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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 benzonaphthothiophenes, 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).

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].

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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 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 equation 1 with the following index markers: (200) Nap, (300) Phe, (400) Chry, and (500) Pic [46].

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

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 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 ± 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 linear significance of correlation coefficients (r) for the retention of isomeric PASHs and MePASHs in RPLC on polymeric C_{18} stationary phases and their L/B values using equation 2:

$$t_{exp} = \frac{|r| \sqrt{df}}{\sqrt{1-r^2}} \quad (2)$$

where df is the degrees of freedom ($n - 2$) and n is the number of data points. Based on the df , a significant linear correlation does exist for the correlation coefficient if $t_{exp} > t_{crit}$ [49]. These concepts will be applied to the linear correlation between the retention of MePASHs on GC stationary phases and their L/B values.

The retention indices for 80 alkyl-substituted PASHs were determined on the following commercial GC stationary phases specially intended for the separation of PAHs: (1) SLB-PAHms, (2) Rxi-PAH, (3) SLB-ILPAH, and (4) LC-50. The column specifications are listed in Table 1. To the best of our knowledge, the retention behavior of isomeric MePASHs has never been investigated on these four GC columns.

The SLB-PAHms is a new GC column with a 50% phenyl stationary phase. The Rxi-PAH is a relatively new GC column that is described as a proprietary high phenyl content stationary phase, with similar retention behavior to a 50% phenyl-MPS stationary phase for isomeric PAHs [2, 3, 8, 35]. The retention index values are reported for both GC columns in Tables 2, 3, and 4; however, all chromatograms identified as 50% phenyl were obtained using the SLB-PAHms column. The chromatograms obtained with the SLB-PAHms column allowed for a direct comparison to previously reported retention data on similar 50% phenyl-MPS stationary phases (DB-17ms) [13, 15]. The slight difference in the retention index values between the two 50% phenyl stationary phases shown in Tables 2, 3, and 4 may be due to a slight difference in phenyl content in the stationary phase. The current study is the first to investigate the correlation between the retention behavior of PASHs with their L/B values on the 50% phenyl phase.

The LC-50 column used in this study has a 50% LC-DMPS stationary phase, which allows for better thermal stability and higher operating temperature limits (270 °C) versus the original smectic liquid crystalline phases (250 °C). Mössner et al. [13] demonstrated previously that the smectic liquid crystalline stationary phase could be useful for the separation of alkyl-substituted PASHs based on shape. Schubert et al. [1] have demonstrated

the shape selectivity characteristics of the 50% LC-DMPS phase for the separation of isomeric PAHs with MM 300 Da. More recently, Nalin et al. [35] have investigated the shape selective characteristics of the 50% LC-DMPS phase for the separation of methyl-substituted PAHs. The current study is the first to investigate the retention behavior of PASHs on the 50% LC-DMPS phase and its correlation with their L/B and T values. The regression calculations for the correlation of L/B and retention on the 50% LC-DMPS and smectic liquid crystalline phases are summarized in Table 5. The correlation data for the smectic liquid crystalline phases were determined using previously reported retention index values by Mössner et al. [13] for 9 of the 10 isomer sets in the present study.

The use of IL as GC stationary phases was first demonstrated by Armstrong et al. [36] to provide unique selectivity differences compared to the traditional 5% and 50% phenyl stationary phases. Antle et al. [38] investigated the separation capabilities of four GC columns with IL stationary phases with various polarities for the following PASH isomer groups: (1) four methyl-substituted DBTs, (2) two ethyl-substituted DBTs, (3) six trimethyl-substituted DBTs, (4) 12 methyl-substituted NTs, (5) 29 methyl-substituted BbNTs, and (6) four methyl-substituted B23P45Ts. In the current study, a newly developed GC column with an IL stationary phase specifically designed for the separation of PAHs was used to obtain retention index values for 80 PASHs. The retention behavior for an additional 23 alkyl-substituted PASHs are reported, which include 15 dimethyl-substituted DBTs that have been previously detected in petroleum samples [14]. The RI values reported in the present study and the study reported by Antle et al. [38] differ for the PASHs investigated in both studies; however, the SLB-ILPAH column is similar to the SLB-IL59 column used in Antle et al. [38] investigation.

3.1. Alkyl-substituted dibenzothiophenes

3.1.1. Methyl- and ethyl-substituted dibenzothiophenes—GC separations for the MeDBTs and three of the four possible EtDBTs are shown in Fig. 2. Good separations were obtained with all of the stationary phases; however, the 2-Me and 4-MeDBT were not resolved with the 50% LC-DMPS phase. It is important to note, the separation on the 50% LC-DMPS phase occurs over ~1 min time range but the separations on the 50% phenyl and IL phases occur over 7 and 11 min, respectively. The 50% phenyl and IL phases provide baseline resolution for all seven compounds. 1-MeDBT represents the only difference in the elution order between these two phases; on the 50% phenyl phase it elutes fourth and on the IL phase it elutes second. In the case of the 50% LC-DMPS phase, the elution order is significantly different. The 50% LC-DMPS is the only phase that has some of the EtDBTs eluting before MeDBTs. A similar observation was made previously [13] for the same PASHs on a smectic liquid crystalline phase; however, the elution order does vary for the MeDBTs with 1-Me eluting first on the smectic liquid crystalline phase but third on the 50% LC-DMPS phase.

