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ELUTION BEHAVIOUR OF PEROPYRENE-TYPE POLYCYCLIC AROMATIC HYDROCARBONS IN VARIOUS CHEMICALLY BONDED STATIONARY PHASES IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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SUMMARY

The elution behaviour of polycyclic aromatic hydrocarbons (PAHs, 13 of the 16 U.S. Environmental Protection Agency priority pollutants and peropyrene types) was studied on several chemically bonded stationary phases (octadecylsilicas, di- and triphenylsilicas, naphthylethylsilica and pyrenylethylsilica) under reversed-phase conditions. The results showed that the elution order of peropyrene-type PAHs is highly dependent on the degree of planarity of the solute and on the orderlines of the bonded phases, whereas no definite differences were found in the retention behaviour of the 13 small PAHs on various stationary phases. The characteristics of all the stationary phases could be classified by statistical cluster analysis.

INTRODUCTION

In high-performance liquid chromatography (HPLC), especially reversed-phase (RP) HPLC, chemically bonded stationary phases are widely used as column packing materials. Although such bonded phases have been prepared and applied to a great variety of separation problems with a high degree of success, it is still of interest to investigate the retention mechanism of RP-HPLC in order to expand further the applicability of the technique.

RP-HPLC has become one of the preferred methods for the separation and analysis of polycyclic aromatic hydrocarbons (PAHs), which occur in many types of carbonaceous material and have important biological effects. Most PAHs are not volatile and are therefore not easily amenable to analysis by gas chromatography. The large number of structural isomers also limits the applicability of other potential analytical techniques, such as mass spectrometry.

TABLE I

COLUMNS AND PACKING MATERIALS USED

No.	*Bonded stationary phase*	*Commercial name*	*Particle diameter (μm)*	*Column size (mm long × mm I.D.)*
1	C_{18}	ODS-224	5	220 × 4.6
2	C_{18}	Vydac 201TPB5	5	500 × 0.35
3	C_{18}	OD-224	5	220 × 4.6
4	C_{18}	FineSIL C-18-10	10	500 × 0.35
5	C_{18}	Finepak SIL C-18S	5	250 × 4.6
6	C_{18}	Develosil ODS-5	5	500 × 0.35
7	C_{18}	Chemcosorb H-ODS-5	5	500 × 0.35
8	C_{18}	(Polymer-based)	7	500 × 0.35
9	Diphenyl	Laboratory-made	5	500 × 0.35
10	Triphenyl		5	500 × 0.35
11	Naphthylethyl		5	500 × 0.35
12	Pyrenylethyl		5	500 × 0.35
13	C_{18} (polymeric)		5	500 × 0.35
14	C_{18} (monomeric)		5	500 × 0.35
15	C_{18} (monomeric) + C_1 end-capped		5	500 × 0.35
16	C_{18} (monomeric) + C_3 end-capped		5	500 × 0.35

A number of papers have recently been published on the elution behaviour of PAHs with various bonded phases. The influence of their physico-chemical properties on their retention has been discussed[1-10]. Previous papers have described the correlation between the logarithm of the capacity factor (log k') of PAHs and several descriptors[11,12], the molecular connectivity index (x)[13], Van der Waals volume (V_w)[14], logarithm of the partition coefficient (log P, Hansch parameter)[15,16] and a correlation factor (F)[17]. Wise *et al.*[18] reported a relationship between the shape of several PAHs defined as the length-to-breadth ratio (L/B) and their retention in RP-HPLC. From the results of these investigations, it has been proposed that the retention of small PAHs (two to five rings) generally increases with increasing F and L/B values in RP-HPLC on octadecylsilica (C_{18}) bonded phases[18,19]. However, it must be pointed out that large PAHs, such as the peropyrene type, show an anomalous elution behaviour on some stationary phases in non-aqueous RP-HPLC. Fetzer and Biggs[20,21] suggested that these anomalies were based on solute–solvent interactions which were a function of the intramolecular steric strain of the PAHs.

