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Journal of Chromatography A, 841 (1999) 207–228

JOURNAL OF CHROMATOGRAPHY A

Gas chromatographic retention behavior of polycyclic aromatic sulfur heterocyclic compounds, (dibenzothiophene, naphtho[*b*]thiophenes, benzo[*b*]naphthothiophenes and alkyl-substituted derivatives) on stationary phases of different selectivity

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Received 12 November 1998; accepted 10 March 1999

Abstract

Retention indices for 80 polycyclic aromatic sulfur heterocyclic compounds (PASHs) were determined by using high-resolution capillary gas chromatography (GC) with three different stationary phases: a 5% (mole fraction) phenyl-substituted methylpolysiloxane column, a 50% (mole fraction) phenyl-substituted methylpolysiloxane column and a smectic liquid crystalline column. Retention data were obtained for the following PASHs: dibenzothiophene, 28 alkyldibenzothiophenes, naphtho[1,2-*b*]thiophene, seven of the eight possible methylnaphtho[1,2-*b*]thiophenes, naphtho[2,1-*b*]thiophene, all eight methylnaphtho[2,1-*b*]thiophenes, naphtho[2,3-*b*]thiophene, the three benzo[*b*]naphthothiophene isomers (benzo[*b*]naphtho[1,2-*d*]thiophene, benzo[*b*]naphtho[2,1-*d*]thiophene and benzo[*b*]naphtho[2,3-*d*]thiophene), and all 30 possible methylbenzo[*b*]naphthothiophene isomers. Molecular descriptors [length, breadth, thickness (T), and length-to-breadth ratio (L/B)] were calculated for all the compounds studied. Correlations for retention on the liquid crystalline phase and solute geometry (L/B and T) ratios were investigated, and the retention was found to be highly correlated with L/B resulting in correlation coefficients ranging from $r=0.68$ to $r=0.98$. Published by Elsevier Science B.V.

Keywords: Retention indices; Stationary phases, GC; Molecular descriptors; Retention behavior; Polycyclic aromatic compounds; Polycyclic aromatic sulfur heterocyclic compounds; Thiophenes; Naphthothiophenes; Benzothiophenes

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widely studied groups of environmental contaminants [1–4]; however, their sulfur analogues, polycyclic aromatic sulfur heterocyclic compounds (PASHs), have received relatively little systematic attention [5], possibly due to the lower levels of

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0021-9673/99/$ – see front matter Published by Elsevier Science B.V.
PII: S0021-9673(99)00363-5

PASHs compared to PAHs in environmental samples and/or the limited availability of authentic reference standards for PASHs. PASHs and to a limited extent alkyl-substituted PASHs, have been determined in fossil fuels [6–12], sediments [13–15], mussels and fish [13,14,16,17], and airborne particulate matter [18,19]. Gas chromatography (GC) has been the preferred analytical technique for the separation and measurement of PASHs in these environmental samples. Because the isomeric structures of the alkyl-substituted PASHs are even more numerous than those of the PAHs, due to the asymmetry imposed by the sulfur atom, the separation and determination of individual alkyl-substituted PASH isomers in environmental samples is a challenging task requiring knowledge about the GC retention behavior of the various isomers on a variety of stationary phases with different selectivity. Relatively few papers have reported extensive GC retention data for PASHs and alkyl-substituted PASHs [20–22].

In this study we report the GC retention behavior of 80 PASHs and alkyl-substituted PASHs on three different GC stationary phases, i.e., two nonpolar phases (5% [mole fraction] phenyl-substituted methylpolysiloxane and 50% [mole fraction] phenyl-substituted methylpolysiloxane) and a smectic liquid crystalline stationary phase. The 5% phenyl-substituted methylpolysiloxane phase is commonly used for the separation of PAHs. The 50% phenyl-substituted methylpolysiloxane phase, while still considered a nonpolar phase, has been shown to exhibit improved separations of some PAH isomers [23,24]. The smectic liquid crystalline phase has been demonstrated to separate PAH isomers based in part on the molecular shape of the solute, and it has been shown to be particularly useful in the separation of methyl-substituted PAH isomers [25–32]. Based on their application for PAH separations, these three stationary phases were investigated and GC retention indices were determined for the separation of 80 PASHs and alkyl-substituted PASHs.

