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# GAS CHROMATOGRAPHIC RETENTION BEHAVIOR OF POLYCYCLIC AROMATIC COMPOUNDS ON SMECTIC LIQUID-CRYSTALLINE POLY-SILOXANE STATIONARY PHASES

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## SUMMARY

Factors affecting gas chromatographic retention on smectic liquid-crystalline phenyl and biphenyl carboxylate ester polysiloxane stationary phases were studied for neutral polycyclic aromatic hydrocarbons (PAHs) and slightly polar sulfur heterocycles. Retention was greatly affected by the molecular geometry of the solutes in addition to other contributions such as solute vapor pressure and polarity. The major geometrical factor was the length-to-breadth ($L/B$) ratio of the solutes, while of less importance, but still significant, was the solute molecular shape. The effect of solute $L/B$ on selectivity was larger in the smectic region than in the nematic region. Furthermore, the selectivity of the smectic phase was generally better than that of the nematic phase. Compounds with at least four aromatic rings annelated in a straight line were retained much longer, and compounds with aromatic rings annelated in a curved or arc-like arrangement were retained much less, than predicted by the $L/B$ ratios for these compounds. Arc-like molecules with groups attached to the outer curved side were, however, retained longer than predicted. Lower chromatographic efficiencies were measured for the arc-like molecules as compared to the latter type of molecules. The latter appear to penetrate the laminar arrangement of the polymer liquid-crystalline side groups more easily, thus leading to better solute diffusion and improved mass transfer.

## INTRODUCTION

Liquid crystals are unique stationary phases in gas chromatography (GC) because of their temperature dependent ordered structures. The rod-like liquid-crystalline molecules retain their orientation with respect to each other with their long axes parallel. Solutes which are also rigid rod-like molecules interact with the ordered structure of the stationary phase[1]. While compounds usually elute in order of their increasing boiling points on conventional, non-polar stationary phases, retention is additionally affected by solute geometry when using liquid-crystalline stationary phases[1].

Polycyclic aromatic compounds (PACs) generally are rigid planar molecules

which have specific structural conformations. Since the first application of liquid-crystalline compounds as stationary phases in GC by Kelker in 1963[2], PACs have been the primary target analytes for these phases. High selectivities have been achieved using liquid-crystalline stationary phases for separation of PACs[3-8].

Liquid crystals can demonstrate nematic, cholesteric, or smectic properties within certain temperature ranges. The cholesteric structure is a twisted nematic form. The smectic phase is more ordered than the nematic phase, and nine different kinds of smectic phases are known. The various smectic phases are designated by the letters A to I according to the chronological order in which they were first observed[9]. It generally has been thought that nematic phases produce better chromatographic resolution than do smectic phases[10]. The smectic phases possessing the best chromatographic properties were the less ordered smectic phases A and C. The more ordered phases (*e.g.*, B and E) were structurally more compact and resisted penetration and dissolution of solutes[10,11].

Until recently, only monomeric rod-like molecules have been utilized as liquid-crystalline stationary phases[1]. Although several high-temperature liquid crystals have been used for packed columns[12,13], it was necessary to develop polymeric liquid-crystalline phases possessing high thermal stability and durability for capillary GC. A polysiloxane with a nematic temperature range of 70–300°C, prepared by Finkelmann and Laub[14] was a successful example[15]. This liquid-crystalline polysiloxane was recently modified to extend the upper temperature of the nematic region[16]. Properties of the monomeric mesogen molecules can be preserved in both linear and cross-linked polymers if flexibility is built into the polymer structure[17].

We have recently reported the synthesis of liquid-crystalline biphenyl carboxylate ester polysiloxanes, one of which demonstrated superior selectivity for isomeric PACs in the smectic range[18]. Since this polymer possessed a narrow smectic temperature range, a new liquid-crystalline polysiloxane stationary phase which could be used over a wide smectic temperature range was synthesized, and unsurpassed resolution of isomeric PACs was demonstrated[19]. For example, all isomers of the methylphenanthrenes, the methylchrysenes, and the 4-ring unsubstituted polycyclic aromatic hydrocarbons (PAHs) were resolved on capillary columns coated with this phase. The influence of hydrocarbon spacer length between the polysiloxane chain and the liquid crystal moiety, percent mesomorphic group substitution, and cross-linking of the stationary phase on liquid-crystalline transition temperatures and on chromatographic performance were also investigated[20].

The relationship between solute molecular geometry and retention on nematic phases has been studied in detail[21]. Radecki *et al.*[22] were able to predict the retention indices of PAHs on nematic phases. Recently, the effect of the molecular structure of the nematic phase on selectivity was reported[23,24]. In contrast, the factors affecting retention on smectic liquid-crystalline stationary phases have not been fully studied.