In this extension of previous work, we have investigated the elution behaviour of several PAHs on various bonded phases in order to understand more precisely the retention mechanism of the separation of PAHs in RP-HPLC.

EXPERIMENTAL

Two different HPLC systems were utilized in this investigation. For commercially available, conventional HPLC columns, a model CCPM pump, coupled with a UV 8000 detector (Toyo Soda, Tokyo, Japan) was used. These columns contained ODS-224 and OD-224 (Brownlee Labs., Santa Clara, CA, U.S.A.) and FineSIL C-18S (Jasco, Tokyo, Japan). For laboratory-made columns (fused-silica capillary columns, 0.35 mm I.D.), a micro-HPLC system, composed of an MF-2 microfeeder (Azuma Electric, Tokyo, Japan) and Jasco Uvidec-100 III detector, was used. The packing materials for these columns were as follows: polymeric C_{18} bonded phase, monomeric C_{18} bonded phase, monomeric C_{18} bonded phase with C_1 end-capping, monomeric C_{18} bonded phase with C_3 end-capping, diphenyl-bonded phase, triphenyl-bonded phase, naphthylethyl-bonded phase and pyrenylethyl-bonded phase. The chemical bonding procedures for these materials have been described elsewhere[22,23]. Four commercial packing materials, Vydac 201 TPB-5 (Separations Group, Hesperia, CA, U.S.A.), FineSIL C-18-10 (Jasco), Develosil ODS-5 (Nomura Chemicals, Seto, Japan) and Chemcosorb H-ODS-5 (Chemco, Osaka, Japan) and polymer-based C_{18} bonded phase (kindley donated by Y. Kato of Toyo Soda, Tokuyama, Japan), were also evaluated in microcapillary columns. The microcolumns were packed by the conventional slurry technique[24]. All the information about the columns utilized in this work is summarized in Table I.

For the study of small PAHs, commercially available compounds were used. For the study of peropyrene-type PAHs, the substances were synthesized by the procedures described in previous papers[20,21]. The purity of these substances was checked by monitoring their UV spectra with a Jasco Multi-320 photodiode-array UV detector. The data analysis was performed with a 16-bit 9801 VM2 microcomputer (Nippon Electric, Tokyo, Japan).

The mobile phases were methanol–water mixtures for the separation of small

TABLE II

CAPACITY FACTORS OF 13 SMALL PAHs OBTAINED WITH VARIOUS STATIONARY PHASES

Compound	*F*	*L/B*	*Capacity factor**								
			1	*2*	*3*	*4*	*6*	*9*	*10*	*11*	*12*
Naphthalene	5.0	1.24	2.11	0.22	1.57	2.98	1.06	3.00	0.75	2.15	1.31
Acenaphthylene	5.5	1.08	2.70	0.28	1.99	3.41	1.28	3.58	0.96	2.66	1.77
Acenaphthene	6.5	1.06	4.48	0.45	3.44	4.53	1.86	4.33	1.24	3.75	2.63
Fluorene	6.5	1.57	4.75	0.45	3.44	4.53	2.05	4.33	1.24	3.89	2.91
Phenanthrene	7.0	1.46	5.49	0.58	3.79	4.85	2.22	4.79	1.37	4.22	3.41
Anthracene	7.0	1.57	6.37	0.74	4.27	5.13	2.22	5.02	1.57	4.51	3.64
Fluoranthene	8.0	1.22	8.83	0.94	5.61	6.24	2.80	5.87	1.73	5.60	5.31
Pyrene	8.0	1.27	10.27	1.11	6.44	6.79	3.05	6.24	1.82	5.76	5.55
Benz[*a*]anthracene	9.0	1.58	17.93	1.54	10.27	8.95	4.17	8.36	2.59	8.75	9.44
Chrysene	9.0	1.72	18.35	2.43	10.00	8.95	4.17	8.36	2.59	8.75	10.24
Benzo[*b*]fluoranthene	10.0	1.40	31.37	3.80	16.01	12.71	5.91	10.33	3.15	12.49	18.80
Benzo[*k*]fluoranthene	10.0	1.48	34.76	4.91	17.07	12.71	5.91	10.93	3.92	12.09	16.33
Benzo[*a*]pyrene	10.0	1.50	39.00	5.54	18.32	13.74	6.33	11.24	3.92	13.45	21.24

* The numbers correspond to bonded stationary phases in Table I.