This extensive data set of retention indices of PASHs is not only useful as an aid in the selection of the appropriate stationary phase and the identification of individual PASH isomers in complex environmental samples, but these data are also useful for investigations of differences in selectivity among stationary phases. For the nonpolar stationary phases the separation is attributed mainly to differences in vapor pressure of the solutes. However, for the liquid crystalline phase the separation of isomeric compounds is related to the molecular shape of the solute, and as a result, this phase provides very different separation selectivity compared to the nonpolar phases. A number of papers have reported the improved separation of PAHs [25–32] and PASHs [22,31–34] on the smectic liquid crystalline stationary phase.

One of the earliest observations concerning solute shape and GC retention for PAHs on a liquid crystalline phase was made by Janini et al. [35], who observed that retention among isomeric PAHs increased with increasing ratio of the length to the breadth of the molecule, as determined by a very rough estimate of these dimensions. Later Radecki et al. [36] proposed a formal shape parameter, defined as the ratio of the length to the breadth (L/B) of a box drawn to enclose the atoms of the PAH molecule, and correlated it with GC retention. The L/B parameter was correlated with reversed-phase liquid chromatographic retention of PAHs on polymeric C_{18} phases by Wise et al. [37]. The L/B value has been used extensively for correlations with retention on liquid crystalline phases in GC [22,26–28] and on C_{18} phases in liquid chromatography (LC) [26,37–42]. The L/B value has become the primary solute shape parameter for such investigations and a detailed discussion of its calculation and use is described elsewhere [41,42]. Solute planarity/thickness has also been observed to influence the separation of PAH isomers on shape-selective phases in both GC and LC [38,39,41]. Wise and Sander [41] calculated the thickness (T) of the solute and used this parameter to quantify the nonplanarity of the PAH solutes as a means of explaining anomalous retention behavior in LC on C_{18} phases and in GC on the smectic liquid crystalline phase.

In this study the investigation of shape selectivity for GC retention on the liquid crystalline phase is extended to PASHs and particularly the alkyl-substituted PASHs. In a companion study [43] the LC retention behavior of these same PASHs is reported and the correlation between LC retention and molecular shape parameters is discussed.

2. Experimental[3]

2.1. Materials

GC retention indices on the three stationary phases were determined for the following three-ring PASHs: dibenzothiophene (DBT) and 28 alkyl-substituted DBTs (all four methyl-substituted DBTs, three of the four possible ethyl-substituted DBTs, 15 of the 16 possible dimethyl-substituted DBTs, and six of the 28 possible trimethyl-substituted DBTs), naphtho[1,2-*b*]thiophene (N12*b*T) and seven of the eight possible methyl-substituted N12*b*Ts, naphtho[2,1-*b*]thiophene (N21*b*T) and all eight methyl-substituted N21*b*Ts, and naphtho[2,3-*b*]thiophene (N23*b*T). Retention data were also obtained for the following four-ring PASHs: the four benzo[*b*]naphthothiophene (BNT) isomers [benzo[*b*]naphtho[1,2-*d*]thiophene (BN12T), benzo[*b*]naphtho[2,1-*d*]thiophene (BN21T), and benzo[*b*]naphtho[2,3-*d*]thiophene (BN23T)], and all 30 possible methyl-substituted benzo[*b*]-naphthothiophene (MeBNT) isomers.

The following PAHs and PASHs were obtained from commercial sources: three dimethyl-substituted DBTs were obtained from Chiron (Trondheim, Norway) and the methyl- and trimethyl-substituted DBTs were purchased from Astec (Münster, Germany). DBT was available from Aldrich (Milwaukee, WI, USA); BN12T, BN21T, BN23T, chrysene, and benzo[*a*]pyrene from the Community Bureau of Reference (BCR) of the Commission of the European Community (Brussels, Belgium); phenanthrene from Fluka (Buchs, Switzerland); picene from Pfaltz and Bauer (Waterbury, CT, USA). Benzo[2,3]phenanthro[4,5-*bcd*]thiophene (B23P45T), all the methyl-substituted BNTs, benzo[*b*]-phenanthro[2,1-*d*]thiophene (BP21T), the ethyl-substituted DBTs, the remaining dimethyl-substituted DBTs, and the naphtho[*b*]thiophene isomers together with their methyl-substituted isomers were synthesized at Brigham Young University (Provo, UT, USA).