A plot of retention on the 50% LC-DMPS phase vs. L/B for the four MeDBT isomers and three EtDBT isomers is shown in Fig. S1A and S1B [13], which have correlation coefficients of $r = 0.22$ and $r = 0.53$, respectively. The correlations are drastically lower than obtained with a smectic liquid crystalline phase (Fig. S2A and B) that provided correlation

coefficients of $r = 0.82$ and $r = 0.55$ for MeDBT and EtDBT, respectively. For both isomer sets, the calculated $t_{\text{exp}} < t_{\text{crit}}$ (Table 5) for both liquid crystalline stationary phases indicating that a significant linear trend was not present for the correlation coefficients [49]. The correlation difference for the MeDBTs can be related to the different elution orders for 1-MeDBT, the correlation coefficient improves to $r = 0.87$ if this data point is removed from the plot in Fig. S1. Although low, the correlation coefficients for the EtDBTs are similar for both liquid crystalline phases. Similar correlations were investigated for the 50% phenyl and IL phases presented in Table 6. A plot of retention on the 50% phenyl phase vs. L/B for the four MeDBT and three EtDBT isomers is shown in Fig. S3A and S3B, which have correlation coefficients of $r = -0.50$ and $r = 0.92$, respectively. A plot of retention on the IL phase vs. L/B for the four MeDBT and three EtDBT isomers is shown in Fig. S4A and S4B, which have correlation coefficients of $r = 0.47$ and $r = 0.83$, respectively [49].

3.1.2. Dimethyl-substituted dibenzothiophenes—GC separations for 15 of the 16 possible DiMeDBTs are shown in Fig. 3. Good separation was obtained on the 50% phenyl phase; however, the following pairs of isomers were not resolved: (1) 1,8- and 3,7-DiMeDBT and (2) 1,3- and 1,7-DiMeDBT isomers. GC separation on the IL phase allowed for the separation of 1,8- and 3,7-DiMeDBT by ~3 mins but co-elution occurred between 1,3- and 1,7-DiMeDBT. In addition, the IL phase had co-elution between the following isomer pairs: (1) 1,6- and 2,4-DiMeDBT, (2) 2,6- and 3,6-DiMeDBT, (3) 2,7- and 2,8-DiMeDBT, and (4) 3,4- and 3,7-DiMeDBT isomers. The most co-elution among the 15 isomers occurred on the 50% LC-DMPS phase, but the separation occurred over a 2 min interval in comparison to 9 min and 12 min intervals for the 50% phenyl and IL phases, respectively. However, all co-eluting isomer pairs discussed above on the other two stationary phases were baseline resolved on the 50% LC-DMPS phase.

Significantly different elution orders were obtained on the 50% LC-DMPS phase than previously reported on the smectic liquid crystalline phase [13], which can be clearly seen in the correlation plots for retention vs. L/B in Fig. 4. The correlation coefficients for the 15 DiMeDBTs on the smectic liquid crystalline and 50% LC-DMPS phases are $r = 0.91$ and $r = 0.71$, respectively. In both cases, the $t_{\text{exp}} > t_{\text{crit}}$ (Table 5) indicating that both correlation coefficient represents a significant linear trend [49]. The lower correlation for the 50% LC-DMPS phase can be explained when the isomer set is divided into smaller subsets based on methyl-substituted position: (1) 1,2-, 1,3-, 1,4-, 1,6-, 1,7-, and 1,8-DiMeDBT, (2) 2,3-, 2,4-, 2,6-, 2,7-, and 2,8-DiMeDBT, and (3) 3,4-, 3,6-, 3,7-, and 4,6-DiMeDBT. The correlation coefficients for the subsets are $r = 0.82$ (1), $r = 0.92$ (2), and $r = 0.95$ (3). Similar to the discussion with 1-MeDBT above, the correlation difference for the DiMeDBTs can be associated with subset 1. If subset 1 is removed from the correlation plot for the 50% LC-DMPS phase in Fig. 4A, the correlation coefficient improves to $r = 0.95$.

A plot of retention on the 50% phenyl and IL phases vs. L/B for the 15 DiMeDBT isomers are shown in Fig. S3C and S4C and have correlation coefficients of $r = 0.08$ and $r = 0.50$, respectively. For both isomer sets, the calculated $t_{\text{exp}} < t_{\text{crit}}$ (Table 6) for the 50% phenyl and IL stationary phases indicating that significant linear trends were not present [49]. In a companion study [44], separation of non-substituted PASH isomers showed some shape selective characteristics on the 50% phenyl and IL phases when dividing the isomers into

smaller subsets based on structural features. A similar comparison was made for the DiMeDBT's isomer set in the present study. The correlation coefficients for the DiMeDBT subsets on the IL phase are $r = 0.82$ (1), $r = 0.55$ (2), and $r = 0.86$ (3); however, the correlation coefficient does not improve if subset 2 is removed from the correlation plot in Fig. S4D.

