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## **Silicas chemically bonded with multidentate phenyl groups as stationary phases in reversed-phase liquid chromatography used for non-planarity recognition of polycyclic aromatic hydrocarbons**

KIYOKATSU JINNO\*, KUNIHICO YAMAMOTO, HIDEO NAGASHIMA, TAKANORI UEDA and KENJI ITOH

*School of Materials Science, Toyohashi University of Technology, Toyohashi 441 (Japan)*

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### ABSTRACT

Multidentate phenyl-bonded phases have been evaluated as stationary phases which can recognize molecular non-planarity of polycyclic aromatic hydrocarbons. The results clearly indicate that these multidentate silicas give a higher non-planarity recognition capability than that with typical octadecylsilicas such as polymeric and monomeric phases. The reason for this mechanism can be interpreted by the molecular–molecular interaction between a solute and a stationary phase and this kind of approach will open the possibility of designing new stationary phases which offer more selective or specific separations.

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### INTRODUCTION

As planarity recognition is directly related to the physico-chemical properties and biological activities of polycyclic aromatic hydrocarbons (PAHs)<sup>1–3</sup>, it is necessary to have good separation and analytical methods for this recognition. Generally in the separation of PAHs by reversed-phase liquid chromatography (LC), which seems to be the most powerful and useful method, chemically bonded octadecylsilica (ODS) phases have been used as the stationary phase of choice because of their capability and applicability. ODS phases can be divided into two categories, one polymeric and the other monomeric. Polymeric phases are normally synthesized by using polyfunctional silanes in the presence of water (or sometimes even under conditions carefully controlled to exclude water) based on polymeric surface modification chemistry, whereas monomeric phases are obtained by using monofunctional silanes as the starting material. A number of papers have reported the differences in the chromatographic properties of the two types of ODS phases for PAH separations<sup>4–10</sup>. The conclusion was that polymeric phases have a greater capability of recognizing molecular planarity of PAHs. Non-planar molecules were eluted faster than planar molecules with polymeric phases because the phases have a “slit-like”

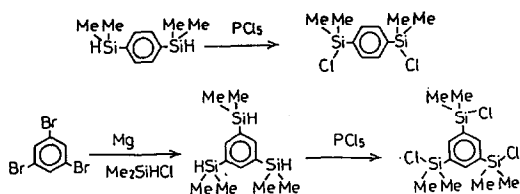
structure on the surface, as described Sander and Wise<sup>4-6</sup>. Solid-state cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS-NMR) spectrometry of various phases clearly revealed that the molecular freedom of the polymeric phases is less than that of the monomeric phases and this limited molecular freedom induces the recognition of the molecular planarity<sup>9,11,12</sup>, where enhancement of the retention for planar molecules would be expected. To enhance planarity recognition more, we investigated the use of dicoronylene as the stationary phase for the separation of PAHs. Dicoronylene has a very flat structure and it can retain planar and exclude non-planar solutes, so that the planarity recognition was enhanced<sup>13,14</sup>. However, one can consider the opposite case, in which stationary phases retain non-planar molecules to a greater extent than planar molecules, so that enhanced selectivity of planar *vs.* non-planar could be also expected.

In this work, newly synthesized phenyl-bonded stationary phases were evaluated for this non-planarity recognition of PAHs. A novel concept of the stationary phase structure has been introduced for synthesizing these phases. The phases use 'bidentate' or 'tridentate' silanes containing one reactive atom on each two or three silicon atoms that are connected through a phenyl ring. Discussions herein indicate that the design of stationary phases which offer high selectivity for particular solute groups will be possible based on the consideration of molecular-molecular interactions between solutes and stationary phase ligands.

## EXPERIMENTAL

New stationary phases were synthesized using reactions developed in our laboratory<sup>15</sup>. Base silica was obtained from Shiseido (Yokohama, Japan). The particle diameter is *ca.* 5  $\mu\text{m}$  and very low metal impurity concentrations are present. The surface area of the silica is *ca.* 270  $\text{m}^2$ . These new materials are *p*-bis(dimethylphenyl) (BP)- and 1,3,5-tris(dimethylphenyl) (TP)-bonded silicas. For comparison, phenyl (P) and methyl (C1) bonded silicas were also synthesized. The procedures for synthesizing them are described elsewhere<sup>15</sup>.