In this paper, the retention characteristics of phenyl- and biphenyl-containing carboxylate ester polysiloxanes with different liquid crystal phase transitions were studied. The effects of degree of phase order (*i.e.*, smectic *vs.* nematic) and solute molecular geometry on retention and retention order were evaluated.

EXPERIMENTAL

The liquid-crystalline polysiloxane stationary phases used in this study (Fig.
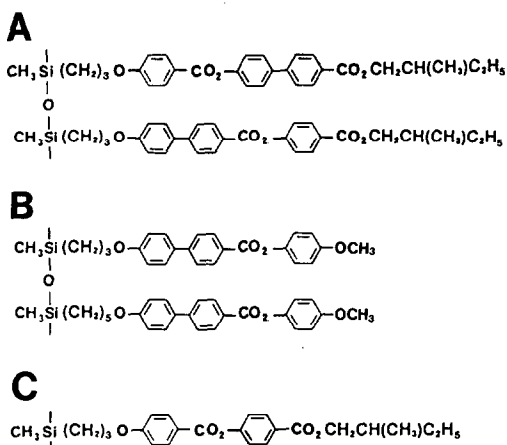
## A

$CH_3\overset{|}{\underset{|}{Si}}(CH_2)_3O-\langle\bigcirc\rangle-CO_2-\langle\bigcirc\rangle\langle\bigcirc\rangle-CO_2CH_2CH(CH_3)C_2H_5$

$\overset{O}{|}$

$CH_3\overset{|}{\underset{|}{Si}}(CH_2)_3O-\langle\bigcirc\rangle\langle\bigcirc\rangle-CO_2-\langle\bigcirc\rangle-CO_2CH_2CH(CH_3)C_2H_5$

## B

$CH_3\overset{|}{\underset{|}{Si}}(CH_2)_3O-\langle\bigcirc\rangle\langle\bigcirc\rangle-CO_2-\langle\bigcirc\rangle-OCH_3$

$\overset{O}{|}$

$CH_3\overset{|}{\underset{|}{Si}}(CH_2)_5O-\langle\bigcirc\rangle\langle\bigcirc\rangle-CO_2-\langle\bigcirc\rangle-OCH_3$

## C

$CH_3\overset{|}{\underset{|}{Si}}(CH_2)_3O-\langle\bigcirc\rangle-CO_2-\langle\bigcirc\rangle-CO_2CH_2CH(CH_3)C_2H_5$

Fig. 1. Structures of liquid-crystalline stationary phases used in this study.

1) were synthesized as previously described[18,19]. Table I lists the transition temperatures for these phases as determined by differential scanning calorimetry using a Perkin-Elmer DSC-2 system, and by visual observation using a Thomas-Kofler hot stage microscope with cross polarizers. Lengths (10–30 m) of fused-silica capillary tubing (0.2 or 0.3 mm I.D., Hewlett-Packard, Avondale, PA, U.S.A.) were statically coated (0.25-$\mu$m film thickness) with the liquid-crystalline stationary phases and a non-polar methylphenyl polysiloxane (SE-54, Applied Science Labs., State College, PA, U.S.A.). The SE-54 column was cross-linked using azo-*tert.*-butane[25]. PAH and polycyclic aromatic sulfur heterocycle (PASH) solutes used in this study were either obtained commercially or synthesized in our laboratories (refer to Table II and Fig. 2). All columns were conditioned at 280°C for 10 h under a slow nitrogen purge before use.

GC retention and efficiency measurements were made using a Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector, and operated in the splitless injection mode with temperature programming, or in the split injection (50:1) mode when under isothermal operation. The carrier gas used was hydrogen.

### RESULTS AND DISCUSSION

The strengths of the interactions between solutes and stationary phases are indicated by retention parameters such as the capacity ratio ($k'$). The $k'$ values of

TABLE I

PHASE TRANSITIONS OF LIQUID-CRYSTALLINE POLYSILOXANES USED IN THIS STUDY

| *Polymer* | *Phase transitions (°C)** |
|-----------|---------------------------|
| A | g 130 s 219 n 235 i |
| B | g 118 s 300      i |
| C |              n 30  i |

* g = glassy, s = smectic, n = nematic and i = isotropic.