3.1.3. Trimethyl-substituted dibenzothiophenes—GC separations for 8 of the 28 possible TriMeDBTs on these three stationary phases are shown in Fig. 5. Good separations were obtained on all three phases, but the following isomer co-elution occurred: 1,3,7- and 3,4,7-TriMeDBT on the 50% phenyl phase; 2,4,6- and 2,4,8-TriMeDBT and 1,4,7- and 2,3,8-TriMeDBT on the 50% LC-DMPS phase; and 2,4,7- and 2,4,8-TriMeDBT and 2,3,7- and 2,3,8-TriMeDBT on the IL phase. 2,4,6-TriMeDBT elutes first on all three phases. A plot of retention on the 50% LC-DMPS vs. L/B for the 8 TriMeDBT isomers is shown in Fig. S1C, a correlation coefficient of $r = 0.84$, which is similar to the correlation coefficient of $r = 0.89$ obtained for 6 of the 8 TriMeDBTs on a smectic LC phase (Fig. S2C, Table 5). For both stationary phases, the calculated $t_{\text{exp}} > t_{\text{crit}}$ (Table 5) indicating that these correlation coefficients do represent a significant linear trend [49]. 1,4,7-TriMeDBT elutes prior to 2,4,7-TriMeDBT on the smectic LC phase but on the 50% LC-DMPS phase the elution order is reversed. Plots of retention on the 50% phenyl and IL phases vs. L/B for the 8 TriMeDBT isomers are shown in Fig. S3D and S4D, which have correlation coefficients of $r = 0.66$ and $r = 0.73$, respectively [49].

3.2. Methyl-substituted naphthothiophenes

GC separations for seven of the eight possible MeN12T and for the eight possible MeN21T isomers are shown in Fig. 6 for these three stationary phases. Baseline resolution was achieved for the seven MeN12T isomers on the 50% phenyl and only partial co-elution occurred between 4-Me and 7-MeN12T isomers on the IL phase. These same two isomers had the opposite elution order on the 50% phenyl (7-Me first) and IL (4-Me first) phases. In the case of the 50% LC-DMPS phase, the elution orders are significantly different and co-elution occurs between the following isomers: (1) 4-Me and 5-MeN12T and (2) 6-Me and 9-MeN12T. In comparison to the smectic liquid crystalline phase [13], 2-Me and 6-MeN12T have a later elution on the 50% LC-DMPS phase.

A plot of retention on the 50% LC-DMPS vs. L/B for the seven MeN12T isomers is shown in Fig. S5A and has a correlation coefficient of $r = 0.47$, which is lower than the correlation coefficient of $r = 0.74$ obtained on the smectic liquid crystalline phase (Table 5, Fig. S5B). It is interesting to note that, 9-MeN12T elutes later than expected based on L/B values. The sulfur atom is located in a *bay*-like-region of the structure. In the case of the smectic liquid crystalline correlation plot, the correlation coefficient is improved to $r = 0.92$ if 9-MeN12T is removed (Fig. S5B). 9-MeN12T eluted later than expect based on the L/B value. The correlation plot for the 50% LC-DMPS phase in Fig. S5A does not improve when 9-MeN12T is removed. A plot of retention on the 50% phenyl and IL phases vs. L/B for the seven MeN12T isomers is shown in Fig. S5C and S5D provided correlation coefficients of $r = -0.65$ and $r = -0.53$, respectively [49].

In the case of MeN21T isomers, all three stationary phases provided significantly different elution orders and co-eluting isomer pairs. A plot of retention on the 50% LC-DMPS vs. L/B for the eight MeN21T isomers is shown in Fig. S6A providing a correlation coefficient of $r = 0.45$ ($t_{\text{exp}} = 1.24$, $t_{\text{crit}} = 2.45$, $n = 8$), which is lower than the correlation coefficient of $r = 0.85$ ($t_{\text{exp}} = 3.21$, $t_{\text{crit}} = 2.45$, $n = 8$), obtained on the smectic liquid crystalline phase (Fig. S6B, Table 5). A plot of retention on the 50% phenyl and IL phases vs. L/B for the eight MeN21T isomers is shown in Fig. S6C and S6D and provides correlation coefficients of $r = -0.50$ and $r = 0.13$, respectively [49].

3.3. Methyl-substituted benzonaphthothiophenes

3.3.1. MeBbN12T isomers—GC separations for BbN12T and 10 MeBbN12T isomers on three different stationary phases are shown in Fig. 7. Dramatic differences are observed in the retention behavior of these isomers on all three stationary phases. In the case of the 50% phenyl phase, the MeBbN12T isomers are separated with co-elution for the following isomer pairs: (1) 6-Me and 8-MeBbN12T isomers and (2) 4-Me and 5-MeBbN12T isomers. The 6-Me and 8-MeBbN12T isomers are completely separated on the 50% LC-DMPS phase and partially separated on the IL phase; however, the elution order is reversed on the IL phase compared to the other two phases. The 4-Me and 5-MeBbN12T isomers also co-elute on the IL phase, but are separated on the 50% LC-DMPS phase, and 5-Me co-elutes with 3-Me and 9-MeBbN12T isomers on the 50% LC-DMPS phase. The largest difference in the retention behavior is observed for the 1-Me and 11-MeBbN12T isomers. Previous studies have observed an early elution for these isomers prior to the unsubstituted parent BbN12T on a smectic liquid crystalline phase, which was attributed to the non-planarity of these two isomers ($T = 4.99$ Å and $T = 5.32$ Å for 11-Me and 1-MeBbN12T, respectively) [13]. Similar observations have been reported for the RPLC separation of these isomers on a polymeric C_{18} stationary phase [48]. However, in the present study 11-MeBbN12T does not elute prior to the unsubstituted BbN12T on the 50% LC-DMPS phase. It is interesting to note that, 1-Me and 11-MeBbN12T do elute prior to the unsubstituted BbN12T on the IL phase; this behavior was not observed on the 50% phenyl phase.