2.2. Molecular descriptors calculations

The calculations for the molecular descriptors [length (L), breadth (B), thickness (T), and length-to-breadth ratio (L/B)] for the PASHs were carried out using commercial molecular modeling programs (PC-Model and MMX, Serena Software, Bloomington, IN, USA) and algorithms developed in this laboratory [40].

2.3. GC retention data

The retention index system originally introduced by Kováts [44] is used to compare retention on different columns. These retention indices (I) are calculated by comparing the retention times of the compounds to the retention times of homologous *n*-alkanes, used as index markers. Van den Dool and Kratz [45] extended this retention index system for the use of temperature-programmed GC runs. Lee et al. [46] reported that more reproducible results could be obtained when retention index markers were selected to resemble the compounds analyzed, and naphthalene, phenanthrene, chrysene and picene were chosen as index markers for PAHs. These compounds were assigned retention indices [I_C – designated as retention indices carbon] values of 200, 300, 400, and 500, respectively. Andersson [21] extended this retention index system for PASHs [I_S – designated as retention indices sulfur] using thiophene ($I_S=100$), benzothiophene (200), DBT (300), BN21T (400), and BP21T (500). The I_C and I_S values in this paper were calculated according to the following equation [46]:

$$I_C/I_S = 100z + 100 \cdot \frac{t_{R(x)} - t_{R(z)}}{t_{R(z+1)} - t_{R(z)}} \quad (1)$$

where x is the compound of interest, t_R the retention time, and z and $z+1$ are the numbers of aromatic rings of the index markers eluting before and after the respective compound of interest.

The five-ring retention index markers, picene and

[3]Certain commercial equipment, instruments, or materials are identified to specify adequately the experimental procedure. such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are the best available for the purpose.

BP21T, did not elute within the temperature limit of the smectic liquid crystalline stationary phase. Therefore, two additional retention index markers were chosen to calculate the retention data for the late-eluting methyl-substituted BNTs. Benzo[*a*]pyrene and benzo[2,3]phenanthro[4,5-*bcd*]thiophene (B23P45T) were selected due to structural similarities and were assigned I_C and I_S values of 450. The I_S value for B23P45T was 455.95, and this is consistent with the use of B23P45T as the retention marker between BN21T (400) and BP21T (500). Benzo[*a*]pyrene has a I_C value of 454.02 [20] and therefore serves as an intermediate retention index marker between chrysene and picene. The following equation was used to calculate retention data on the smectic column for compounds eluting between chrysene and benzo[*a*]pyrene and BN21T and B23P45T:

$$I_C/I_S = 100z + 50 \cdot \frac{t_{R(x)} - t_{R(z)}}{t_{R(z+1)} - t_{R(z)}} \quad (2)$$

where x is the compound of interest, t_R the retention time, and z and $z+1$ are the numbers of aromatic rings of the index markers eluting before and after the respective compound. Reported values are the mean of at least three measurements. The standard deviation of a single measurement of the retention times was typically less than 0.03 min on all three columns. For all three columns baseline resolution is achieved for differences in I_C or I_S values of generally 0.5 to 0.7 index units for the three-ring isomers and differences of 0.9 to 1.2 index units for the BNT isomers.

