered points in the lower right-hand part of figure 9. Their location is connected with the fact that the molecules in question have practically fully lost coplanarity, so that only one of the two phenyl-nuclei is localized close to an Al^+ site.

Contrasted to the rather flexible amorphous silicagel the rigid crystalline structure of alumina prevents the attraction of more than one phenyl-nucleus during the adsorption process.

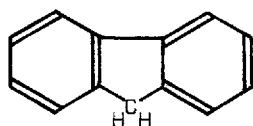
Evidence from UV-spectral Data

In the thirties extensive studies were performed on the UV-light absorption of biphenyls (10, 11), particularly in view

TABLE 2
Ultra-violet Data of Methylsubstituted Biphenyls
(C-band Absorptions)

Biphenyl	λ_{\max}	log ϵ
unsubstituted	248 nm	4.23
fluorene	260 "	4.28
4-methyl	252 "	4.28
4,4'-dimethyl	255 "	4.32
2-methyl	237 "	4.01
2,2'-dimethyl	228 ⁱ "	3.78
2,6-dimethyl	231 ⁱ "	3.75
2,6,2'-trimethyl	230 ⁱ "	3.60
2,6,2',6'-tetramethyl	absent	
2,4,6,2',4',6'-hexamethyl	absent	

Note: i = inflection (shoulder)



fluorene

of the correct understanding of resonance-decoupling phenomena caused by steric effects.

The available data reveals that two different types of spectral changes induced by steric inhibition of coplanarity between the composing resonating moieties in a molecule should be distinguished:

a) steric effects causing decreases in wavelength of the conjugative absorption band (i.e., increase of transition energy) combined with decreases in absorption intensity (i.e., lowering of transition probabilities);

b) steric effects mainly causing decreases in absorption intensity;

Biphenyls appear to belong to the first category as becomes apparent from the small compilation of data given in Table 2 (10). Biphenyl shows a well-developed conjugation band (C-band)

blue-shifted by 12 nm compared with fluorene in which the two phenyl groups must be practically uniplanar in order to correctly accommodate the methylene bridge. The observed blue-shift for biphenyl indicates a slight distortion from the coplanar situation in solution (here ethanol) of the same magnitude as observed by Dhar (12) in the solid crystalline state but it does by no means cover an interplanar angle as high as 45° reported by Bastiansen (13) for gaseous biphenyl.

We are of opinion that our conclusions drawn from the described adsorption phenomena are well in line with the above memorized UV-data and that the figures 6-9 represent realistic attachment patterns of the investigated structures on the two adsorbents: an interplanar angle of $\approx 15^{\circ}$ between the two phenyl groups was applied for non-orthosubstituted biphenyls in drawing figures 6 and 8 where both rings have an attaching function. Fig. 7 visualizes the binding of a maximally distorted biphenyl structure on silicagel; one ring fully attached and the second ring deprived of attaching possibilities. What remains for this second ring is some secondary impact on its partner ring; by means of the negative phenyl effect the attached ring will lose in effective binding power and this is the reason that 2,4,6,2',4',6'-hexamethylbiphenyl takes such exceptional position (see Fig.3).

The 'deformation' of the attachment pattern is pregnant when the hexamethylbiphenyl is adsorbed on alumina. Owing to the rigidity of the alumina structure the phenyl group seeking for attachment will be lifted up too far to find reasonable accommodation (see Figs. 4 and 9).

POLY-AROMATICS

Retention of a Selection of Poly-aromatics on Silicagel

Results displayed in the preceding sections confirm our previous finding (2) that binding of the three series of compounds to silica as well as to alumina depends on the availa-

bility of a suitable π -electronic system. In order to collect some more decisive information we investigated the retentional behaviour of a selection of poly-aromatics on slightly 'moistened' silicagel. The aromatic parent structures already studied in the above sections were included in this investigation so that Table 3 overviews log k' -values obtained for seventeen hydrocarbons. Due comparison with their total number of π -electrons (n_{π}) suggests a close relationship. For the first six items from the table following equation can be derived:

$$\log k' = 0.067(\pm 0.006) n_{\pi} - 0.907(\pm 0.086) \quad (\text{eq. 12})$$

$$n = 6 \quad r = 0.998 \quad s = 0.024 \quad F = 861$$

Application of this equation to Nrs 7-17 enables us to trace four apparent outliers: coronene, ortho-terphenyl, ortho-quaterphenyl and 1,3,5-triphenylbenzene. The remaining aromatics all give a satisfying fit into eqn. 12 as shown in the last column but one of Table 3.