Typical starting silane compounds for BP and TP phases are produced by the following reactions (Me = methyl):



The basic difference between these phases and the generally commercially available phases is the structure on the silica surface. As shown in Fig. 1, BP and TP have a unique structure which covers the silica surface horizontally, whereas P, C1 and general ODS phases are attached vertically to the silica surface by siloxane bonding. As the bidentate or tridentate reagents can form two or three bonds to the silica surface for each molecule of silane and these multi-bonds produce a multi-membered

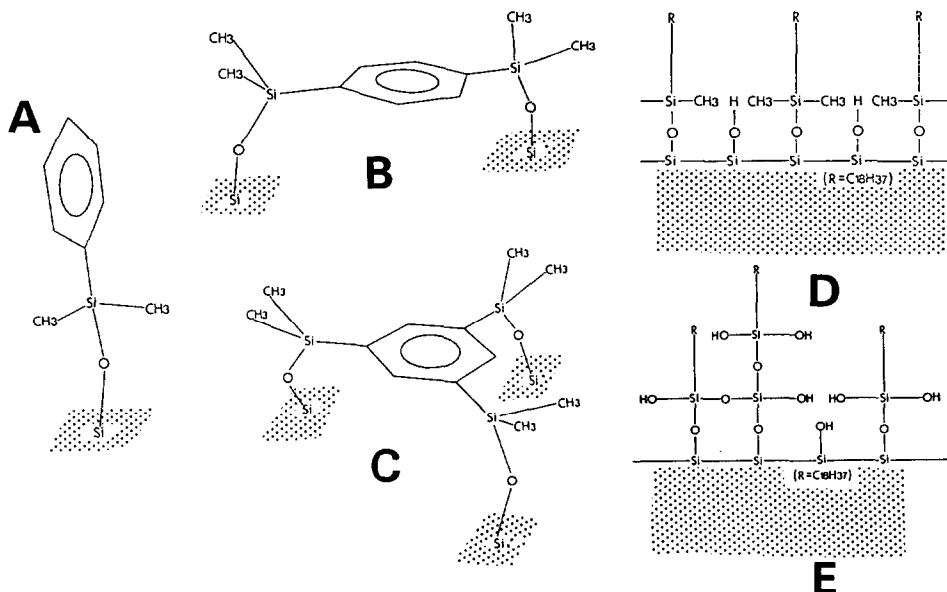


Fig. 1. Bonded-phase structures investigated. (A) P; (B) BP; (C) TP; (D) monomeric ODS; (E) polymeric ODS.

ring with the silica structure, they should lead to increased stability of the attached ligand. The materials synthesized are summarized in Table Ia, which presents the data for elemental analysis of carbon. An important consideration with the multidentate silanes is whether each silicon atom from the silane has reacted with the surface SiOH groups for a true multidentate attachment, or whether the silane connects by only one Si-O-Si bond to the surface. In order to confirm the structural differences of the three phenyl-group-bonded phases, P, BP and TP, both solution- and solid-state NMR measurements were performed.

$^{13}\text{C}$  MAS-NMR spectra were obtained on a Model JNM GX270 FT-NMR spectrometer (JEOL, Tokyo, Japan). The magic angle was set by minimizing the line width of the side-bands of the  $^{79}\text{Br}$  or  $^{81}\text{Br}$  satellite transitions in KBr. For  $^{13}\text{C}$  CP-MAS-NMR, the Hartmann-Hahn matching condition for cross-polarization was calibrated with adamantane and, in order to eliminate spinning side-bands, the TOSS method was used. The measurement conditions used were basically the same as those reported by Kirkland *et al.*<sup>16</sup>. Solution-state NMR measurements were performed on the same NMR spectrometer.

Fig. 2 shows the  $^{29}\text{Si}$  solution-state NMR spectra of the authentic methoxysilanes (although in the actual synthetic reactions we used chlorosilanes instead of the methoxysilanes), *i.e.*, phenyldimethylmethoxysilane for P, *p*-bis(dimethylmethoxysilyl)benzene for BP and 1,3,5-tri(dimethylmethoxysilyl)benzene for TP. The spectra indicate that they have almost identical structures with regard to the silicon atoms, because a *ca.* 10-ppm signal can be assigned to the silicon atom desired. The signal at -4 ppm is due to 1,1',3,3'-tetramethylsiloxane as the internal standard.

The similar chemical shifts in these spectra suggest that the three silanes have the same silicon structure because the silicon atoms are connected to two methyl, one

TABLE I  
STATIONARY PHASES USED IN THIS WORK

(a) Newly synthesized phases<sup>a</sup>

Abbrev.	Bonded phase	Carbon content (wt.-%)
P	Phenyl	8.04
BP	<i>p</i> -Bis-phenyl	7.97
TP	1,3,5-Tris-phenyl	7.46
Cl	Methyl	4.46

(b) Other phases<sup>b</sup>

Abbrev.	Bonded phase	Remarks
DP	Diphenyl	Ref. 17
DC18	Octadecyl	Develosil-ODS, monomeric
VC18	Octadecyl	Vydac 201 TPB5-ODS, polymeric
LC18	Octadecyl	LC Packings RP-18 180JC89 <sup>c</sup>
FC18	Octadecyl	FineSIL C18T-5 <sup>d</sup>
CC18	Octadecyl	Capcell Pak C <sub>18</sub> , monomeric <sup>e</sup>

<sup>a</sup> All phases were packed into the 150 mm × 0.53 mm I.D. fused-silica capillary by the slurry technique.

<sup>b</sup> All phases except LC18 were packed into the 150 mm × 0.53 mm I.D. fused-silica capillary by the slurry technique.

<sup>c</sup> Commercially available microcolumn (150 mm × 0.32 mm I.D.).