A plot of retention on the 50% LC-DMPS phase vs. L/B for the MeBbN12T isomers is shown in Fig. S7A, which results in a correlation coefficient of $r = 0.60$ ($t_{\text{exp}} = 2.12$, $t_{\text{crit}} = 2.31$, $n = 10$). Surprisingly, this correlation coefficient is the highest of the three MeBbNT isomer sets on the 50% LC-DMPS phase. The correlation coefficient for the separation on the smectic liquid crystalline phase is $r = 0.74$ (Fig S7B, $t_{\text{exp}} = 2.71$, $t_{\text{crit}} = 2.31$, $n = 10$), which is the lowest of the three BbNT isomer sets. 1-Me and 11-MeBbN12T isomers elute much earlier on the liquid crystalline phases than predicted based on L/B values (see Fig 7) but affects the linear trend significantly more for the 50% LC-DMPS phase. The correlation coefficient improves to $r = 0.74$ ($t_{\text{exp}} = 2.71$, $t_{\text{crit}} = 2.45$, $n = 10$) for the 50% LC-DMPS phase if 1-Me and 11-MeBbN12T are removed from the correlation plots in Fig S7A. Plots of retention on the 50% phenyl and IL phases vs. L/B for the 10 MeBbN12T isomers are shown in Fig. S7C and S7D, which have correlation coefficients of $r = 0.40$ and $r = 0.30$, respectively [49].

3.3.2. MeBbN21T isomers—GC separations for BbN21T and 10 MeBbN21T isomers on the three different stationary phases are shown in Fig. 8. Of the three stationary phases investigated, the 50% LC-DMPS phase provided the most comprehensive separation of the MeBbN21T isomers with only partial co-elution between 1-Me and 4-MeBbN21T and complete co-elution between 2-Me and 3-MeBbN21T isomers. In comparison, the 50% phenyl-DMPS phase allowed for the separation of 6 of the 10 isomers, while the IL phase provided separation for only 3 of the 10 isomers. 10-MeBbN21T isomer elutes first on all three stationary phases. On the 50% LC-DMPS phase, 1-MeBbN21T elutes sixth but on the 50% phenyl and IL phases it elutes last (10th).

The correlation of retention on the 50% LC-DMPS phase vs. L/B value for the MeBbN21T isomers is shown in Fig. S8A. The correlation coefficient on the 50% LC-DMPS phase for the MeBbN21T isomer set is $r = 0.42$, which is lower than the smectic liquid crystalline phase correlation coefficient of $r = 0.79$ (Fig. S8B, Table 5). Both phases provided significantly different retention behavior for several isomers in this isomer set. On the smectic liquid crystalline phase, 5-MeBbN21T elutes before the unsubstituted BbN21T for no apparent reason because the thickness (4.22 Å) indicates structural planarity. On the 50% LC-DMPS phase, 5-MeBbN21T elutes after BbN21T and 10-MeBbN21T. 2-MeBbN21T elutes fourth on the smectic liquid crystalline phase but ninth on the 50% LC-DMPS phase. Similar to 9-MeN12T previously discussed, 1-MeBbN21T elutes later than expected based on L/B values. The sulfur atom is located in a *bay*-like-region of the structure for 1-MeBbN21T. Correlation studies are shown in Fig. S8C and S8D for the separation of MeBbN21T isomers on the 50% phenyl and IL phases with correlation coefficients of $r = -0.53$ and $r = -0.17$, respectively [49].

3.3.3. MeBbN23T isomers—GC separations for BbN23T and 10 MeBbN23T isomers on three different stationary phases are shown in Fig. 9. Unfortunately, some of the reference standards of the MeBbN23T isomers contained impurities. 11-MeBbN23T elutes at the end of the separation on all three phases but co-elutes with 3-MeBbN23T on the 50% LC-DMPS phase. 4-MeBbN23T elutes first on the 50% phenyl and IL phases, but it elutes sixth on the 50% LC-DMPS phase. The correlation of retention on the 50% LC-DMPS phase vs. L/B for the MeBbN23T isomers is shown in Fig. S9A. The correlation coefficient on the 50% LC-DMPS phase for the MeBbN23T isomer set is $r = 0.56$ ($t_{\text{exp}} = 1.91$, $t_{\text{crit}} = 2.31$, $n = 10$) [49]. Previous studies have shown that the separation of these isomers on a smectic liquid crystalline phase was significantly better and provided a correlation coefficient of $r = 0.79$ (Fig. S9B, $t_{\text{exp}} = 2.86$, $t_{\text{crit}} = 2.31$, $n = 10$) [49]. From examining the correlation plots for this isomer set, it can be seen clearly that 10-Me and 11-MeBbN23T elute significantly different than expected based on L/B values (1.57 Å and 1.59 Å, respectively), for which no apparent reason can be identified. The correlation coefficients improve to $r = 0.83$ and $r = 0.91$ when these two isomers are removed from the plots in Fig. S9A and S9B for the 50% LC-DMPS and smectic liquid crystalline phases, respectively. Fig. S9C and S9D show correlation plots for the separation of MeBbN23T isomers on the 50% phenyl and IL phases with correlation coefficients of $r = -0.28$ and $r = -0.06$, respectively [49].