TABLE III

NORMALIZED CAPACITY FACTORS OF 13 SMALL PAHs WITH VARIOUS STATIONARY PHASES

Compound	*F*	*L/B*	*Normalized capacity factor**								
			1	*2*	*3*	*4*	*6*	*9*	*10*	*11*	*12*
Naphthalene**	5.0	1.24									
Acenaphthylene	5.5	1.08	0.02	0.01	0.03	0.04	0.04	0.07	0.07	0.05	0.02
Acenaphthene	6.5	1.06	0.06	0.04	0.11	0.14	0.15	0.16	0.15	0.14	0.07
Fluorene	6.5	1.57	0.07	0.04	0.11	0.14	0.19	0.16	0.15	0.15	0.08
Phenanthrene	7.0	1.46	0.09	0.07	0.13	0.17	0.22	0.22	0.20	0.18	0.11
Anthracene	7.0	1.57	0.12	0.10	0.16	0.20	0.22	0.25	0.26	0.21	0.12
Fluoranthene	8.0	1.22	0.18	0.14	0.24	0.30	0.33	0.35	0.31	0.31	0.20
Pyrene	8.0	1.27	0.22	0.17	0.29	0.35	0.38	0.39	0.34	0.32	0.21
Benz[a]anthracene	9.0	1.58	0.43	0.25	0.52	0.55	0.59	0.65	0.58	0.58	0.41
Chrysene	9.0	1.72	0.44	0.42	0.50	0.55	0.59	0.65	0.58	0.58	0.45
Benzo[b]fluoranthene	10.0	1.40	0.79	0.67	0.86	0.90	0.92	0.89	0.76	0.92	0.88
Benzo[k]fluoranthene	10.0	1.48	0.89	0.88	0.93	0.90	0.92	0.96	1.00	0.88	0.75
Benzo[a]pyrene	10.0	1.50	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

* The numbers correspond to bonded stationary phases in Table I.

** The value of the normalized capacity factor for naphthalene should be zero, as this solute was eluted first.

PAHs and methanol–dichloromethane mixtures for the separation of peropyrene-type PAHs.

RESULTS AND DISCUSSION

Retention behaviour of small PAHs

Several workers have studied the influence of the molecular structure (size and shape) of PAHs on their RP chromatographic retentions[4,10–12,18,19]. In this work, 13 PAHs (13 of 16 U.S. Environmental Protection Agency priority pollutants) were used in an investigation of the retention characteristics of small PAHs. A typical chromatogram of the separation of these PAHs is shown in Fig. 1. Table II lists the capacity factors (k') obtained with various separation systems. It seemed appropriate to investigate the correlation between the physico-chemical properties of the solutes and their capacity factors. The PAHs in the test mixture can be classified according to their F and L/B values. The data in Table II indicate that the retention of the 13 PAHs generally increases with increasing F and L/B values. Therefore, multiregression analyses between log k' and these parameters were carried out for each data set. The correlation coefficients obtained were very high (>0.99) in all instances. As each of these stationary phases differed in particle properties (particle diameter, pore size and surface coverage), a normalized capacity factor, k'_{ni}, was used in order to continue the evaluations of retention behaviour. This is defined as

$$k'_i = (k'_i - k'_n)/(k'_{n+1} - k'_n) \qquad (1)$$

where i represents the solute i and n and $n + 1$ represent the solutes that give the lowest and highest capacity factors, respectively, on the corresponding phase. The normalized capacity factors calculated for the 13 PAHs are given in Table III.