<sup>d</sup> Trifunctional phase but looks like a monomeric phase.

<sup>e</sup> Polymer-coated C<sub>18</sub> phase.

phenyl and one methoxy group as the active site, although the tris-phenylsilane has three silicon atoms, the bis-phenylsilane has two and the phenylsilane has only one.

Fig. 3 illustrates the <sup>13</sup>C solution-state NMR spectra for these three silanes. Depending on the location of carbon atoms within these silanes, the signals around 130–150 ppm are different from each other. The spectra clearly indicate that TP and BP have two positionally different carbon atoms, whereas P has four chemically different carbon atoms, although the signal intensities do not accurately suggest the number of these carbon atoms. In Fig. 4 <sup>13</sup>C CP-MAS-NMR spectra are summarized for the three bonded silicas. Even though the signal peaks are much broader than those of the authentic silanes because these are solid-state NMR spectra, the signals are consistent with those which appeared in the solution-state spectra. The correspondence can be found by the peak numbers marked in Figs. 3 and 4.

The <sup>29</sup>Si CP-MAS-NMR spectra shown in Fig. 5 suggest some different information about the synthesized phases. The signals appearing at *ca.* 2 ppm for P, BP and TP can be assigned to silicon atoms connected to the phenyl ring and the silica surface by siloxane bonds and the two signals around –100 ppm are caused by SiOH and SiO– bondings in the substrate silica. The spectrum for P suggests that it has only one such connecting silicon atom, whereas the spectra of TP and BP indicate that they have another type of silicon atom in their structure because of the signals at *ca.* 1.6 ppm.

As Kirkland *et al.*<sup>16</sup> reported similar <sup>29</sup>Si NMR spectra for bidentate bonded

phases, it seems that these spectra are not unusual. The presence of the two low-field peaks could be explained by the following two assumptions: dimerization of TP and BP occurred in the synthetic reaction or different bond angles and conformations of the Si–O–Si bonds led to positionally different silicon atoms. However, it is apparent from the spectrometric data that the synthesized bonded phases are the desired materials.

For comparison, five different commercially available ODS phases, Develosil-ODS (Nomura Chemicals, Seto, Japan; DC18), Vydac 201 TPB5-ODS (Separations Group, Hesperia, CA, U.S.A.; VC18), LC Packings RP-18 (Zurich, Switzerland; LC18), FineSIL C18T-5 (Jasco, Tokyo, Japan; FC18) and Capcell Pak C<sub>18</sub> (Shiseido, Yokohama, Japan; CC18), and a diphenyl (DP) phase synthesized in a previous study<sup>17</sup> were also evaluated. The reason for adding the DP phase for comparison is that it has been found to have some unique chromatographic properties when compared with ODS phases. These phases are listed in Table Ib.

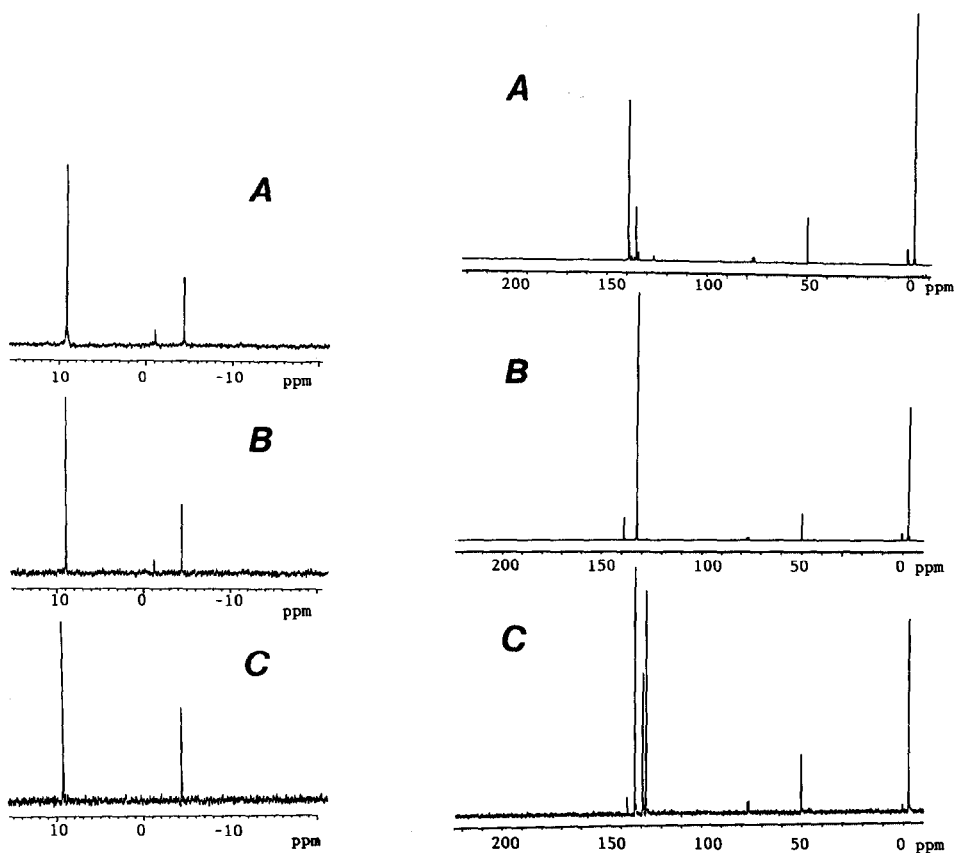


Fig. 2. <sup>29</sup>Si solution-state NMR spectra of the authentic silanes. (A) 1,3,5-Tris(dimethylmethoxysilyl) benzene; (B) *p*-bis(dimethylmethoxysilyl)benzene; (C) dimethylmethoxysilylbenzene.