3.4. Methyl-substituted tetraphenothiopenes

GC separations for B23P45T and 5 Me B23P45T isomers on three different stationary phases are shown in Fig. 10. This isomer set is the only *peri*-condensed PASHs included in the present study. The 50% phenyl and 50% LC-DMPS phases provided baseline resolution for the five Me B23P45T isomers, but the IL phase had partial co-elution between 9-Me and 5-Me B23P45T isomers. The elution order was the same on the 50% phenyl and IL phases: 1-Me, 9-Me, 5-Me, 7-Me, and 3-Me B23P45T. On the 50% LC-DMPS phase, 5-Me eluted second before 9-Me B23P45T. The correlation of retention on the 50% LC-DMPS phase and L/B for the Me B23P45T isomers is shown in Fig. S10A. The correlation coefficient on the 50% LC-DMPS phase for the Me B23P45T isomer set is $r = 0.67$ ($t_{\text{exp}} = 1.57$, $t_{\text{crit}} = 3.18$, $n = 5$) [49]. Unlike the previous isomer sets in this study, the Me B23P45T isomers have not been separated on a smectic liquid crystalline phase previously. Correlation plots for the 50% phenyl and IL phase are shown in Fig. S10B and S10C, respectively, with a correlation coefficient for both phases of $r = 0.30$ [49].

4. Conclusion

GC retention indices were generated for 80 alkyl-substituted PASHs on a 50% phenyl, 50% LC-DMPS, and IL stationary phases. Similar to the behavior of non-substituted PASHs [44], all three stationary phases have distinct selectivity differences for alkyl-substituted PASHs. Correlation between the molecular shape parameters of PASHs (L/B and T) and GC retention on the three phases was investigated. In the case of the IL and 50% phenyl phase, both phases appear to have a limited correlation between PASH retention and L/B values. The currently available 50% LC-DMPS phase does provide some correlations to L/B with correlation coefficients ranging from $r = 0.22$ (MeDBTs) to $r = 0.84$ (TriMeDBTs). Direct comparisons were made between the 50% LC-DMPS phase and previously available smectic liquid crystalline phase, which provided correlation coefficients ranging from $r = 0.55$ (EtDBTs) to $r = 0.91$ (DiMeDBTs). Additional retention behavior differences were observed for the non-planar alkyl-substituted PASHs. 1-Me ($T = 5.28$ Å) and 11-MeBbN12T ($T = 4.99$ Å) elute prior to BbN12T on the smectic liquid crystalline phase but only 1-MeBbN12T eluted prior to BbN12T on the 50% LC-DMPS phase. The shape selective separation characteristic of the 50% LC-DMPS phase is affected by the addition of the DMPS linker for the alkyl-substituted PASHs in this study. It was interesting to note, on the IL phase the retention behavior for the 1-Me and 11-MeBbN12T isomers was similar to the smectic liquid crystalline phase.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Molecular structures of the three-ring and four-ring PASHs included in the present study.

Fig. 2.
GC separations of the four MeDBT isomers (m/z 198) and three EtDBT isomers (m/z 212) on three different stationary phases.

Fig. 3.

GC separations of 15 DiMeDBT isomers (m/z 212) on three different stationary phases. Numbers identify the DiMeDBT isomers.

Fig. 4. Plots of retention (RI values) on the smectic LC (A) [13] and 50% LC-DMPS (B) phases vs. L/B values for 15 DiMeDBTs. Number identify the specific DiMeDBT isomers.

Fig. 5.
GC separations of eight TriMeDBT isomers (m/z 226) on three different stationary phases.
Numbers identify the TriMeDBT isomers.

Fig. 6. GC separations of seven MeN12T isomers and 8 MeN21T isomers (m/z 198) on three different stationary phases. Numbers identify the MeN12T and MeN21T isomers.

Fig. 7.
GC separations of BbN12T (m/z 234) and 10 MeBbN12T isomers (m/z 248) on three different stationary phases. Numbers identify the MeBbN12T isomers.

Fig. 8. GC separations of BbN21T (m/z 234) and 10 MeBbN21T isomers (m/z 248) on three different stationary phases. Numbers identify the MeBbN21T isomers. Impurities in the reference standards are indicated with an *.

Fig. 9.

GC separations of BbN23T (m/z 234) and 10 MeBbN23T isomers (m/z 248) on three different stationary phases. Numbers identify the MeBbN23T isomers. Impurities in the reference standards are indicated with an *.

Fig. 10.

GC separations of B23P45T (m/z 258) and five Me B23P45T isomers (m/z 272) on three different stationary phases. Numbers identify the Me B23P45T isomers.

Table 1

GC/MS operating parameters.

Gas Chromatograph	
Inlet	Cool on-column (with electronic pressure control)
Injection Volume	1 μ 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 μ m film thickness
	Rxi-PAH, ~50% phenyl phase (Restek, Bellefonte, PA)
	60 m $\times$ 0.25 mm i.d. $\times$ 0.10 μ m film thickness
	SLB-ILPAH, ionic liquid phase (Supelco, Bellefonte, PA)
Carrier Gas Flow	20 m $\times$ 0.18 mm i.d. $\times$ 0.05 μ m film thickness
	LC-50, 50% LC-DMPS phase (Restek, Bellefonte, PA)
	20 m $\times$ 0.25 mm i.d. $\times$ 0.10 μ 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 Temperature	300 °C
MS Temperatures	Ion source: 230 °C and Quadrupole: 150 °C
Solvent Delay	6 min
SIM Mode	<i>m/z</i> 184, 198, 212, 226, 234, 248, 258, 272

Table 2

GC retention indices for the alkyl-substituted isomers of DBT.