We then used a correlation matrix to facilitate a numerical comparison of each data set in Table III, because examination of the correlations between the retention

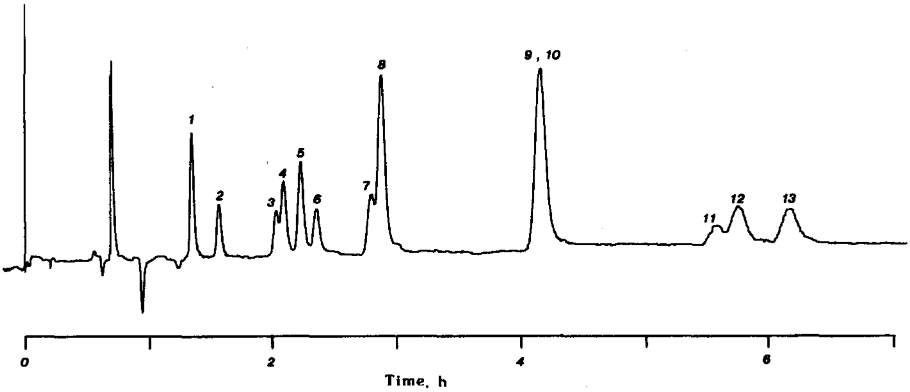


Fig. 1. Typical chromatogram of 13 small PAHs. Column, 500 mm × 0.35 mm I.D. packed with naphthylethyl-bonded phase, Mobile phase, methanol–water (8:2); flow-rate, 1 µl/min; detection, UV (254 nm). Peak assignments: 1 = naphthalene; 2 = acenaphthylene; 3 = acenaphthene; 4 = fluorene; 5 = phenanthrene; 6 = anthracene; 7 = fluoranthene; 8 = pyrene; 9 = benz[*a*]anthracene; 10 = chrysene; 11 = benzo[*k*]fluoranthene; 12 = benzo[*b*]fluoranthene; 13 = benzo[*a*]pyrene.

data measured on the various stationary phases show that there might be a similarity in the retention mechanism on each stationary phase. The results are shown in Table IV. Almost all the correlation coefficients in this matrix indicate a great similarity in the retention behaviour of small PAHs among the nine different stationary phases. To determine more clearly whether there are any differences among the various stationary phases, a hierarchical cluster analysis was performed. This indicated no apparent differences in the retention characteristics of the 13 PAHs with the stationary phases investigated. This result is consistent with a retention mechanism in which the size and the shape of a solute are the dominant factors controlling retention on any RP column material.

Retention behaviour of peropyrene-type PAHs

Fetzer and Biggs[20,21] reported that large PAHs such as the peropyrene type showed a characteristic elution behaviour on some stationary phases in non-aqueous RP-HPLC. As an extension of this work, we investigated the elution behaviour of peropyrene-type PAHs on various reversed phases.

The structure of the large PAHs could generally be classified into two groups. Four of them coronene, dibenzo[*cd,lm*]perylene, benzo[*ghi*]naphtho[8,1,2-*cde*]perylene and naphtho[8,1,2-*abc*]coronene, always have a planar conformation, whereas the other PAHs are non-planar under suitable conditions.

The capacity factor of the solutes were measured with methanol–dichloromethane (8:2) as the mobile phase. A typical chromatogram of the separation of the large PAHs is shown in Fig. 2. The normalized capacity factors for these test solutes on the chemically bonded phases were then calculated from eqn. 1 and are summarized in Table V. In Figs. 3 and 4, the capacity factors obtained on various stationary phases are plotted against the corresponding solutes. Some prominent changes in the elution sequence of large PAHs are seen for this set of stationary phases. The two most conspicuous solutes are benzo[*ghi*]naphtho[8,1,2-*cde*]perylene and tetrabenzo[*a,cd,j,lm*]perylene; the former is planar and the latter is non-planar. Close examination of the experimental data shows that tetrabenzo[*a,cd,j,lm*]perylene was weakly retained, while benzo[*ghi*]naphtho[8,1,2-*cde*]perylene was eluted very late from the

TABLE IV

CORRELATION MATRIX OF THE RETENTION DATA FOR 13 SMALL PAHs

The numbers 1–12 correspond to bonded stationary phases in Table I.