TABLE II

LENGTH-TO-BREADTH ($L/B$) RATIOS AND RELATIVE RETENTION TIMES FOR ISOMERIC
GROUPS OF PAHs AND PASHs

| Compound | $L/B$ | Relative retention time[*] | |
|---|---|---|---|
| | | Liquid crystal polysiloxane[**] | SE-54 |
| 1-Methylphenanthrene | 1.45 | 2.029 | 0.962 |
| 2-Methylphenanthrene | 1.58 | 2.084 | 0.930 |
| 3-Methylphenanthrene | 1.37 | 1.820 | 0.924 |
| 4-Methylphenanthrene | 1.25 | 1.854 | 0.959 |
| 9-Methylphenanthrene | 1.25 | 1.891 | 0.959 |
| Chrysene | 1.72 | 3.693 | 1.471 |
| Benzo[c]phenanthrene | 1.22 | 2.988 | 1.403 |
| Triphenylene | 1.12 | 3.294 | 1.471 |
| Benz[a]anthracene | 1.58 | 3.534 | 1.431 |
| Naphthacene | 1.89 | 4.265 | 1.597 |
| 1-Methylchrysene | 1.71 | 4.040 | 1.606 |
| 2-Methylchrysene | 1.85 | 4.140 | 1.583 |
| 3-Methylchrysene | 1.63 | 3.878 | 1.577 |
| 4-Methylchrysene | 1.51 | 3.848 | 1.596 |
| 5-Methylchrysene | 1.48 | 3.778 | 1.596 |
| 6-Methylchrysene | 1.48 | 3.745 | 1.596 |
| Dibenzo[c,g]phenanthrene | 1.12 | 4.032 | 0.998 |
| Dibenz[a,c]anthracene | 1.24 | 14.531 | 1.933 |
| Benzo[g]chrysene | 1.32 | 9.826 | 1.644 |
| Dibenzo[b,g]phenanthrene | 1.33 | 9.052 | 1.548 |
| Benzo[c]chrysene | 1.47 | 10.930 | 1.686 |
| Dibenz[a,j]anthracene | 1.47 | 12.540 | 1.782 |
| Pentaphene | 1.73 | 15.700 | 1.956 |
| Benzo[a]naphthacene | 1.77 | 36.140 | 3.042 |
| Dibenz[a,h]anthracene | 1.79 | 15.700 | 1.933 |
| Benzo[b]chrysene | 1.84 | 18.360 | 2.027 |
| Picene | 1.99 | 20.090 | 2.066 |
| Pentacene | 2.18 | 48.850 | 3.489 |
| 1-Methyldibenzo[b,d]thiophene | 1.34 | 1.752 | 0.758 |
| 2-Methyldibenzo[b,d]thiophene | 1.54 | 1.754 | 0.744 |
| 3-Methyldibenzo[b,d]thiophene | 1.65 | 1.933 | 0.745 |
| 4-Methyldibenzo[b,d]thiophene | 1.44 | 1.754 | 0.732 |
| 6-Methylnaphtho[1,2-b]thiophene | 1.42 | 1.891 | 0.757 |
| 7-Methylnaphtho[1,2-b]thiophene | 1.55 | 1.943 | 0.767 |
| 8-Methylnaphtho[1,2-b]thiophene | 1.36 | 1.726 | 0.742 |
| 9-Methylnaphtho[1,2-b]thiophene | 1.23 | 1.891 | 0.743 |
| 6-Methylnaphtho[2,1-b]thiophene | 1.36 | 2.141 | 0.706 |
| 7-Methylnaphtho[2,1-b]thiophene | 1.48 | 2.064 | 0.726 |
| 8-Methylnaphtho[2,1-b]thiophene | 1.36 | 1.871 | 0.760 |
| 9-Methylnaphtho[2,1-b]thiophene | 1.20 | 1.987 | 0.779 |

[*] Retention times relative to $n$-$C_{20}$. These values are the average of two measurements. Both
measurements agreed to within $\pm$ 0.004. Temperature program: 240°C to 280°C at 2°C min$^{-1}$ for the 5-
ring PAHs; 100°C to 265°C at 4°C min$^{-1}$ for all of the other compounds.
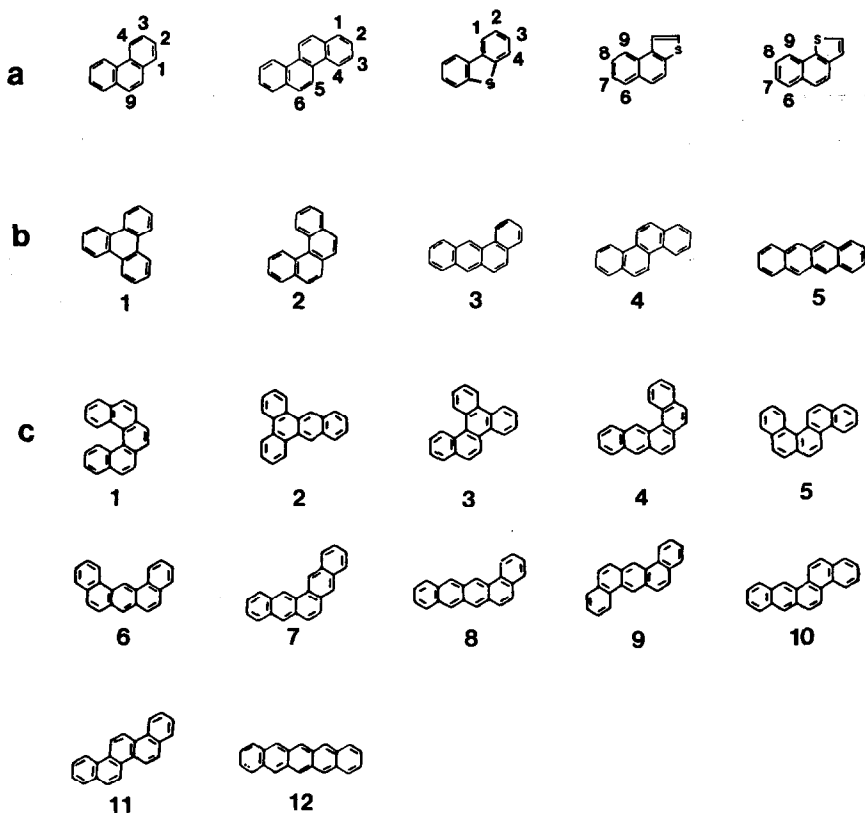  [**] PAHs and PASHs were measured on liquid-crystalline phases B and A, respectively.