PASHs	Molecular Shape Parameters			RI Values				
	<i>T</i> (Å)	<i>L/B</i>	<i>R</i> _{xi} -PAH	50% Phenyl ^d		<i>I</i> _L ^b	50% LC ^c	
				<i>R</i> _{xi} -PAH	SLB-PAH			
DBT	4.06	1.45	290.76	291.23	283.18	289.68		
1-MeDBT	4.24	1.31	309.73	312.09	302.61	302.56		
2-MeDBT	4.21	1.51	306.02	307.40	303.48	301.26		
3-MeDBT	4.21	1.59	306.81	308.46	305.29	303.30		
4-MeDBT	4.21	1.42	304.56	305.69	296.95	301.17		
2-EtDBT	4.22	1.65	313.86	316.36	311.83	301.93		
3-EtDBT	4.23	1.71	315.59	318.40	313.40	305.29		
4-EtDBT	4.23	1.28	312.03	314.38	311.09	302.28		
1,2-DiMeDBT	4.36	1.44	327.49	331.96	323.31	310.51		
1,3-DiMeDBT	4.23	1.44	321.29	325.15	316.95	307.41		
1,4-DiMeDBT	4.23	1.25	318.85	322.50	311.43	305.29		
1,6-DiMeDBT	4.26	1.32	319.18	322.85	312.25	305.86		
1,7-DiMeDBT	4.23	1.44	321.56	325.46	317.27	308.03		
1,8-DiMeDBT	4.23	1.32	318.45	321.57	315.29	305.04		
2,3-DiMeDBT	4.22	1.52	322.58	326.55	324.91	308.12		
2,4-DiMeDBT	4.23	1.34	313.91	316.76	311.78	303.83		
2,6-DiMeDBT	4.24	1.46	314.56	317.47	313.31	305.20		
2,7-DiMeDBT	4.21	1.60	317.47	320.75	319.11	307.62		
2,8-DiMeDBT	4.22	1.37	316.31	319.37	318.88	303.81		
3,4-DiMeDBT	4.26	1.57	320.67	324.52	319.60	309.36		
3,6-DiMeDBT	4.23	1.56	315.46	318.56	313.92	307.19		
3,7-DiMeDBT	4.22	1.73	318.32	321.54	319.45	311.18		
4,6-DiMeDBT	4.21	1.41	312.88	315.60	307.89	303.43		
1,3,7-TrMeDBT	4.24	1.57	335.36	339.78	331.81	317.31		
1,4,7-TrMeDBT	4.24	1.36	332.45	336.85	326.36	313.18		
2,3,7-TrMeDBT	4.23	1.69	337.61	342.07	340.49	319.08		

PASHs	Molecular Shape Parameters				RI Values		
	<i>T</i> (Å)	<i>L/B</i>	50% Phenyl ^d			IL ^b	50% LC ^c
			Rxi-PAH	SLB-PAH			
2,3,8-TriMeDBT	4.22	1.52	336.29	340.57		340.49	313.17
2,4,6-TriMeDBT	4.22	1.41	324.03	327.83		322.59	307.62
2,4,7-TriMeDBT	4.21	1.54	327.22	331.24		328.01	311.74
2,4,8-TriMeDBT	4.22	1.40	325.97	329.83		327.97	307.84
3,4,7-TriMeDBT	4.22	1.70	335.21	339.65		335.11	320.93

^aBaseline resolution on the 50% phenyl phase is achieved with a RI difference of approximately 0.70.

^bBaseline resolution on the IL phase is achieved with a RI difference of approximately 0.75.

^cBaseline resolution on the 50% LC-DMPS phase is achieved with a RI difference of approximately 0.60.

Table 3

GC retention indices for the methyl-substituted isomers of N12T and N21T.

PASHs	Molecular Shape Parameters			RI Values			
	<i>T</i> (Å)	<i>L/B</i>	50% Phenyl ^a		IL ^b	50% LC-DMPS ^c	
			Rxi-PAH	SLB-PAH			
N12T	4.16	1.40	292.90	293.49	289.08	289.34	
2-MeN12T	4.33	1.54	305.75	307.36	305.97	302.46	
4-MeN12T	4.20	1.23	308.41	310.79	307.62	301.98	
5-MeN12T	4.22	1.21	309.57	312.20	308.83	302.03	
6-MeN12T	4.23	1.42	310.13	312.85	309.34	302.94	
7-MeN12T	4.21	1.54	306.99	309.04	307.94	303.96	
8-MeN12T	4.21	1.35	306.47	308.22	306.70	301.17	
9-MeN12T	4.23	1.22	313.01	316.49	311.01	302.99	
N21T	4.06	1.40	301.03	301.47	297.61	299.83	
1-MeN21T	4.23	1.24	313.67	316.96	312.08	303.34	
2-MeN21T	4.21	1.43	308.86	311.01	311.75	303.12	
4-MeN21T	4.21	1.25	309.20	311.52	309.47	302.63	
5-MeN21T	4.22	1.20	313.36	316.64	314.09	303.43	
6-MeN21T	4.21	1.40	313.83	317.18	314.75	304.80	
7-MeN21T	4.21	1.52	310.39	313.05	313.08	305.33	
8-MeN21T	4.21	1.39	309.51	311.80	312.86	302.85	
9-MeN21T	4.24	1.24	315.76	319.55	313.73	304.49	

^aBaseline resolution on the 50% phenyl phase is achieved with a RI difference of approximately 0.6.^bBaseline resolution on the IL phase is achieved with a RI difference of approximately 0.7.^cBaseline resolution on the 50% LC-DMPS phase is achieved with a RI difference of approximately 0.5.

Table 4

GC retention indices for methyl-substituted isomers of BbN12T, BbN21T, BbN23T, and B23P45T.