Instead of the number of π -electrons, we may use as well delocalisation energies; expressed in β -units ($\beta \approx -20$ kcal/Mol), these energies ($E_D(\beta)$) can be correlated with our observed retention values by means of following equation:

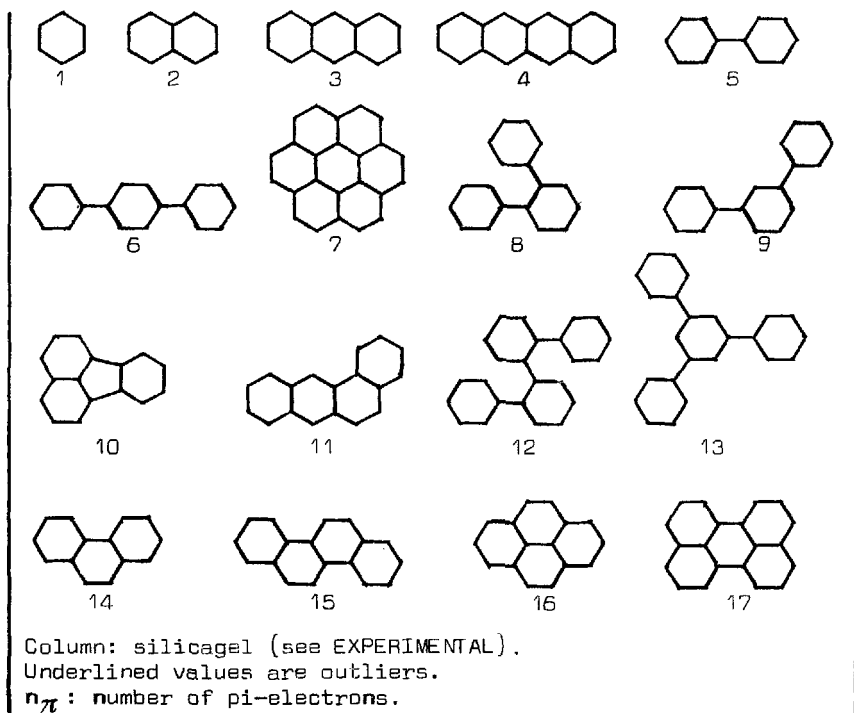
$$\log k' = 0.158(\pm 0.011) E_D(\beta) - 0.807(\pm 0.072) \quad (\text{eq. 13})$$

$$n = 13 \quad r = 0.994 \quad s = 0.031 \quad F = 882$$

Proper $E_D(\beta)$ -values required for drafting eqn. 13 were collected from literature (14, 15). The inability of the above mentioned four outliers to fit eqn. 13 (see also Fig. 10) could have following reasons: for coronene the non-availability of sufficient space on the adsorbent to assert its excessive π -field and for ortho-terphenyl, ortho-quaterphenyl and 1,3,5-triphenylbenzene matters of non-planarity could be of importance. Steric effects in the first two compounds are evident (16) and the small though significant deviation for 1,3,5-triphenylbenzene finds support in investigations done by Orelkin and Lansdale (17).

TABLE 3
 Retention of Aromatics versus Delocalization Energy

No	Aromatic	$\log K'_{\text{obs}}$	$n\pi$	$\log K'_{\text{est}}$	$E_D(\beta)$
1	benzene	-0.53	6	-0.51	2.00
2	naphthalene	-0.21	10	-0.24	3.68
3	anthracene	0.04	14	0.03	5.31
4	tetracene	0.31	18	0.30	6.93
5	biphenyl	-0.08	12	-0.10	4.38
6	<u>para</u> -terphenyl	0.28	18	0.30	6.77
7	coronene	0.55	24	<u>0.70</u>	<u>10.57</u>
8	<u>ortho</u> -terphenyl	0.16	18	<u>0.30</u>	<u>6.77</u>
9	<u>meta</u> -terphenyl	0.24	18	<u>0.30</u>	<u>6.77</u>
10	fluoranthene	0.22	16	0.17	6.50
11	benzanthrene	0.31	18	0.30	7.10
12	<u>ortho</u> -quaterphenyl	0.32	24	<u>0.70</u>	<u>9.16</u>
13	1,3,5-triphenyl-benzene	0.49	24	<u>0.70</u>	<u>9.15</u>
14	phenanthrene	0.07	14	0.03	5.45
15	chrysene	0.35	18	0.30	7.19
16	pyrene	0.15	16	0.17	6.51
17	perylene	0.47	20	0.43	8.25