2.4. Gas chromatographic conditions

The PASH retention data were obtained by using a GC–mass spectrometry (MS) system (Hewlett-Packard, Palo Alto, CA, USA). Samples were introduced by on-column injection, and helium was used as carrier gas. Analyses were performed in the single ion monitoring (SIM) mode. Retention data of various PASHs were obtained using three different GC stationary phases: a 5% phenyl-substituted methylpolysiloxane phase (DB-5MS: 60 m×0.25 mm I.D., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA), a 50% phenyl-substituted methylpolysiloxane phase (DB-17: two coupled 30 m columns, 0.25 mm I.D. each, 0.25 μm film thickness each, both from J&W Scientific), and a liquid crystalline polysiloxane phase (SB-Smectic: 25 m×0.20 mm I.D., 0.15 μm film thickness, Dionex, Salt Lake City, UT, USA).

The temperature program used with the DB-5MS column had an initial isothermal period of 1 min at 60°C, then an increase at 45°C/min to 150°C, followed by an isothermal period of 2 min at 150°C, then an increase at 2°C/min to 300°C with an isothermal period of 25 min at 300°C. The temperature program used with the DB-17 column had an initial isothermal period of 1 min at 60°C, then an increase at 35°C/min to 190°C, followed by an isothermal period of 1 min at 190°C, then an increase at 1°C/min to 320°C. For the SB-Smectic the initial isothermal period was 1 min at 60°C, then an increase at 35°C/min to 190°C, followed by an isothermal period of 1 min at 190°C, then an increase at 1°C/min to 260°C. The temperature programs above were developed to provide optimal separations for the determination of these PASHs in fossil-fuel samples [6]. Although two isothermal and two temperature programmed periods were used for our retention indices measurements, all compounds eluted within the main (second) temperature programmed zone, therefore justifying the use of the equation introduced by Van den Dool and Kratz [45]. This same approach has been reported previously in the literature [22,27].

3. Results and discussion

The structures of the PASH compounds studied are shown in Fig. 1 with the numbering of the positions available for substitution. The molecular shape parameters (L, B, T and L/B ratio) for each three-ring and four-ring PASH compound of interest and the alkyl-substituted isomers are summarized in Tables 1 and 2, respectively. The retention indices for 80 three-ring and four-ring PASH compounds were determined on three different stationary phases and are reported in Tables 3 and 4, respectively. To our knowledge, the GC retention indices in Tables 3 and 4 represent the most extensive compilation of GC retention data on different stationary phases for

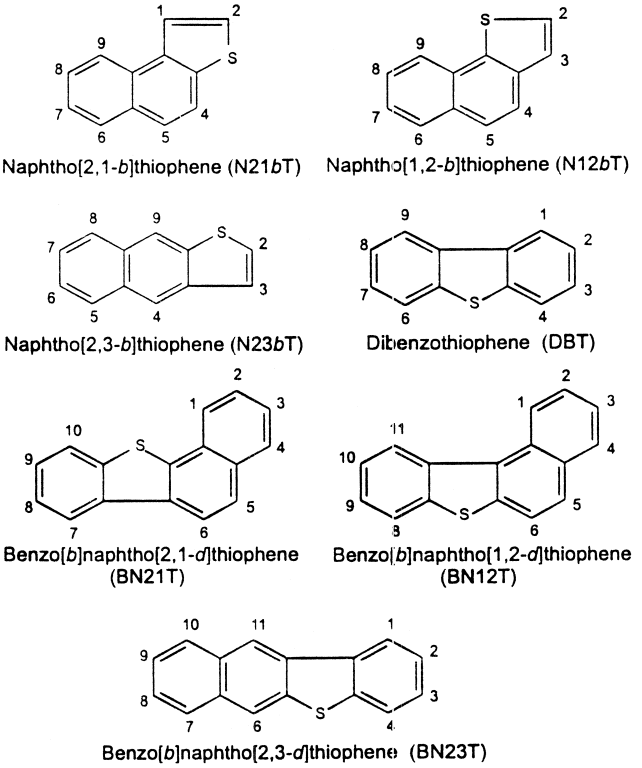

Fig. 1. Structures and substitution position numbering for the PASHs of interest.

PASHs, particularly for alkyl-substituted PASHs, and will serve as a valuable resource in the identification of individual alkyl-substituted PASH isomers in complex environmental mixtures. Mössner and Wise [6] recently used these retention data to identify and quantify most of these 80 PASHs in three fossil fuel-related samples (coal tar, crude oil and decant oil).