Fig. 2. Structures of PAH and PASH solutes used in this study.

$n$-C$_{20}$ at 180°C on columns (10 m × 0.2 mm I.D.) coated with SE-54 and liquid crystalline phase B (Fig. 1) were 35.7 and 5.2, respectively. Remarkably small $k'$ values were observed for $n$-alkane solutes on the smectic liquid-crystalline phases. Also, the relative retention or separation factor ($\alpha$) of $n$-C$_{20}$/phenanthrene was measured at the same temperature of 180°C on the two columns. The $\alpha$ value was 1.28 on SE-54, while it was 0.617 on the liquid-crystalline phase. $n$-Alkane molecules are generally flexible, random coils in the vapor state, while the geometrical shapes of most of the PAHs are fixed by annelated aromatic rings. High chromatographic selectivity for the PAHs has been ascribed to the fitting of the planar molecules into the ordered laminar moieties of the liquid-crystalline stationary phases[26,27]. Therefore, it is reasonable to expect that interactions with the ordered stationary phase are weak for alkanes, but strong for the PAHs. Although there are many kinds of interactions between solutes and phases, these results suggest that solute shape and rigidity are of major importance in interactions between solutes and liquid-crystalline phases.

Various retention phenomena have been observed at transition temperatures of thermotropic monomeric liquid-crystalline stationary phases[28,29]. Some phases showed large, abrupt variations in retention times and orders at these temperatures. Measurements made on the liquid-crystalline polymers reported here showed no sig-

nificant deviations at the transition temperatures, and no temperature hysteresis as a result of supercooling[28,30].

The degree of order of liquid-crystalline side chain polysiloxanes was determined from birefringence and dichroism measurements by Finkelmann *et al.*[31]. The degree of order ($S$) is described by the following equation:

$$S = \frac{1}{2} [3 \cos^2\theta - 1] \qquad (1)$$

where $\theta$ is the angle between the molecular axis of the side chain and the director, and the brackets indicate the average of the side chain orientation. This parameter is 1 for perfect alignment, 0 for complete randomness, and normally between 0 and 1. The $S$ parameters of liquid-crystalline side chain polysiloxanes were determined to be about 10% lower than those of the corresponding monomeric liquid crystals. The $S$ parameter increased by approximately 5% when making the transition from the smectic to cholesteric states. Similar measurements at the smectic/nematic transition temperatures for our polymers corresponded to the results reported by Finkelmann *et al.*[31]; $\alpha$ temporarily increased by approximately 1–3% at the transitions from the smectic to nematic or nematic to isotropic regions. This increase in $\theta$ is expected to have little effect on compound retention in chromatography.

The resolution of isomeric PACs was greatly improved in the smectic region as shown in our earlier work[18]. In Fig. 3, the retention of four cata-condensed 4-ring PAH isomers (naphthacene did not elute at these temperatures) relative to $n$-$C_{20}$ on phases A and C were plotted for temperatures which lie in the smectic, nematic, and isotropic ranges of phase A. Phase C is isotropic at these temperatures and was included for comparison.

For a relatively short temperature range, $\alpha$ is related to temperature by the following equation[32]:

$$\alpha = A T + B \qquad (2)$$

where column temperature $T$ is expressed in °C, and $A$ and $B$ are constants. Relative retention times measured on the isotropic phase (phase C), which is structually similar to phase A, decreased nearly linearly with respect to temperature as expressed by eqn. 2, while those on phase A deviated more significantly from a linear slope. Deviations in the smectic range were larger than those in the nematic range, and the order of solute deviation was coincident with increasing length-to-breadth ($L/B$) ratio.