	1	*2*	*3*	*4*	*6*	*9*	*10*	*11*	*12*
1	1.000								
2	0.989	1.000							
3	0.997	0.977	1.000						
4	0.992	0.968	0.998	1.000					
6	0.987	0.961	0.995	0.999	1.000				
9	0.983	0.955	0.992	0.995	0.996	1.000			
10	0.988	0.974	0.990	0.986	0.985	0.991	1.000		
11	0.989	0.961	0.995	0.999	0.998	0.995	0.983	1.000	
12	0.989	0.971	0.988	0.989	0.985	0.974	0.964	0.990	1.000

TABLE V

NORMALIZED CAPACITY FACTORS OF PEROPYRENE-TYPE PAHs

Compound	*F*	*L/B*	*Normalized capacity factor**										
			1	*2*	*3*	*4*	*5*	*7*	*8*	*9*	*10*	*11*	*12*
Coronene**	12	1.000											
Dibenzo[*cd,lm*]perylene	13	1.726	0.18	0.24	0.13	0.17	0.10	0.11	0.15	0.26	0.17	0.13	0.11
Benzo[*ghi*]naphtho[8,1,2-*cde*]perylene	14	1.207	0.30	0.44	0.38	0.35	0.44	0.40	0.48	0.48	0.17	0.34	0.40
Naphtho[8,1,3-*abc*]coronene	15	1.207	1.00	1.00	1.00	1.00	1.00	1.00	0.99	0.56	0.50	0.62	1.00
Tribenzo[*a,cd,lm*]perylene	15	1.347	0.10	0.05	0.26	0.19	0.41	0.33	0.38	0.56	0.56	0.42	0.18
Tetrabenzo[*a,cd,j,lm*]perylene	17	1.207	0.07	0.01	0.27	0.25	0.83	0.60	0.60	1.00	1.00	0.83	0.33
Dibenzo[*a,cd*]naphtho[,8-*jk*]-perylene	17	1.312	0.67	0.71	0.80	0.69	0.96	0.93	1.00	0.89	0.94	1.00	0.64
Benzo[*rst*]phenanthro[1,10,9-*cde*]-pentaphene	17	1.546	0.30	0.44	0.80	0.69	0.99	0.89	1.00	0.85	0.97	0.88	0.78

* The numbers correspond to bonded stationary phases in Table I.

** The value of the normalized capacity factor for coronene should be zero, as this solute was eluted first.

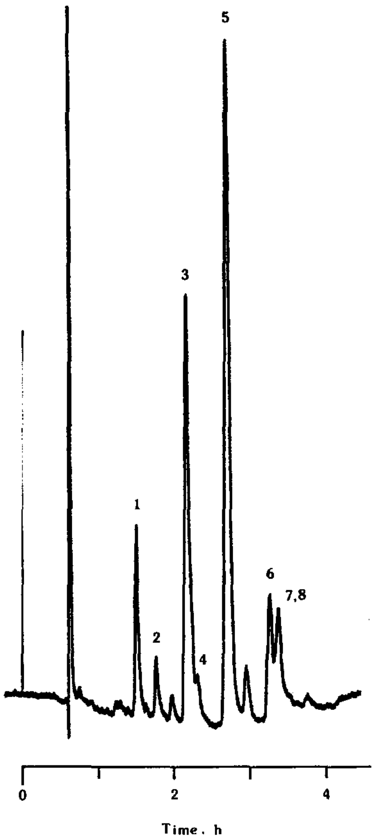


Fig. 2. Typical chromatogram of peropyrene-type PAHs. Column, 500 mm × 0.35 mm I.D., packed with polymer C_{18} bonded phase. Mobile phase, methanol–dichloromethane (8/2); flow-rate, 1 μl/min; detection, UV (340 nm). Peak assignments: 1 = coronene; 2 = dibenzo[*cd,lm*]perylene; 3 = tribenzo[*a,cd,lm*]perylene; 4 = benzo[*ghi*]naphtho[8,1,2-*cde*]perylene; 5 = tetrabenzo[*a,cd,lm*]perylene; 6 = naphtho[8,1,2-*abc*]coronene; 7 = dibenzo[*a,cd*]naphtho[1,8-*jk*]perylene; 8 = benzo[*rst*]phenanthro[1,10,9-*cde*]pentaphene.