PASHs	Molecular Shape Parameters				RI Values			
	<i>T</i> (Å)	<i>L/B</i>	50% Phenyl ^d		IL ^b	50% LC-DMPS ^c		
			Rxi-PAH	SLB-PAH				
BbN12T	4.06	1.37	388.69	390.30	383.82	357.22		
1-MeBbN12T	5.28	1.32	400.23	399.44	377.04	351.51		
2-MeBbN12T	4.21	1.27	401.09	400.25	392.86	365.42		
3-MeBbN12T	4.21	1.49	406.02	405.18	396.79	387.84		
4-MeBbN12T	4.22	1.46	410.70	410.46	398.53	391.00		
5-MeBbN12T	4.22	1.30	410.79	410.73	398.47	387.15		
6-MeBbN12T	4.21	1.22	405.63	403.72	394.21	373.93		
8-MeBbN12T	4.21	1.45	404.22	403.86	393.68	381.47		
9-MeBbN12T	4.21	1.48	406.43	406.01	397.08	388.20		
10-MeBbN12T	4.21	1.30	402.31	401.51	393.17	366.35		
11-MeBbN12T	4.99	1.34	401.73	401.14	379.70	357.87		
BbN21T	4.06	1.68	383.32	385.62	380.70	370.83		
1-MeBbN21T	4.23	1.47	411.23	411.55	396.61	401.40		
2-MeBbN21T	4.21	1.56	402.43	401.69	391.83	403.37		
3-MeBbN21T	4.21	1.82	402.69	401.69	393.31	403.37		
4-MeBbN21T	4.23	1.71	406.60	406.35	395.13	401.65		
5-MeBbN21T	4.22	1.47	404.92	404.58	394.81	384.47		
6-MeBbN21T	4.29	1.46	407.13	406.93	393.42	391.71		
7-MeBbN21T	4.23	1.58	407.59	407.13	393.17	397.71		
8-MeBbN21T	4.21	1.74	401.65	401.03	393.22	396.31		
9-MeBbN21T	4.21	1.82	403.07	402.41	393.33	402.41		
10-MeBbN21T	4.21	1.62	398.95	398.32	388.29	379.98		
BbN23T	4.06	1.70	393.07	393.96	388.36	380.01		
1-MeBbN23T	4.24	1.54	410.20	410.68	396.55	397.56		
2-MeBbN23T	4.21	1.64	407.03	407.99	401.56	396.54		
3-MeBbN23T	4.21	1.84	409.79	409.95	400.92	406.75		

PASHs	Molecular Shape Parameters			RI Values			
	<i>T</i> (Å)	<i>L/B</i>	50% Phenyl ^a			IL ^b	50% LC-DMPS ^c
			Rxi-PAH	SLB-PAH			
4-MeBbN23T	4.20	1.70	405.73	406.11		393.16	401.52
6-MeBbN23T	4.21	1.55	409.61	409.94		397.79	400.00
7-MeBbN23T	4.22	1.67	411.01	411.36		398.85	398.71
8-MeBbN23T	4.21	1.84	408.60	408.95		400.72	405.29
9-MeBbN23T	4.21	1.80	408.21	408.52		400.62	401.74
10-MeBbN23T	4.22	1.57	407.85	407.82		397.26	386.44
11-MeBbN23T	4.24	1.59	420.09	421.14		402.81	406.62
B23P45T	4.05	1.46	441.37	443.50		431.90	422.36
1-MeB23P45T	4.20	1.44	451.20	452.42		439.73	426.41
3-MeB23P45T	4.22	1.55	460.80	461.99		448.22	439.03
5-MeB23P45T	4.21	1.30	456.92	458.00		445.33	428.21
7-MeB23P45T	4.22	1.48	459.19	460.31		446.35	432.35
9-MeB23P45T	4.19	1.51	455.27	456.18		444.83	430.38

^aBaseline resolution on the 50% phenyl phase is achieved with a RI difference of approximately 0.7.

^bBaseline resolution on the IL phase is achieved with a RI difference of approximately 0.8.

^cBaseline resolution on the 50% LC-DMPS phase is achieved with a RI difference of approximately 0.8.

Table 5
Correlation coefficients relating retention on the liquid crystalline stationary phases versus L/B .

