



# Retention behavior of alkyl-substituted polycyclic aromatic sulfur heterocycle isomers in gas chromatography on stationary phases of different selectivity



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## ABSTRACT

Retention indices for 10 sets of alkyl-substituted polycyclic aromatic sulfur heterocycles (PASHs) isomers (total of 80 PASHs) were determined using gas chromatography with three different stationary phases: a 50% phenyl phase, a 50% liquid crystalline dimethylpolysiloxane (LC-DMPS) phase, and an ionic liquid (IL) phase. Correlations between the retention behavior on the three stationary phases and PASH geometry [length-to-breadth ( $L/B$ ) and thickness ( $T$ )] were investigated for the following PASHs: 4 methyl-substituted dibenzothiophenes (DBTs), 3 ethyl-substituted DBTs, 15 dimethyl-substituted DBTs, 8 trimethyl-substituted DBTs, 15 methyl-substituted naphthothiophenes, 30 methyl-substituted benzophanthothiophenes, and 5 methyl-substituted tetrapheno[1,12-*bcd*]thiophene. Correlation coefficients for retention on the 50% phenyl phase vs  $L/B$  ranged from  $r = -0.28$  (MeBbN23Ts) to  $r = 0.92$  (EtDBTs). Correlation coefficients for retention on the IL phase vs  $L/B$  ranged from  $r = 0.13$  (MeN12Ts) to  $r = 0.83$  (EtDBTs). Correlation coefficients for retention on the 50% LC-DMPS phase vs  $L/B$  ranged from  $r = 0.22$  (MeDBTs) to  $r = 0.84$  (TriMeDBTs).

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## 1. Introduction

Gas chromatography/mass spectrometry (GC/MS) using ~50% phenyl-substituted methylpolysiloxane (phenyl-MPS) or phenyl-substituted dimethylpolysiloxane (phenyl-DMPS) stationary phases has been shown to provide excellent separations of isomeric polycyclic aromatic hydrocarbons (PAHs) [1–12] and polycyclic aromatic sulfur heterocycles (PASHs) [10,13–16]. However, the non-polar 5% phenyl phases are still commonly used for the separation of PAHs [7,11,12,17–22] and PASHs [13,23–27]. Previous studies by Mössner et al. [13] investigated the separation capabilities of a 5% phenyl-MPS phase and a 50% phenyl-MPS phase for nine alkyl-substituted three- and four-ring PASHs. For almost all isomer sets, the elution orders were similar on both phenyl-MPS phases; however, the 50% phenyl-MPS phase provided

significantly better separation for all isomer sets. In addition to the phenyl-MPS phases, Mössner et al. also evaluated a smectic liquid crystalline phase for the separation of the same isomer sets.

Previous work has shown that a smectic liquid crystalline phase can separate isomeric PAHs [17,28–33] and PASHs [13,29,32,34] based on their molecular shape, which was defined as the length-to-breadth ( $L/B$ ) ratio [33]. In most cases, isomer retention was observed to increase with increasing  $L/B$  values except for isomers with high degree of non-planarity as indicated by a thickness ( $T$ ) parameter. Due to thermal instability at higher temperature limits (250 °C), these stationary phases are no longer commercially available. More recently, a 50% liquid crystalline DMPS (50% LC-DMPS) stationary phase has been made commercially available with improved thermal stability and a higher temperature limit (270 °C). Nalin et al. have recently investigated the shape selective characteristics of the 50% LC-DMPS stationary phase for the separation of isomeric methyl-substituted PAHs [35].

More recently, GC columns with an ionic liquid (IL) stationary phase have been developed for separating a wide range of analytes [36–42]. IL stationary phases consist of two or more organic cations joined by an anion linker, which can be either organic

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or inorganic. IL stationary phases provide several distinct advantages over phenyl-substituted phases, such as no active hydroxyl groups, ease of modification for desired selectivity, and function as either a polar or non-polar stationary phase. IL stationary phases have a higher temperature limit (300 °C) than the 50% LC-DMPS phase (270 °C). Antle et al. [38] investigated the selectivity differences of four IL stationary phases with different polarities for a large number of alkyl-substituted PASHs: (1) 9 two-ring PASHs, (2) 24 three-ring PASHs, (3) 35 four-ring PASHs, and (4) 4 five-ring *peri*-condensed PASHs. Recently, a new GC column using IL as the stationary phase (SLB-ILPAH) has become commercially available specifically intended for separating mixtures of PAHs.

In the current study, three different GC stationary phase types (50% phenyl, 50% LC-DMPS, and IL) were evaluated for the separation of alkyl-substituted PASH isomers. GC retention indices were determined for 30 alkyl-substituted dibenzothiophenes (DBT), 15 methyl-substituted naphthothiophenes (NTs), 30 methyl-substituted benzonaphthothiophenes (BbNTs), and 5 methyl-substituted benzo[2,3]phenanthro[4,5-*bcd*]thiophene (B23P45Ts). Retention indices for GC has been reported for alkyl-substituted PASH isomers on 5% phenyl stationary phase [13,26,43], 50% phenyl stationary phases [13,26,27], smectic liquid crystalline stationary phases [13], and IL stationary phases [24]. To our knowledge, this investigation is the first to report the GC separations of alkyl-substituted PASH isomers on the 50% LC-DMPS stationary phase, the new 50% phenyl phase, and IL phase introduced for PAH analysis. RI values are valuable in the selection of the appropriate GC stationary phase and can be used to identify unknown peaks in the chromatographic analysis of real samples when authentic reference standards are not available. Correlation for PASH geometry ( $L/B$  and  $T$ ) and retention on the 50% LC-DMPS phase used in the present study and previous data [13] obtained using a smectic LC phase are compared. In a companion study, the GC retention behavior on the 50% phenyl, 50% LC-DMPS, and IL stationary phases and shape selectivity correlations are reported for three-, four-, and five-ring non-substituted PASHs [44].