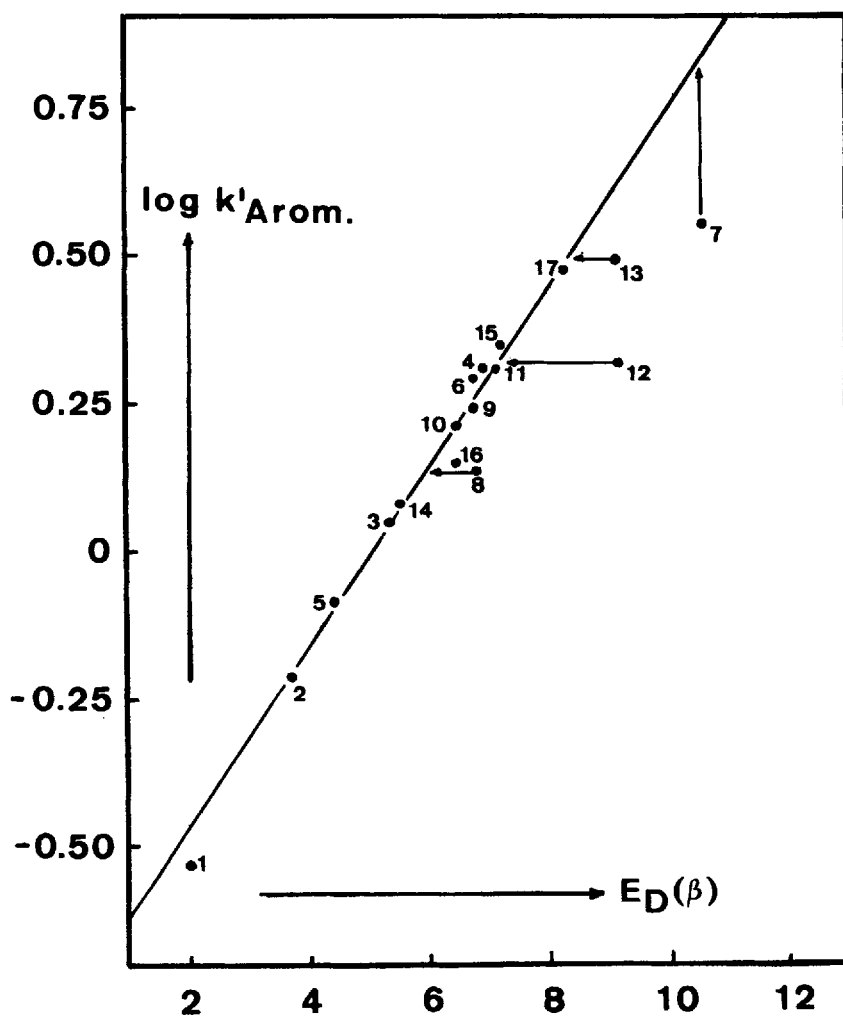


FIGURE 10. Plot of $\log k'$ for a series of aromatics versus delocalisation energies (expressed in β -units. The numbering is as given in Table 3. Column: silica gel under "moist" conditions. Four arrows suggest how the outliers 7, 8, 12 and 13, if proper corrections could be applied, will fit the regression line.

CONCLUSION

Retention-values (expressed as $\log k'$ (capacity-factors)) obtained on normal-phase silicagel and alumina columns for methyl-naphthalenes and methylbiphenyls follow the same rules as those established in a previous study for methylbenzenes.

Each methyl group has a constant impact on $\log k'$ and deviations, particularly those observed for biphenyls on alumina, are mainly attributable to steric influences on resonance. For compounds with a sufficient number of ortho-methyl groups this will result in a mutual perpendicular position of the phenyl moieties. Our ideas concerning the adsorption are visualized in a number of pictures.

The described impact of a methyl group originates in the positive mesomeric effect of this group (negative Hammett σ) which is responsible for an increase of the π -electronic 'activity' of the aromatic ring(s).

That ' π -binding' to the adsorbents is virtually the principal factor in the achievement of the attachments, finds due support in additional retention studies on a selection of polyaromatics. The correlation between $\log k'$ and delocalisation energies which are decisive for the π -electron 'activity' of the aromatics is of the expected statistical significance ($r = 0.994$).

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