PASHs	n^a	Equation	r^b	df^c	$t\text{-test } \alpha = 0.05$		
Smectic Liquid Crystalline d							
MeDBT	4	$y = 20.83x + 272.65$	0.82	2	4.30	2.03	No
EtDBT	3	$y = 10.37x + 289.65$	0.55	1	12.71	0.65	No
DiMeDBT	15	$y = 45.03x + 247.01$	0.91	13	2.16	7.81	Yes
1,-DiMeDBT	6	$y = 47.06x + 246.20$	0.90	4	2.78	2.89	Yes
2,-DiMeDBT	5	$y = 48.01x + 240.86$	0.99	3	3.18	12.25	Yes
3,-/4,-DiMeDBT	4	$y = 67.41x + 211.25$	0.98	2	4.30	6.92	Yes
TriMeDBT	6	$y = 76.15x + 207.64$	0.89	4	2.78	2.79	Yes
MeN12T	7	$y = 10.42x + 288.90$	0.74	5	2.57	1.91	No
MeN21T	8	$y = 23.27x + 274.53$	0.85	6	2.45	3.21	Yes
MeBbN12T	10	$y = 102.1x + 230.91$	0.74	8	2.31	2.71	Yes
MeBbN21T	10	$y = 56.03x + 302.41$	0.79	8	2.31	3.17	Yes
MeBbN23T	10	$y = 64.79x + 289.09$	0.76	8	2.31	2.86	Yes
MeB23P45T	-	-	-	-	-	-	-
50% LC-DMPS							
MeDBT	4	$y = 1.88x + 299.33$	0.22	2	4.30	0.32	No
EtDBT	3	$y = 4.20x + 296.67$	0.53	1	12.71	0.62	No
DiMeDBT	15	$y = 13.56x + 287.11$	0.71	13	2.16	3.66	Yes
1,-DiMeDBT	6	$y = 20.73x + 278.66$	0.82	4	2.78	2.88	Yes
2,-DiMeDBT	5	$y = 17.70x + 279.91$	0.92	3	3.18	4.09	Yes
3,-/4,-DiMeDBT	4	$y = 24.28x + 269.72$	0.95	2	4.30	4.33	Yes
TriMeDBT	8	$y = 31.88x + 265.35$	0.84	6	2.45	3.81	Yes
MeN12T	7	$y = 2.86x + 298.62$	0.47	5	2.57	1.19	No
MeN21T	8	$y = 3.82x + 298.66$	0.45	6	2.45	1.24	No
MeBbN12T	10	$y = 87.20x + 256.22$	0.60	8	2.31	2.12	No
MeBbN21T	10	$y = 24.63x + 356.21$	0.42	8	2.31	1.31	No
MeBbN23T	10	$y = 28.71x + 352.06$	0.56	8	2.31	1.91	No

<u>t-test $\alpha = 0.05$</u>						
PASHs	<i>n</i> ^a	Equation	<i>r</i> ^b	<i>df</i> ^c	<i>t</i> _{crit}	<i>t</i> _{exp} Significant
MeB23P45T	5	<i>y</i> = 34.19 <i>x</i> + 381.49	0.67	3	3.18	1.57 No

^a *n* = number of data points.
^b *r* = correlation coefficient.
^c *df* = degrees of freedom.
^d Correlation graphs were calculated using RI values for a smectic liquid crystalline phase obtained with the same retention index markers used in the present study [13].
^e Retention data was not obtained in the previous study for the MeTeP112T isomer set.

Table 6

Correlation coefficients relating retention on the 50% phenyl and IL stationary phases versus L/B .

PASHs	n^a	Equation	r^b	df^c	t_{crit}	t_{exp}	Significant
50% phenyl							
MeDBT	4	$y = -11.21x + 324.74$	-0.50	2	4.30	0.81	No
EtDBT	3	$y = 7.94x + 304.10$	0.92	1	12.71	2.36	No
DiMeDBT	15	$y = 2.66x + 318.18$	0.08	13	2.16	0.29	No
1,-DiMeDBT	6	$y = 32.51x + 280.43$	0.71	4	2.78	2.03	No
2,-DiMeDBT	5	$y = 20.69x + 290.01$	0.57	3	3.18	1.20	No
3,-/4,-DiMeDBT	4	$y = 18.82x + 290.54$	0.64	2	4.30	1.18	No
TriMeDBT	6	$y = 28.29x + 292.88$	0.66	4	2.78	1.76	No
MeN12T	7	$y = -14.05x + 330.07$	-0.65	5	2.57	1.91	No
MeN21T	8	$y = -14.05x + 333.46$	-0.50	6	2.45	1.41	No
MeBbN12T	10	$y = 16.16x + 382.21$	0.40	8	2.31	1.23	No
MeBbN21T	10	$y = -14.64x + 427.97$	-0.53	8	2.31	1.76	No
MeBbN23T	10	$y = -9.67x + 426.44$	-0.28	8	2.31	0.82	No
MeB23P45T	5	$y = 11.42x + 441.16$	0.30	3	3.18	0.55	No
IL							
MeDBT	4	$y = 14.10x + 281.53$	0.47	2	4.30	0.76	No
EtDBT	3	$y = 4.18x + 305.64$	0.83	1	12.71	1.48	No
DiMeDBT	15	$y = 18.46x + 289.56$	0.50	13	2.16	2.07	No
1,-DiMeDBT	6	$y = 42.23x + 258.29$	0.82	4	2.78	2.88	Yes
2,-DiMeDBT	5	$y = 27.01x + 278.22$	0.55	3	3.18	1.13	No
3,-/4,-DiMeDBT	4	$y = 36.32x + 258.28$	0.86	2	4.30	2.38	No
TriMeDBT	8	$y = 37.43x + 274.58$	0.73	6	2.45	2.99	Yes
MeN12T	7	$y = -6.11x + 316.50$	-0.53	5	2.57	1.39	No
MeN21T	8	$y = 1.81x + 310.31$	0.13	6	2.45	0.32	No
MeBbN12T	10	$y = 23.56x + 360.03$	0.30	8	2.31	0.89	No
MeBbN21T	10	$y = -2.73x + 397.75$	-0.17	8	2.31	0.49	No
MeBbN23T	10	$y = 7.33x + 386.75$	-0.30	8	2.31	0.89	No

<u>t-test $\alpha = 0.05$</u>							
PASHs	n^a	Equation	r^b	df^c	t_{crit}	t_{exp}	Significant
MeB23P45T	5	$y = 9.72x + 430.74$	0.30	3	3.18	0.55	No

^a n = number of data points.

^b r = correlation coefficient.

^c df = degrees of freedom.