A comparison between the I_C/I_S values for the methyl and dimethyldibenzothiophenes presented in Table 3 for the liquid crystalline phase with similar I_C/I_S values reported by Budzinski et al. [22] indicates that our values were consistently lower (0.5% to 2.5%). These differences in I_C/I_S values can be attributed to differences in the smectic liquid crystalline phase columns and the difficulties in preparing reproducible liquid crystalline stationary phases [28]. The differences in the retention index values also reflect differences in selectivity, i.e., isomers that were separated on our column were sometimes not separated on their column and vice versa [22]. The I_C/I_S values reported by Lee et al. [20] in 1982 using a methylpolysiloxane phase (SE-52) coated on a fused-silica capillary column are generally up to 1.0% higher than the I_C/I_S values reported in this study on the 5% phenyl methylpolysiloxane phase (DB-5MS) (see Tables 3 and 4), which is a similar nonpolar stationary phase. These small differences may be due to the different temperature programs used. The order of elution is, with only a few exceptions, identical in both studies.

The GC retention characteristics of the three stationary phases and the correlations between the retention on the liquid crystalline phase and the shape parameters are discussed in detail for each isomeric group of PASHs in the following sections. Regression calculations were performed to correlate the retention on the smectic phase with L/B ratio and solute thickness T; the correlation coefficients are summarized in Table 5. Correlation of retention vs. L/B and T resulted in correlation coefficients ranging from $r=0.68$ to 0.98 and $r=0.11$ to 0.99, respective-

Table 1
Molecular shape parameters for the three-ring PASHs: dibenzothiophene (DBT), C_1–C_3-substituted DBTs, naphtho[*b*]thiophenes (N*b*Ts), and C_1-substituted N*b*Ts

Compounds	Length (*L*) (Å)	Breadth (*B*) (Å)	Thickness (*T*) (Å)	*L*/*B*
DBT	11.58	7.99	4.06	1.45
N12*b*T	11.32	8.06	4.06	1.40
N21*b*T	11.10	8.03	4.06	1.38
N23*b*T	11.63	7.45	4.06	1.56
1-MeDBT	11.22	8.55	4.23	1.31
2-MeDBT	11.97	8.20	4.21	1.46
3-MeDBT	12.69	7.99	4.21	1.59
4-MeDBT	11.56	8.05	4.21	1.44
1-EtDBT[a]	11.20	9.69	5.08	1.16
2-EtDBT	12.32	8.65	4.26	1.42
3-EtDBT	13.74	7.99	5.13	1.72
4-EtDBT	12.68	8.11	4.22	1.56
1,2-DiMeDBT	12.28	8.52	4.36	1.44
1,3-DiMeDBT	12.30	8.54	4.23	1.44
1,4-DiMeDBT	11.58	9.24	4.23	1.25
1,6-DiMeDBT	11.26	8.54	4.26	1.32
1,7-DiMeDBT	12.33	8.54	4.23	1.44
1,8-DiMeDBT	12.05	9.10	4.23	1.32
1,9-DiMeDBT[a]	11.42	9.03	5.21	1.26
2,3-DiMeDBT	12.51	8.21	4.22	1.52
2,4-DiMeDBT	11.96	8.94	4.23	1.34
2,6-DiMeDBT	11.96	8.20	4.24	1.46
2,7-DiMeDBT	13.08	8.20	4.21	1.60
2,8-DiMeDBT	12.04	8.78	4.22	1.37
3,4-DiMeDBT	12.67	8.05	4.26	1.57
3,6-DiMeDBT	12.63	8.08	4.23	1.56
3,7-DiMeDBT	13.80	7.99	4.22	1.73
4,6-DiMeDBT	11.58	8.24	4.21	1.41
1,3,7-TriMeDBT	13.42	8.54	4.24	1.57
1,4,7-TriMeDBT	12.68	9.24	4.25	1.37
2,4,6-TriMeDBT	11.95	8.95	4.23	1.34
2,4,7-TriMeDBT	13.07	8.94	4.22	1.46
2,4,8-TriMeDBT	12.08	9.08	4.22	1.33
3,4,7-TriMeDBT	13.78	8.05	4.31	1.71
2-MeN12*b*T	12.42	8.05	4.21	1.54
3-MeN12*b*T[a]	11.94	8.07	4.21	1.48
4-MeN12*b*T	11.31	9.30	4.21	1.22
5-MeN12*b*T	11.30	9.29	4.21	1.22
6-MeN12*b*T	11.47	8.06	4.22	1.42
7-MeN12*b*T	12.43	8.05	4.21	1.54
8-MeN12*b*T	11.54	8.53	4.21	1.35
9-MeN12*b*T	11.39	9.24	4.23	1.23
1-MeN21*b*T	11.04	8.89	4.23	1.24
2-MeN21*b*T	11.97	8.34	4.21	1.44
4-MeN21*b*T	11.04	9.12	4.21	1.21
5-MeN21*b*T	11.10	9.27	4.22	1.20
6-MeN21*b*T	11.22	8.03	4.22	1.40
7-MeN21*b*T	12.21	8.01	4.20	1.52
8-MeN21*b*T	11.69	8.42	4.21	1.39
9-MeN21*b*T	10.84	8.73	4.50	1.24