ODS-224 and Vydac 201 TPB-5 columns. It is also interesting that the elution order of PAHs on several stationary phases, such as diphenyl, triphenyl and naphthylethyl, generally follows the order of increasing *F* and *L*/*B* values. Particularly on diphenyl and triphenyl phases the retention behaviour is almost identical. This trend is very similar to that seen with the small PAHs.

An explanation of these observations could be that the diphenyl and triphenyl phases present a uniform surface to PAHs, and therefore planar and non-planar solutes behave similarly. On an ordered phase, there are spaces which only planar PAHs can enter easily[25]. The non-planar solutes are not flat enough to enter the spaces. As ODS-224 and Vydac 201 TPB-5 are polymeric C_{18} phases, they are more retentive towards planar PAHs. Other phases also behaved in this manner. OD-224, FineSIL C-18S, Chemcosorb ODS-H-5, polymer C_{18} and pyrenylethyl phases showed similar behaviour but were different from each other. They all tended to

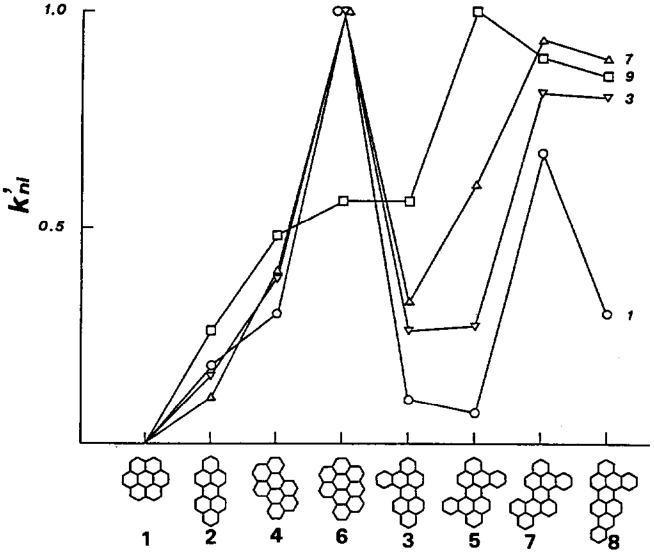


Fig. 3. Structure of peropyrene-type PAHs *versus* respective normalized capacity factors on C_{18} bonded phases. The numbers against the lines correspond to the stationary phases in Table I. The numbers of the structures correspond to those in the caption of Fig. 2.

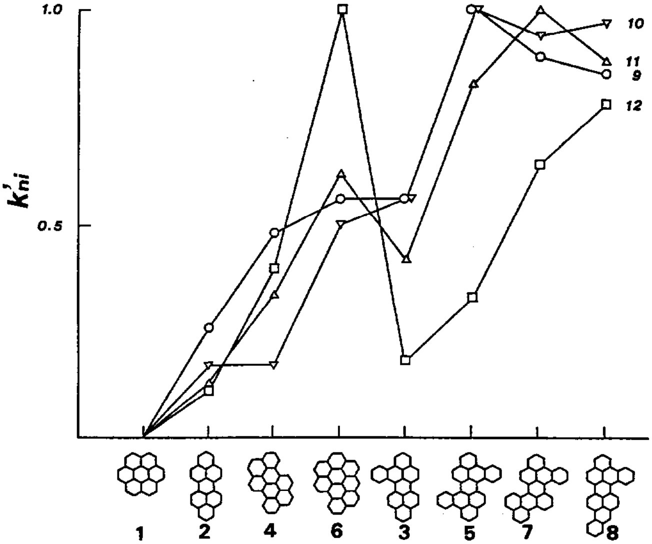


Fig. 4. Structure of peropyrene-type PAHs *versus* respective normalized capacity factors on phenyl-bonded phases. The numbers against the lines correspond to the stationary phases in Table I. The numbers of the structures correspond to those in the caption of Fig. 2.