Fig. 3. <sup>13</sup>C solution-state NMR spectra of the authentic silanes. (A) 1,3,5-Tris(dimethylmethoxysilyl) benzene; (B) *p*-bis(dimethylmethoxysilyl)benzene; (C) dimethylmethoxysilylbenzene.

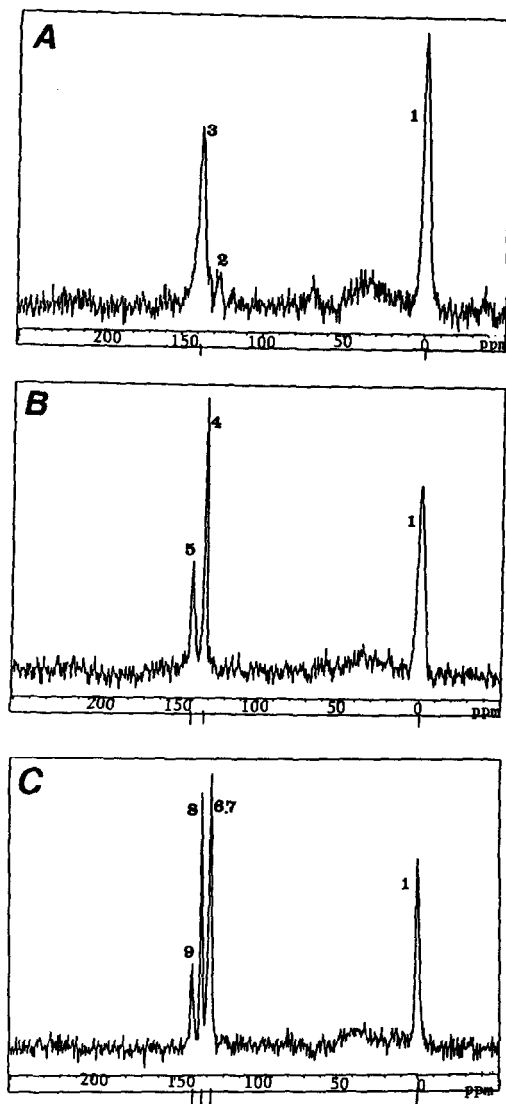


Fig. 4.  $^{13}\text{C}$  CP-MAS solid-state NMR spectra of the chemically modified silicas. (A) TP; (B) BP; (C) P.

All the phases except LC18 were packed into fused-silica capillaries of (150 mm  $\times$  0.53 mm I.D.) by a slurry technique. LC18 was used as supplied by the manufacturer in a 150 mm  $\times$  0.32 mm I.D. fused-silica capillary.

The microcolumn LC system consisted of a microfeeder MF-2 as a pump (Azuma Electric, Tokyo, Japan), a Rheodyne (Cotati, CA, U.S.A.) Model 7513 injector and a Jasco Uvidec 100-III UV detector set at 254 nm. The mobile phases were mixtures of methanol and water and the typical flow-rate used was 2  $\mu\text{l}/\text{min}$ . Chromatographic measurements were performed at least in triplicate. The retention data used

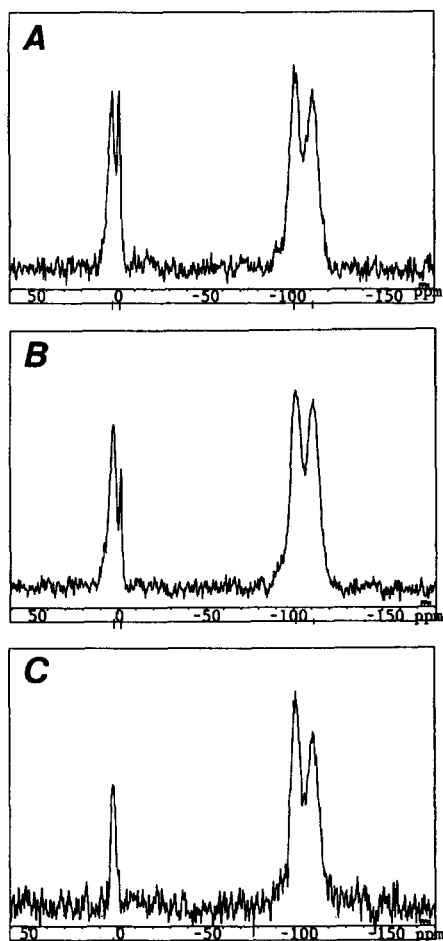


Fig. 5.  $^{29}\text{Si}$  CP-MAS solid-state NMR spectra of the chemically modified silicas. (A) TP; (B) BP; (C) P.

for the evaluation were mean values of these experimental data. For the column dead-volume measurements, sodium nitrite solution (100 ppm) was used.