[a] Reference standard was not available; therefore GC retention data was not obtained for this compound.

Table 2
Molecular shape parameters for the four-ring PASHs: benzo[*b*]naphthothiophenes (BNTs) and C_1-substituted BNTs

Compounds	Length (*L*) (Å)	Breadth (*B*) (Å)	Thickness (*T*) (Å)	*L*/*B*
BN12T	12.54	9.23	4.39	1.36
1-MeBN12T	12.27	9.36	5.56	1.31
2-MeBN12T	12.36	9.85	4.60	1.26
3-MeBN12T	13.64	9.23	4.44	1.48
4-MeBN12T	13.37	9.25	4.74	1.45
5-MeBN12T	12.36	9.56	4.58	1.29
6-MeBN12T	12.50	10.35	4.45	1.21
8-MeBN12T	13.25	9.23	4.50	1.44
9-MeBN12T	13.60	9.22	4.53	1.47
10-MeBN12T	12.29	9.51	4.63	1.29
11-MeBN12T	12.28	9.22	5.24	1.33
BN21T	13.65	8.09	4.08	1.69
1-MeBN21T	13.64	9.13	4.23	1.49
2-MeBN21T	13.64	8.73	4.21	1.56
3-MeBN21T	14.77	8.09	4.21	1.82
4-MeBN21T	13.82	8.09	4.23	1.71
5-MeBN21T	13.65	9.30	4.22	1.47
6-MeBN21T	13.65	9.34	4.23	1.46
7-MeBN21T	13.51	8.54	4.23	1.58
8-MeBN21T	14.15	8.22	4.21	1.72
9-MeBN21T	14.76	8.09	4.21	1.82
10-MeBN21T	13.62	8.36	4.21	1.63
BN23T	13.85	8.18	4.06	1.69
1-MeBN23T	13.84	9.03	4.23	1.53
2-MeBN23T	14.22	8.76	4.21	1.62
3-MeBN23T	14.96	8.19	4.21	1.83
4-MeBN23T	13.84	8.19	4.21	1.69
6-MeBN23T	13.86	8.97	4.22	1.55
7-MeBN23T	13.89	8.37	4.22	1.66
8-MeBN23T	14.94	8.19	4.21	1.83
9-MeBN23T	14.45	8.33	4.21	1.74
10-MeBN23T	13.53	8.65	4.22	1.56
11-MeBN23T	13.64	8.52	4.61	1.60

ly. Although solute shape influences retention on the liquid crystalline phase, other factors also contribute to the retention. In the most general case, solute retention can be considered in terms of enthalpic and entropic contributions to the free energy of the retention process. The SB-Smectic stationary phase consists of a siloxane polymer with approximately 50% substitution with 3-[4′-(4-methoxyphenoxycarbonyl)biphenyl-4-yloxy]propyl groups [30]. Because the stationary phase retains considerable nonpolar character in addition to the liquid crystalline substituents, solute retention may involve dispersive-type interactions in addition to shape-selective interactions.