retain non-planar PAHs strongly. For example, from stationary phases such as OD-224, FineSIL C-18-10 and pyrenylethyl-bonded phases, tetrabenzo[*a*,*cd*,*j*,*lm*]perylene was eluted as the fourth peak. From Finepak SIL C-18S, Chemcosorb ODS-H-5 and polymer C_{18}, this solute was eluted behind benzo-[*ghi*]naphtho[8,1,2-*cde*]perylene. The naphthylethyl phase seems to be intermediate between diphenyl/triphenyl and polymeric C_{18} phases in its behaviour, probably because the bonded moieties have less rotational freedom than phenyl groups. The naphthylethyl groups in that phase are large enough to be sterically hindered and must remain in a fairly rigid (or ordered) arrangement. Owing to the larger size of a pyrenylethyl moiety, this phase is more orderly than the naphthylethyl phase and hence the behaviour is similar to that on monomeric C_{18} phases.

To clarify the differences, the correlation matrix for each data set was calculated. The results are shown in Table VI. It can be seen that all the bonded phases can be classified into four groups, as follows: (A) ODS-224 and Vydac 201 TPB-5; (B) OD-224, FineSIL C-18-10 and pyrenylethyl; (C) Finepak SIL C-18S, Chemcosorb ODS-H-5 and polymer C_{18}; and (D) diphenyl, triphenyl and naphthylethyl phases. These results suggest that the correlation matrix detected the different characteristics of all the bonded phases investigated. Cluster analysis was then performed, and the results are illustrated in Fig. 5. In contrast to the small PAHs, differences in retention characteristics among the various stationary phases are clearly present. Peropyrene-type PAHs are large enough to generate such differences.

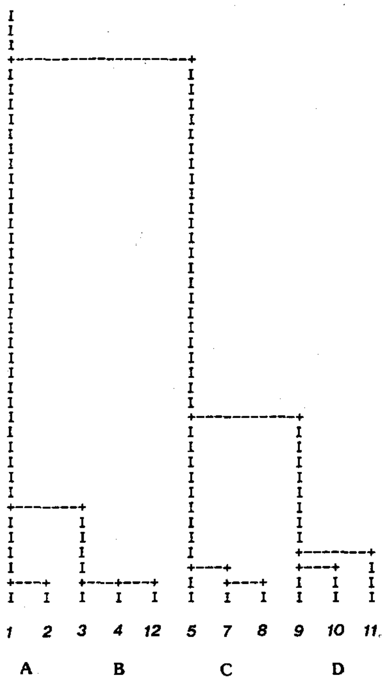
To confirm the classification, four more stationary phases were synthesized, monomeric C_{18} without end-capping, monomeric C_{18} with C_1 end-capping, monomeric C_{18} with C_3 end-capping and polymeric C_{18}. Each was evaluated by experiments similar to those described above. The normalized capacity factors obtained are summarized in Table VII. Again, the retention data for all the stationary phases, including the four synthesized phases, were evaluated by performing cluster analysis, and the results are illustrated in Fig. 6. According to their properties, the four phases can be categorized into the following groups (as in Fig. 5): polymeric C_{18} into group

TABLE VI

CORRELATION MATRIX OF THE RETENTION DATA FOR PEROPYRENE-TYPE PAHs

The numbers 1–12 correspond to bonded stationary phases in Table I.