PAHs used for the evaluation were commercially available, except benzo[*a*]pyrene (BaP), tetrabenzonaphthalene (TBN) and phenanthro[3,4-*c*]phenanthrene (PhPh), which were obtained as a gift from J.C. Fetzer of Chevron Research (Richmond, CA, U.S.A.).

## RESULTS AND DISCUSSION

### *Recognition of molecular size*

To understand the basic chromatographic characteristics of the synthesized materials, the separation of four small, planar PAHs, naphthalene, anthracene, pyrene and chrysene, was attempted. The retention data obtained with methanol-water (70:30) as the mobile phase are summarized in Table II. The chromatogram obtained

TABLE II

CAPACITY FACTORS  $k'$  FOR PLANAR POLYCYCLIC AROMATIC HYDROCARBONS WITH VARIOUS BONDED PHASES

Solute	$F$	$k'$									
		Stationary phase									
		$P$	$BP$	$TP$	$DP$	$C1$	$DC18$	$VC18$	$LC18$	$FC18$	$CC18$
Naphthalene	5	1.17	1.46	1.18	0.67	0.29	4.27	1.17	2.00	1.93	3.82
Anthracene	7	2.17	3.31	2.09	1.25	0.65	13.82	4.75	5.67	5.21	11.09
Pyrene	8	2.75	4.39	2.55	1.50	0.77	21.73	7.33	8.67	7.71	16.82
Chrysene	9	3.92	6.69	3.46	2.00	1.18	39.55	19.50	13.67	12.50	28.64

on the TP phase is shown in Fig. 6. The separation capability of this phase seems very good. BP, P, C1 and six other reference phases were also evaluated. In general, the retention of these PAHs in reversed-phase LC has a high correlation with the  $F$  number proposed by Schabron *et al.*<sup>18</sup> in 1977<sup>19-22</sup> as follows:

$$\log k' = AF + B \quad (1)$$

where  $k'$  is the capacity factor of the solute,  $F$  is defined as the number of double bonds plus the number of primary or secondary carbons minus 0.5 times the number of non-aromatic rings and  $A$  and  $B$  are regression coefficients.

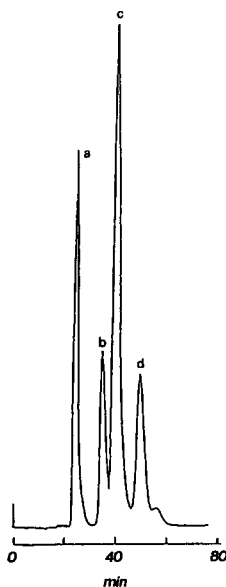


Fig. 6. Typical chromatogram for the separation of PAHs with the TP phase. Mobile phase, methanol-water (70:30); flow-rate, 2  $\mu$ l/min; detection, UV (254 nm). Peaks: a = naphthalene; b = anthracene; c = pyrene; d = chrysene.



TABLE III

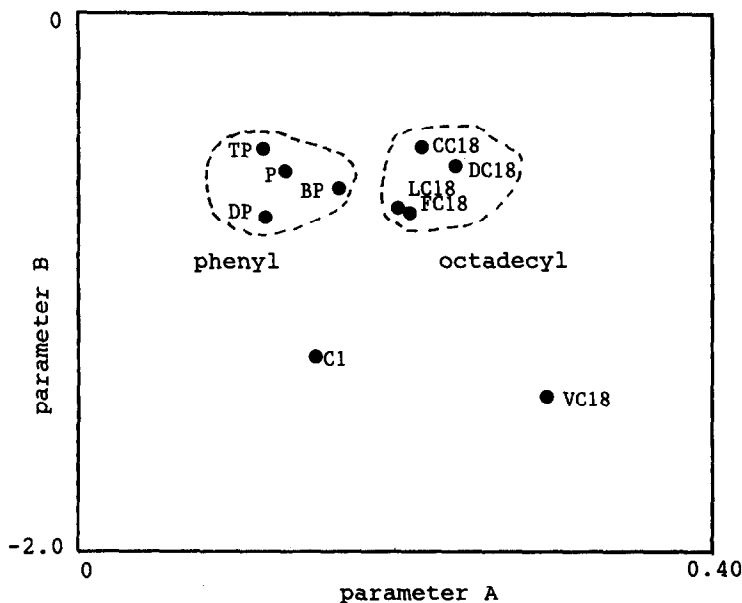
RESULTS OF THE REGRESSION ANALYSIS FOR THE CORRELATION BETWEEN LOG  $k'$  AND  $F$ 

$$\text{Log } k' = AF + B.$$

Stationary phase	$A$	$B$	$r$	$F\text{-ratio}^a$
P	0.1292	-0.5772	0.999	669
BP	0.1630	-0.6440	0.998	529
TP	0.1150	-0.4996	0.998	532
C1	0.1482	-1.2663	0.992	128
DP	0.1173	-0.7501	0.996	254
DC18	0.2393	-0.5590	0.999	1015
VC18	0.2953	-1.4159	0.994	158
LC18	0.2087	-0.7304	0.999	922
FC18	0.2015	-0.7143	0.999	1179
CC18	0.2169	-0.4953	0.999	1128

<sup>a</sup>Statistical significance.