Table III lists the separation factors for 2-/1-methylphenanthrene on phase A. The retention times of 1-methylphenanthrene in the isotropic and nematic regions were larger than those of 2-methylphenanthrene. However, when the temperature was decreased into the smectic region, the retention order for them was reversed. Clearly, the solute geometrical factor ($L/B$) was a significant factor, in addition to the boiling points of the solutes, for the separation of these isomers in the smectic region; 2-methylphenanthrene ($L/B = 1.58$, b.p. $= 352$°C) eluted later than 1-methylphenanthrene ($L/B = 1.45$, b.p. $= 359$°C). Similarly, two pairs of sulfur heterocyclic isomers which coeluted in the nematic and isotropic regions were separated in the smectic region as previously reported[18]. It generally has been thought that ne-
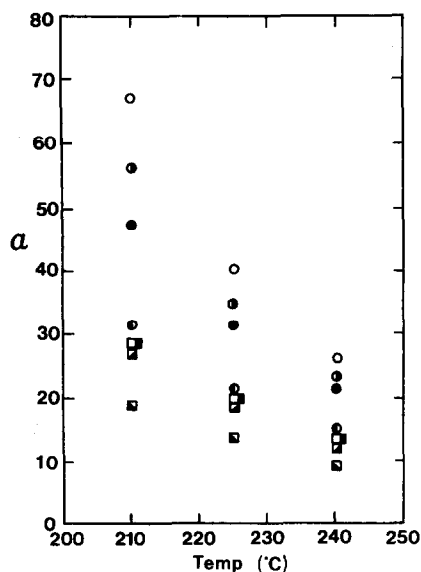
Fig. 3. Plot of relative retention time (relative to $n$-$C_{20}$) $vs.$ temperature for chrysene (O, □), benz[$a$]anthracene (◑, ◪), triphenylene (●, ■) and benzo[$c$]phenanthrene (◐, ◪) on liquid-crystalline phases A and C. Circles: on phase A; squares: on phase C.

matic phases provide better resolution than smectic phases, as mentioned in the Introduction, due to the compact arrangement of liquid-crystalline side groups which leads to resistence to penetration and dissolution of solutes. However, polymeric phase A demonstrated better selectivity in the smectic region than in the less ordered nematic region.

A number of attempts have been made to relate chromatographic retention properties to the detailed molecular properties of the solutes. It is well known that in isothermal GC, graphs of the logarithm of retention times against boiling points are linear for given homologous series. This behavior is simply a consequence of the

TABLE III

SEPARATION FACTORS FOR 2-/1-METHYLPHENANTHRENE ON PHASE A

| Temp. ($°C$) | Adjusted retention time (min)* | | Separation factor ($\alpha$) 2-/1-Methyl-phenanthrene |
|---|---|---|---|
| | 1-Methylphenanthrene | 2-Methylphenanthrene | |
| 170 | 13.86 | 14.34 | 1.03 |
| 180 | 9.63 | 9.82 | 1.02 |
| 190 | 6.87 | 6.87 | 1.00 |
| 200 | 4.94 | 4.94 | 1.00 |
| 210 | 3.64 | 3.64 | 1.00 |
| 220 | 2.78 | 2.72 | 0.978 |
| 230 | 2.16 | 2.09 | 0.968 |
| 240 | 1.70 | 1.63 | 0.959 |

* These values are the average of two measurements. Both measurements agreed to within ± 0.05.

thermodynamic relation between retention volume and vapor pressure of the solute[33]. Randic[34] introduced an easily computable parameter, the connectivity index ($\chi$), which includes molecular descriptors in addition to other physical/chemical data, which can be used to predict retention. However, it generally has found little use in GC, since the major component of the predictor is the boiling point. The prediction of reversed-phase liquid chromatography (LC) retention data for PAHs has been examined with respect to various molecular structure descriptors such as $L/B$, molecular connectivity, van der Waals volume, logarithm of partition coefficient[35-37], and the correlation factor as defined by Hurtubise et al.[38]. It was found that all of these descriptors, except $L/B$, showed high correlation with LC retention for a wide range of PAH solutes. This is not surprising since all these descriptors, except $L/B$, include a molecular weight factor as discussed by Wise et al.[39]. However, within a series of isomers, there is high correlation of LC retention with $L/B$. In contrast to LC, the solute vapor pressure (or boiling point) is important for inclusion in the prediction for GC retention.