	1	*2*	*3*	*4*	*5*	*7*	*8*	*9*	*10*	*11*	*12*
1	1.000										
2	0.973	1.000									
3	0.861	0.873	1.000								
4	0.909	0.915	0.987	1.000							
5	0.574	0.539	0.841	0.798	1.000						
7	0.729	0.708	0.939	0.907	0.973	1.000					
8	0.694	0.697	0.942	0.896	0.962	0.992	1.000				
9	0.012	−0.038	0.358	0.267	0.786	0.646	0.648	1.000			
10	0.021	−0.041	0.391	0.297	0.772	0.650	0.655	0.954	1.000		
11	0.306	0.272	0.630	0.544	0.910	0.840	0.848	0.938	0.934	1.000	
12	0.833	0.849	0.977	0.983	0.852	0.930	0.923	0.355	0.362	0.594	1.000



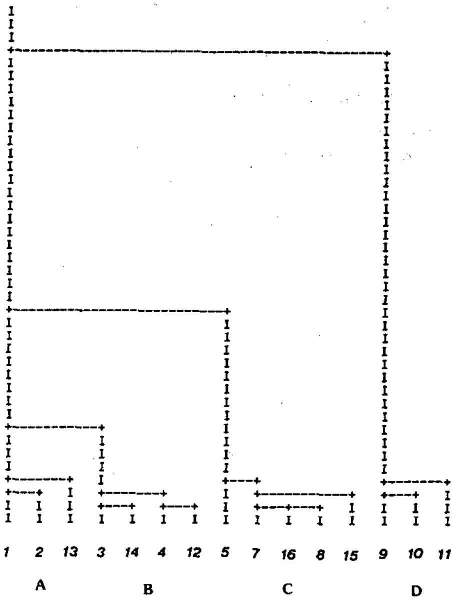


Fig. 5. Dendrogram of cluster analysis for the retention data of peropyrene-type PAHs with various stationary phases. The numbers correspond to the stationary phases in Table I.

Fig. 6. Dendrogram of cluster analysis for the retention data of peropyrene-type PAHs with 15 stationary phases. The numbers correspond to the stationary phases in Table I.

TABLE VII

NORMALIZED CAPACITY FACTORS OF THE RETENTION DATA FOR PEROPYRENE-TYPE PAHs WITH FOUR LABORATORY-MADE STATIONARY PHASES

Compound	*F*	*L/B*	*Normalized capacity factor**			
			13	*14*	*15*	*16*
Coronene**	12	1.000				
Dibenzo[*cd,lm*]perylene	13	1.726	0.09	0.11	0.15	0.12
Benzo[*ghi*]naphtho[8,1,2-*cde*]perylene	14	1.207	0.29	0.48	0.36	0.45
Naphtho[8,1,2-*abc*]coronene	15	1.207	1.00	1.00	1.00	1.00
Tribenzo[*a,cd,lm*]perylene	15	1.347	0.16	0.28	0.33	0.36
Tetrabenzo[*a,cd,j,lm*]perylene	17	1.207	0.16	0.41	0.48	0.66
Dibenzo[*a,cd*]naphtho[1,8-*jk*]perylene	17	1.312	0.55	0.88	0.86	0.93
Benzo[*rst*]phenanthro[1,10,9-*cde*]pentaphene	17	1.546	0.43	0.88	0.82	0.91

* The numbers correspond to bonded stationary phases in Table I.

** The values of the normalized capacity factor for coronene should be zero, as this solute was eluted first.

A, monomeric C_{18} into group B and monomeric C_{18} with C_1 and C_3 end-capping into group C. Hence it may be concluded that the clusters of A, B, C and D in Fig. 5 are categorized as polymeric C_{18}, monomeric C_{18} without end-capping, monomeric C_{18} with end-capping and phenyl group bonded phases, respectively.

CONCLUSION

The retention behaviour of PAHs with various chemically bonded reversed phases has been investigated. For small PAHs it appears that retention is controlled by the size and shape of the solute molecule, where increases of F and L/B values for small PAHs induce greater retention. No differences due to the different types of bonded phases are seen. For large PAHs the elution behaviour appears to be controlled by two major factors: (1) orderliness of the bonded phase and (2) degree of planarity of the solute. Statistical cluster analysis has shown this, and it is concluded that the elution behaviour of large PAHs can be used to categorize the characteristics of the bonded phase.

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