Therefore, the correlation study on the data in Table II was performed by using a multiregression analysis. The results are summarized in Table III, where regression coefficients  $A$  and  $B$ , correlation coefficients  $r$  and statistical  $F$ -ratio values are given. The correlation coefficients in all instances are extremely high ( $> 0.992$ ). However, close examination of the data reveals the difference between ODS phases and phenyl-bonded phases. The regression coefficients  $A$  and  $B$  in the eqn. 1 were plotted as shown in Fig. 7. Two main clusters are found: one for ODS phases and the other for

Fig. 7. Plot of parameter  $A$  vs. parameter  $B$ .

phenyl-bonded phases. C1 and VC18 are located far from these two groups. These two unique points can be explained as follows: VC18 has been reported to be a unique stationary phase for PAH separations<sup>7-10</sup> and C1 is a totally different stationary phase to the various alkyl-chain-bonded phases with regard to its surface coverage and properties. The large difference between the phenyl-bonded phases and the ODS phases should come from the retention mechanisms, where the hydrophobic interactions and  $\pi$ - $\pi$  interactions are dominant for the former but only hydrophobic interactions are the main contributor to retention for the latter.

It is clear that, even though TP and BP have unique structures on the silica surface compared with the P and DP phases, the molecular size recognition capability of the former is similar to that of the latter but slightly different to that for the ODS phases.

#### Recognition of molecular planarity

Tanaka and co-workers<sup>23-25</sup> investigated the differences in the chromatographic properties of various ODS phases with regard to PAH planarity recognition capability, and found that ODS phases can be categorized into two main groups, one with a strong and the other with a low planarity recognition capability. They used the separation factor between triphenylene and *o*-terphenyl ( $k'_{\text{triphenylene}}/k'_{\text{o-terphenyl}}$ ) as the indicator, where the former is a planar solute and the latter is non-planar. The ratio of the capacity factors of these two PAHs suggests that the values for polyfunctional ODS phases are larger than 2.0 and those for monofunctional phases are less than 2.0. This measure can be useful for evaluating the PAH non-planarity recognition capability of the newly synthesized materials.

TABLE IV

CAPACITY FACTORS  $k'$  FOR TRIPHENYLENE (Tri) AND *o*-TERPHENYL (Ote) AND THE SEPARATION FACTORS ( $\alpha$ ) WITH THREE MOBILE PHASE COMPOSITIONS FOR TEN STATIONARY PHASES

Mobile phases: methanol-water (80:20, 70:30 and 60:40).

Stationary phase	$k'$						$\alpha = k'_{\text{Tri}}/k'_{\text{Ote}}$		
	Tri			Ote			80:20	70:30	60:40
	80:20	70:30	60:40	80:20	70:30	60:40			
P	1.23	3.50	11.00	1.08	3.92	13.67	1.14	0.89	0.80
BP	1.53	5.58	16.58	1.27	5.50	17.33	1.20	1.01	0.96
TP	0.92	3.36	14.82	1.08	4.55	22.91	0.85	0.74	0.65
DP	0.69	1.83	5.00	0.77	2.00	5.42	0.90	0.92	0.92
C1	<sup>a</sup>	1.00	4.80	<sup>a</sup>	1.29	7.07	<sup>a</sup>	0.78	0.68
DC18	7.50	30.18	115.4	4.67	20.00	69.25	1.61	1.51	1.67
VC18	3.08	10.75	38.50	1.15	4.50	15.42	2.68	2.39	2.50
LC18	3.33	11.33	41.67	2.50	9.83	39.00	1.33	1.15	1.07
FC18	3.46	11.64	- <sup>b</sup>	2.39	8.43	-	1.45	1.38	-
CC18	-	24.82	-	-	19.00	-	-	1.31	-

<sup>a</sup> Not retained

<sup>b</sup> -, Not examined.

The experimental data obtained with the phases listed in Table I are summarized in Table IV, where the capacity factors of triphenylene and *o*-terphenyl and the separation factors with three different compositions of methanol-water mobile phases are shown. It is remarkable that the elution order of the two solutes on the ODS phases is reversed with the TP phase.