The connectivity index has been used as a predictor of retention for various isotropic phases[40,41]. In general, the retention indices ($I$) can be expressed as follows for non-polar compounds

$$I_1 = a\chi + b \tag{3}$$

where $a$ and $b$ are constants. For the nematic liquid.crystalline phases, the shape parameter $\eta$ was introduced into eqn. 3[22,42]

$$I_2 = c'\eta + a'\chi + b' \tag{4}$$

where $a'$, $b'$, and $c'$ are constants. The parameter $\eta$ was defined as the ratio of the longer to the shorter side of a rectangle having a minimum area, which could envelope the molecule ($\eta = L/B$ for most of the compounds). If constant $a$ is approximately equal to $a'$, eqn 5 is obtained from eqns. 3 and 4.

$$\Delta I = I_2 - I_1 \approx c'\eta + (b' - b) \tag{5}$$

In this study, the dependence of retention on the $L/B$ ratio for the smectic liquid-crystalline polysiloxane (phase B) was investigated based on eqn. 5 in order to compensate for the boiling points of the solutes. Relative retention measurements on SE-54 and the smectic phase were chosen for $I_1$ and $I_2$, respectively. As can be seen from the structures given in Fig. 1, these phases contain polar functionalities such as esters and ethers. Consequently, the dipole-induced dipole interactions between phases and PAH solutes are important. Since the molecular polarizabilities are approximately equal for PAHs with the same number of aromatic rings[43,44], dipole-induced dipole interactions were ignored in this study for simplicity, and correlations were made only within isomeric groups.

Fig. 4 shows the $L/B$ dependence of retention order for the methylphenanthrene and methylchrysene isomers (see Table II). The differences in relative retention times (relative to $n$-$C_{20}$) of the PAHs on SE-54 and on phase B were plotted vs. their $L/B$ ratios. The retention order of the methylchrysenes on nematic liquid-crystalline phases[7,15,35] followed the values of $L/B$ except for the 3- and 4-methyl isomers (see
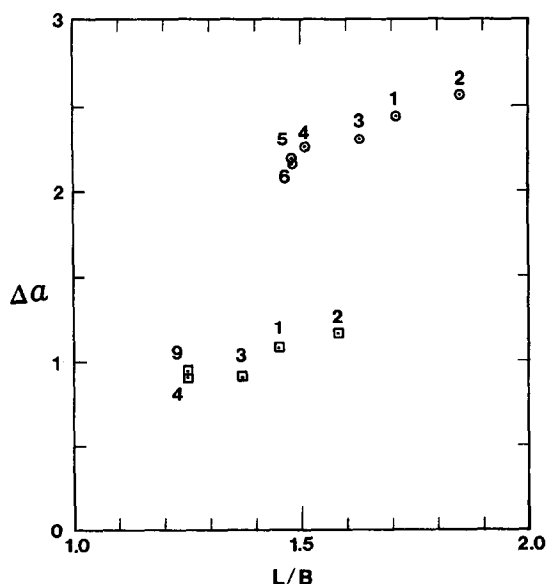
Fig. 4. Plot of the difference in relative retention times on phase B and SE-54 (relative to $n\text{-}C_{20}$) vs. length-to-breadth ratio for all methylphenanthrene ($\square$) and methylchrysene ($\bigcirc$) isomers. Numbers denote the position of methyl group substitution (see Fig. 2).

Table IV). However, the retention order of the 3- and 4-methylchrysenes on phase B was consistent with $L/B$. Fig. 5 shows the dependence of retention on $L/B$ for all of the unsubstituted cata-condensed 4- and 5-ring PAH isomers[45]. Reversed-phase LC retention data for the cata-condensed 5-ring PAHs were recently reported by Wise and Sander[39]. In general, the elution order followed increasing $L/B$ values in LC. However, several isomers had different retentions than were predicted from $L/B$

TABLE IV

RELATIVE RETENTION TIMES AND LENGTH-TO-BREADTH ($L/B$) RATIOS FOR METHYL-CHRYSENE ISOMERS

BBBT = N,N'-Bis[p-n-butoxybenzylidene]α,α'-bi-p-toluidine; BPhBT = N,N'-bis[p-biphenyl]α,α'-bi-p-toluidine.

| Isomer | $L/B$ | Stationary phase | | |
|---|---|---|---|---|
| | | BBBT* | BPhBT** | Phase B*** |
| 6-Methylchrysene | 1.48 | 1.37 | 1.124 | 1.014 |
| 5-Methylchrysene | 1.48 | 1.44 | 1.164 | 1.023 |
| 4-Methylchrysene | 1.51 | 1.62 | 1.253 | 1.042 |
| 3-Methylchrysene | 1.63` | 1.55 | 1.235 | 1.050 |
| 1-Methylchrysene | 1.71 | 1.92 | 1.515 | 1.094 |
| 2-Methylchrysene | 1.85 | 2.17 | 1.720 | 1.121 |