## 2. Experimental

### 2.1. Chemicals

The following PAHs and PASHs were purchased from commercial sources with high purity (>95%): DBT (Acros Organics, Springfield, NJ); 1-, 2-, and 4-MeDBT, 2,8- DiMeDBT, 1,4,7-, 3,4,7-, 2,3,7-, 2,3,8-, 2,4,7-, 2,4,8-, 2,4,6-, and 1,3,7-TriMeDBT (Jan Andersson, Munster, Germany); 2-EtDBT, 3-EtDBT, and 4-EtDBT (Chiron AS, Trondheim, Norway); and BbN12T, BbN21T, BbN23T, chrysene (Chry), and picene (Pic) (BCR, Brussels, Belgium); naphthalene (Nap) and phenanthrene (Phe) (Fluka, Buchs, Switzerland). The remaining PASHs were synthesized in the laboratories of M.L.L. at Brigham Young University (Provo, UT).

### 2.2. Molecular shape parameter calculations

The molecular modeling programs and procedure for calculating the molecular shape parameters have been described in detail previously [45].

### 2.3. Gas chromatographic retention data

GC retention index (RI) values were calculated according to Eq. (1) with the following index markers: (200) Nap, (300) Phe, (400) Chry, and (500) Pic [46].

$$RI = 100z + 100 \frac{t_{R(x)} - t_{R(z)}}{t_{R(z+1)} - t_{R(z)}} \quad (1)$$

**Table 1**  
GC/MS operating parameters.

Gas Chromatograph	
Inlet	Cool on-column (with electronic pressure control)
Injection Volume	1 $\mu$ L
Inlet Temperature	Tracking oven temperature (3 °C above actual oven temperature)
Column Guard	5 m $\times$ 0.25 mm i.d.
Columns	SLB-PAHms, 50% phenyl phase (Supelco, Bellefonte, PA) 60 m $\times$ 0.25 mm i.d. $\times$ 0.25 $\mu$ m film thickness Rxi-PAH, ~50% phenyl phase (Restek, Bellefonte, PA) 60 m $\times$ 0.25 mm i.d. $\times$ 0.10 $\mu$ m film thickness SLB-ILPAH, ionic liquid phase (Supelco, Bellefonte, PA) 20 m $\times$ 0.18 mm i.d. $\times$ 0.05 $\mu$ m film thickness LC-50, 50% LC-DMPS phase (Restek, Bellefonte, PA) 20 m $\times$ 0.25 mm i.d. $\times$ 0.10 $\mu$ m film thickness
Carrier Gas Flow	1.2 mL/min of helium
Oven Program	
SLB-PAHms and Rxi-PAH	Isothermal at 60 °C for 1 min, with 35 °C/min to 190 °C, with 1 °C/min to 300 °C, isothermal at 300 °C for 60 min
LC-50	Isothermal at 60 °C for 1 min, with 35 °C/min to 190 °C, with 1 °C/min to 250 °C, isothermal at 250 °C for 50 min
SLB-ILPAH	Isothermal at 60 °C for 1 min, with 35 °C/min to 100 °C, with 1 °C/min to 300 °C
Mass Spectrometer	
Interface	Direct coupling
Transfer Line	300 °C
Temperature	
MS Temperatures	Ion Source: 230 °C and Quadrupole: 150 °C
Solvent Delay	6 min
SIM Mode	$m/z$ 184, 198, 212, 226, 234, 248, 258, 272

where  $x$  represents the solute of interest,  $t_R$  represents the retention time, and  $z$  and  $z + 1$  represent the numbers of aromatic rings of the index markers eluting before and after the solute of interest. Mössner et al. [13] previously reported RI values using the same retention index markers used in present study; however, Pic with a MM of 278 Da did not elute within the temperature limits of the smectic LC phase used in their study. More recently, Nalin et al. [35] have demonstrated that the addition of the DMPS linker to the LC phase allow for the elution of PAHs with MM  $\geq$  302 Da. The RI values reported here are based on three measurements obtained from reference standards. The precision (standard deviation) of the RI values was equal or less than  $\pm 0.02$  RI units.

### 2.4. Instrumentation and chromatographic conditions

GC/MS analysis was performed on a gas chromatograph (HP 6890 series GC, Agilent, Avondale PA) coupled to a quadrupole mass spectrometer with electron impact (EI) ionization (HP 5973 MSD, Agilent). The GC was equipped with an on-column injector and an autosampler. GC column specifics and separation conditions are listed in Table 1. The GC retention index data (RI) were determined using these conditions.

## 3. Results and discussion

The molecular structures for the seven PASHs studied are shown in Fig. 1 including the numbering of the positions available for substitution. Tables 2, 3, and 4 summarize the molecular shape parameters ( $T$  and  $L/B$ ) and retention indices for the alkyl-substituted dibenzothiophenes, naphthothiophenes, and benzonaphthothiophenes and tetraphenothiophenes in the present study, respectively. The regression calculations for the correlation of  $L/B$  and retention on all four stationary phases are summarized in Tables 5 and 6. Wilson et al. [47,48] have recently demonstrated the use of statistical  $t$ -test for determining the lin-

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