As reported by Tanaka and co-workers<sup>23-25</sup>, polymeric VC18 gave separation factors larger than 2.0 and monomeric ODS phases gave the values between 1 and 1.7. The values in Table IV for the ODS phases are in good agreement with those reported by them<sup>23-25</sup>. For the phenyl-bonded phases, the separation factors are smaller than those for the ODS phases. P, BP and DP gave similar values and it appears that they do not have any recognition capability for the planarity difference between triphenylene and *o*-terphenyl. The TP phase, however, shows a unique property among the phenyl-bonded phases in its non-planarity recognition capability. The separation factors are smaller than 0.90, especially with the mobile phase methanol-water (60:40), where the value is 0.65. This means that *o*-terphenyl has an almost 50% larger retention than triphenylene.

The reason for this unique enhancement of the retention of *o*-terphenyl with the TP phase can be explained by interpretation of molecular-molecular interactions between the two solutes and the TP. In Fig. 8 a computer molecular graphics technique was applied to this problem. Fig. 8A shows that the methyl groups favour the planar solute by hydrophobic interaction and they maintain the distance between the solute and TP to reduce possibility of  $\pi$ - $\pi$  interactions, where triphenylene can interact with the phenyl ring of the TP phase. However, as shown in Fig. 8B, *o*-terphenyl

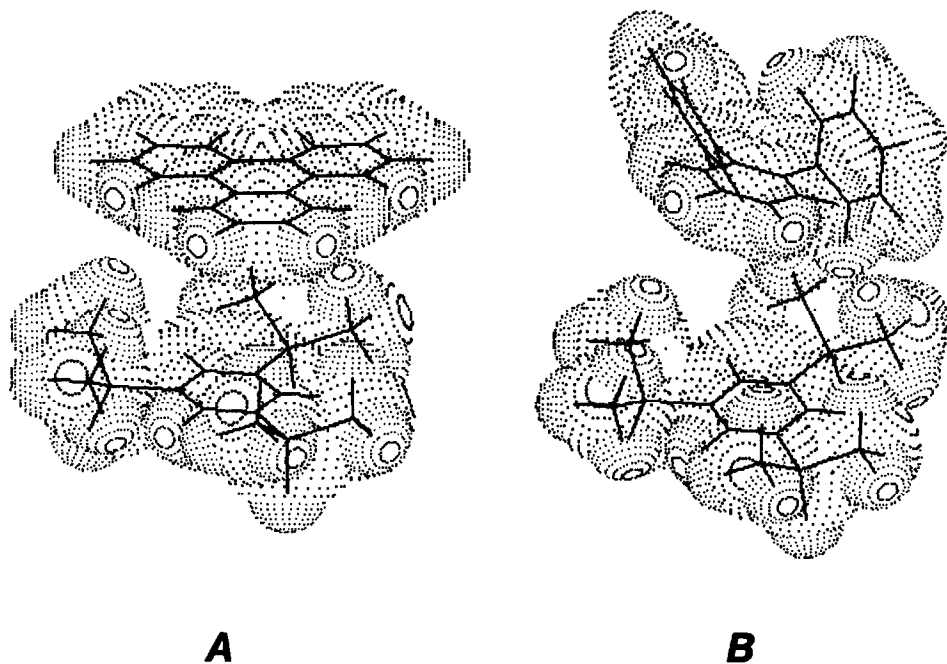


Fig. 8. Molecular-molecular interactions drawn by computer graphics. (A) Interaction between triphenylene and the TP phase; (B) interaction between *o*-terphenyl and the TP phase.

has a suitable steric structure which can interact well with the phenyl ring of the TP phase. *o*-Terphenyl has a high possibility of retention with the TP phase by two mechanisms, hydrophobic interaction of the methyl groups with two phenyl rings of the solute and  $\pi$ - $\pi$  interaction of the phenyl ring of the phase with the central phenyl ring. This means that, in addition to the hydrophobic interaction between the methyl groups and the solute, more pronounced  $\pi$ - $\pi$  interactions induce a larger retention of *o*-terphenyl with the TP phase than those with other phases.

This theory can also explain the small difference in the separation factors observed with C1 and with TP, where the factors with TP are smaller than those with C1. The larger absolute retention for the solutes with TP than those with C1 should also be noted.

Interpretation of the experimentally obtained data by using the concept of molecular-molecular interaction clearly explains the retention mechanism that occurs in the separation system and this kind of theoretical approach can open up the possibility of designing new stationary phases suitable for particular separation problems such as isomer separations or chiral separations.

The difference between BP and TP is also found in the experimental data. BP is more similar to the DP than the P phase with respect to the separation factor between triphenylene and *o*-terphenyl. However, other information in Table V indicates a very complicated similarity among these stationary phases. The separation factors between triphenylmethane and *o*-terphenyl are almost identical for seven phases but small differences are seen between P and DP and between BP and TP. The separation factors between *p*-terphenyl and *o*-terphenyl show some differences among the phases. VC-18 prefers to retain rod-like molecules and DC18 also has a similar but smaller preference. DP, P and C1 also have similar preference and TP and BP have intermediate preference between the former and the latter phases. Therefore, the molecular recognition properties of the stationary phases are related to each other in a complex manner.