    * Retention times relative to benz[a]anthracene = 1.00. Ref. 35.
    ** Retention times relative to chrysene = 1.00. Ref. 7.
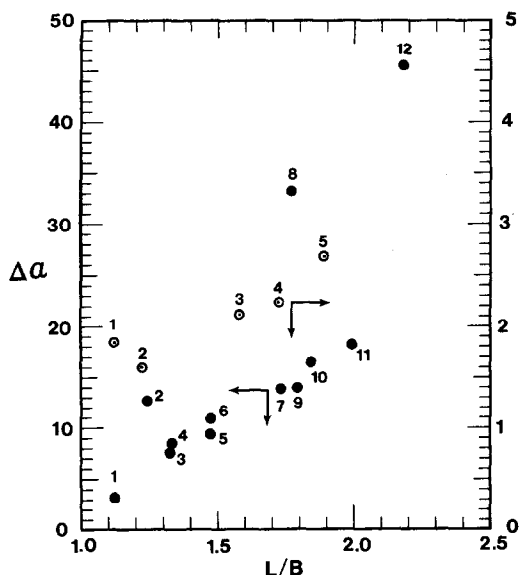    *** Retention times relative to chrysene = 1.00.

Fig. 5. Plot of the difference in relative retention times on phase B and SE-54 (relative to $n$-$C_{20}$) *vs.* length-to-breadth ratio for all 4- (○) and 5-ring (●) PAH isomers. Numbers refer to structures listed in Fig. 2.

values. One isomer with an apparent anomalous behavior was dibenz[$a,c$]anthracene. It was explained that benzo[$g$]chrysene and dibenzo[$b,g$]phenanthrene, which contain the non-planar benzo[$c$]phenanthrene structure, eluted earlier than expected due to solute non-planarity. Another isomer with anomalous behavior was benzo[$a$]naphthacene which had greater retention than would be predicted by the $L/B$ value. It was proposed that the naphthacene structure (four rings with linear annelation) had a greater influence on retention than the overall $L/B$ value of the PAHs. Interestingly, these same two isomers were also retained longer than expected on the smectic phase in GC.

As can be seen in Figs. 4 and 5, a number of solutes deviate from the $L/B$ prediction. Naphthacene, benzo[$a$]naphthacene, and pentacene, which contain a straight line 4-ring annelation, were retained longer than predicted. Furthermore, 9-methylphenanthrene, triphenylene, and dibenz[$a,c$]anthracene were retained longer, while 3-methylphenanthrene and 6-methylchrysene eluted earlier. These observations cannot be explained by the $L/B$ factor alone. The separation and retention of these compounds seem to be dependent on the molecular shapes of the solutes in addition to $L/B$. After careful study of subtle structural correlations, it was found that molecules with aromatic rings annelated in a curved arc-like arrangement (*e.g.*, 3-methylphenanthrene) eluted earlier than expected, while arc-like molecules with groups attached to the outer curved side (*e.g.*, 9-methylphenanthrene, triphenylene, and dibenz[$a,c$]anthracene) were retained longer than predicted.

Since there are many more isomeric sulfur heterocycles compared to PAHs, several isomeric groups of the slightly polar sulfur heterocycles were chromatographed in order to obtain more information about the relationship between structure and retention. The relative retention times (relative to $n$-$C_{20}$) for various 3-ring
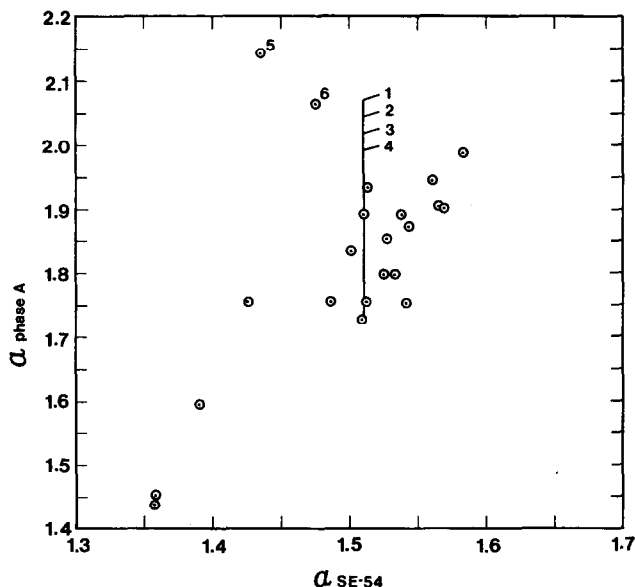
Fig. 6. Plot of relative retention times (relative to $n$-$C_{20}$) of 3-ring sulfur heterocycles on phase A vs. SE-54. Key: 1 = 3-methyldibenzothiophene, 2 = 9-methylnaphtho[1,2-$b$]thiophene, 3 = 2-methyldibenzothiophene, 4 = 8-methylnaphtho[1,2-$b$]thiophene, 5 = 6-methylnaphtho[2,1-$b$]thiophene, 6 = 7-methylnaphtho[2,1-$b$]thiophene.

sulfur heterocycles on the smectic phase A were plotted against those on SE-54 (Fig. 6). Although a linear relationship was obtained in the isotropic region of this phase (above 235°C), this was not the case in the smectic region. Four isomers, 3-methyldibenzothiophene, 9-methylnaphtho[1,2-$b$]thiophene, 2-methyldibenzothiophene, and 8-methylnaphtho[1,2-$b$]thiophene, coeluted on SE-54, but were separated on phase A. Although compounds with large $L/B$ ratios tended to be more retained, the retention of these compounds was not exactly dependent on $L/B$ (see Table II). The molecular shape of 3-methyldibenzothiophene is arc-like with an outside substituent, and was more retained, while 2-methyldibenzothiophene and 8-methylnaphtho[1,2-$b$]-thiophene are arc-like molecules and were eluted earlier. Additionally, 6-methylnaphtho[2,1-$b$]thiophene and 7-methylnaphtho[2,1-$b$]thiophene are also arc-like with outside methyl groups, and were more retained.

Van Deemter curves for 2- and 3-methylphenanthrene, and 2- and 3-methyl-dibenzothiophene, measured on phase A in the smectic region are shown in Fig. 7. In both cases, better efficiency was obtained for the arc-like molecule with an outside methyl group (2-methylphenanthrene and 3-methyldibenzothiophene) than for the smooth arc-like molecules (3-methylphenanthrene and 2-methyldibenzothiophene). Therefore, it appears as though the resistance to mass transfer of 2-methylchrysene is less than that of 3-methylchrysene, and it can more easily diffuse into the smectic liquid-crystalline phase. Similarly, other arc-like molecules with outside methyl groups, e.g., 2-methyldibenzothiophene, 2-methylchrysene, 3-methyldibenzothio-phene, triphenylene, and dibenz[$a,c$]anthracene, were more retained. Likewise, PACs with the straight line 4-ring annelation apparently fit well into the liquid-crystalline structure.

Recently, it was reported that selectivity on a nematic liquid-crystal with a lateral substituent was worse than that without it[23]. It was explained that the lateral
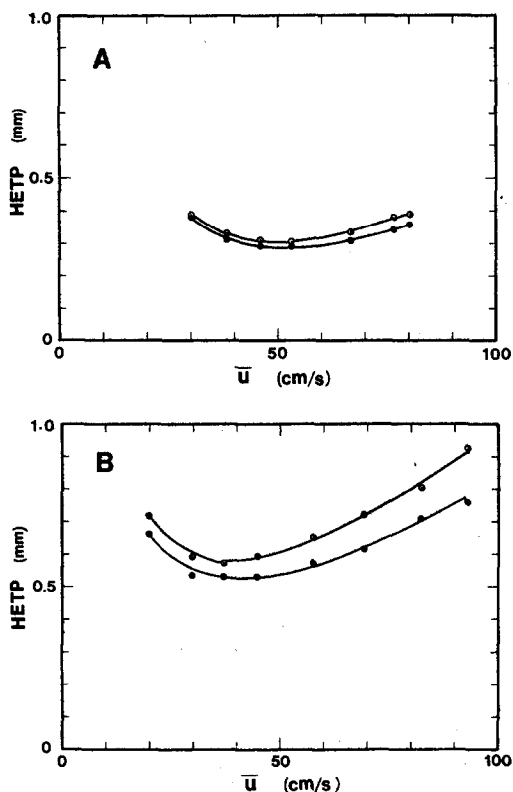
Fig. 7. Van Deemter plots for (A) 2- (●) and 3-methylphenanthrene (○) and (B) 2- (○) and 3-methyl-dibenzothiophene (●) on liquid crystalline phase A.

substituent interfered with substrate molecules entering into the mesomorphic structure of the phase. Ziólek et al.[24] reported that minor changes in the liquid crystal molecular structure affected the properties of the liquid-crystalline stationary phases. Similarly, our results show that small changes in the molecular structures of solutes as well as changes in the stationary phases affect retention.

The main purpose of our work in this area is to find the best stationary phases for the resolution of isomeric PACs or other similar molecules, and to predict their retention properties. Newly developed smectic liquid-crystalline polysiloxanes have been found to be extremely useful for the analysis of PACs in a variety of samples[45–47]. It is expected that these stationary phases will become increasingly more popular as further important separations in which added selectivity based on molecular structure are discovered.

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