In summary, the TP phase has a unique property of recognizing non-planar solutes in addition to a size recognition capability. Some properties are similar to those of ODS, but some are similar to those of normal phenyl- or diphenyl-bonded

TABLE V

RETENTION RATIOS AMONG TRIPHENYLMETHANE, *o*-TERPHENYL AND *p*-TERPHENYL WITH VARIOUS STATIONARY PHASES

Mobile phase: methanol-water (60:40).

Stationary phase	Retention ratio	
	Triphenylmethane/ <i>o</i> -terphenyl	<i>p</i> -Terphenyl/ <i>o</i> -terphenyl
P	1.44	1.25
BP	1.22	1.55
TP	1.22	1.53
C1	1.19	1.32
DP	1.37	1.29
DC18	1.20	2.20
VC18	1.21	4.38

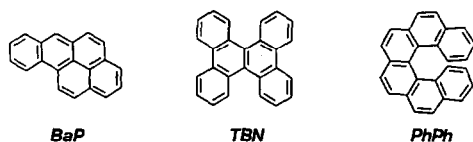


Fig. 9. Three PAHs used in the stationary phase evaluation.

phases with a characteristic non-planarity recognition capability. Differences between C1 and TP are also found.

Another useful factor for indicating the planarity recognition capability of stationary phases is the capacity factor ratio between BaP and TBN, suggested by Sander and Wise<sup>6,10,26</sup>. They proposed a new solute group for the evaluation of the capability of planarity recognition in reversed-phase LC, which consists of three PAHs as shown in Fig. 9. BaP is a planar molecule, TBN is bulky and rather non-planar and PhPh is more non-planar than TBN. These three PAHs can be used to categorize various ODS phases with respect to their capability to recognize molecular planarity.

In order to evaluate the capability of the new phases, measurements have been performed by using these three PAHs as test samples with methanol-water (90:10) as the mobile phase. The results are shown in Table VI. As Sander and Wise suggested that the separation factor between TBN and BaP should be lower than 0.7 for polymeric ODS phases and larger than 1.0 for monomeric phases, the experimental data in Table VI seem to be in reasonable agreement for VC18 and DC18, because the former is a polymeric and the latter a monomeric ODS phase. As the values for the TP and C1 phases are similar to that for DC18, it seems that there is no difference in properties between C1 and TP. They have similar properties with respect to molecular size discrimination to the monomeric ODS phases. However, one can calculate other separation factors between PhPh and BaP and between PhPh and TBN in order to obtain more information about these differences. The separation factors between PhPh and BaP indicate the degree of capability for molecular size and planarity recognition. There are some differences between P and TP, because the values are different from each other. ODS phases gave a more pronounced planarity recognition

TABLE VI

RETENTION DATA FOR BaP, TBN AND PhPh WITH VARIOUS STATIONARY PHASES

Mobile phase: methanol-water (90:10).

Stationary phase	$k'$			$\alpha$		
	BaP	TBN	PhPh	TBN/BaP	PhPh/BaP	PhPh/TBN
P	0.23	0.48	0.28	2.09	1.22	0.58
TP	0.35	0.58	0.47	1.66	1.34	0.81
C1	0.13	0.24	0.18	1.85	1.38	0.75
DC18	6.06	9.86	3.60	1.63	0.59	0.37
VC18	6.79	3.64	1.43	0.54	0.21	0.39

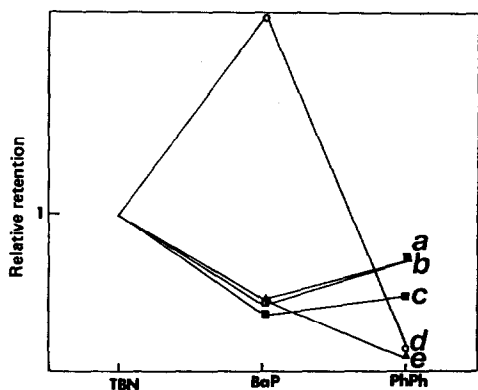


Fig. 10. Relative retentions of three PAHs with various phases. (a) TP; (b) C1; (c) P; (d) VC18; (e) DC18.

for BaP. With TP, P and C1, the retention of PhPh is larger than that of BaP. This phenomenon was also observed in the retention study on triphenylene and *o*-terphenyl. The C1 phase seems to behave similarly to TP in this instance. Therefore, hydrophobic interactions between PhPh and the methyl groups of C1 and TP may be the main contributors to the retention. The ratio for PhPh and TBN suggests some small difference between C1 and TP. As *o*-terphenyl is retained longer with TP than with C1, the same retention mechanism caused by  $\pi$ - $\pi$  interaction should be added to this problem for the TP system. As PhPh is more non-planar than TBN, it can be concluded that TP has a much higher non-planarity recognition capability than has C1.

Fig. 10, where the relative retentions of PhPh and BaP to TBN are plotted, illustrates the above discussion more clearly. The similarity between TP and C1 seems to be very high. However, it is possible to conclude that the TP phase is much superior to the C1 phase in chromatographic performance, because the absolute retentions with TP are higher than those with C1 and Kirkland *et al.*<sup>16</sup> reported that multidentate phases are more stable towards long-term usage for separations.

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