3.1. Methyldibenzothiophenes (MeDBTs) and ethyldibenzothiophenes (EtDBTs)

GC separations of DBT, the MeDBTs, and three of the four possible EtDBTs are shown in Fig. 2. Good separations were obtained with all of the columns; however, the 2-Me and 3-MeDBT were not resolved with the 5% phenyl methylpolysiloxane column, and the elution order on the liquid crys-

Table 3
GC retention indices (I_C and I_S) for the three-ring PASHs: dibenzothiophene (DBT), C_1–C_3-substituted DBTs, naphtho[*b*]thiophenes (N*b*Ts), and C_1-substituted N*b*Ts on three stationary phases (DB-5MS, DB-17 SB-Smectic)

Compounds	DB-5MS		DB-17		SB-Smectic	
	I_C	I_S	I_C	I_S	I_C	I_S
DBT	293.59	300.00	296.19	300.0	297.58	300.00
N12*b*T	293.28	299.80	295.96	301.37	297.23	299.13
N21*b*T	299.79	304.28	302.27	306.95	299.87	302.34
N23*b*T	304.33	309.09	306.76	311.83	304.69	308.18
1-MeDBT	317.10	322.86	317.27	322.90	300.94	304.08
2-MeDBT	313.71	319.21	310.36	315.39	302.01	305.38
3-MeDBT	313.98	319.51	311.51	316.65	307.53	312.09
4-MeDBT	310.76	316.05	308.08	312.91	301.57	304.85
2-EtDBT	328.54	335.15	322.76	328.87	302.80	306.34
3-EtDBT	329.77	336.47	324.71	330.99	310.80	316.06
4-EtDBT	324.59	330.91	320.13	326.01	303.48	307.17
1,2-DiMeDBT	341.29	348.92	339.40	346.94	316.74	322.92
1,3-DiMeDBT	334.73	341.81	332.09	338.96	311.41	316.53
1,4-DiMeDBT	332.53	339.51	328.91	335.55	306.02	310.08
1,6-DiMeDBT	332.80	339.74	329.33	336.01	308.55	313.10
1,7-DiMeDBT	335.55	342.67	331.78	338.67	314.32	320.01
1,8-DiMeDBT	332.86	339.77	328.29	334.87	306.50	310.66
2,3-DiMeDBT	337.58	344.94	332.62	339.58	314.69	320.46
2,4-DiMeDBT	328.05	334.62	321.13	327.09	305.56	309.52
2,6-DiMeDBT	328.83	335.47	322.16	328.21	310.83	315.83
2,7-DiMeDBT	332.02	338.89	325.70	332.06	317.23	323.50
2,8-DiMeDBT	332.00	338.86	324.28	330.51	306.02	310.08
3,4-DiMeDBT	335.09	342.21	330.61	337.39	318.99	325.60
3,6-DiMeDBT	329.25	335.90	323.23	329.38	317.65	324.00
3,7-DiMeDBT	332.23	339.11	326.52	332.95	326.34	334.41
4,6-DiMeDBT	325.75	332.15	320.42	326.33	304.69	308.49
1,3,7-TriMeDBT	352.37	360.82	345.70	354.11	328.35	336.85
1,4,7-TriMeDBT	350.56	358.87	342.79	350.94	319.48	326.11
2,4,6-TriMeDBT	342.49	350.18	333.66	341.04	310.40	315.09
2,4,7-TriMeDBT	345.94	353.90	336.83	344.48	321.36	328.38
2,4,8-TriMeDBT	345.76	353.70	335.50	343.03	310.73	315.50
3,4,7-TriMeDBT	352.91	361.40	345.56	353.96	339.36	350.20
2-MeN12*b*T	312.11	317.46	309.89	315.23	304.81	308.32
4-MeN12*b*T	314.82	320.38	314.64	320.38	301.01	303.45
5-MeN12*b*T	316.24	321.91	316.29	322.18	300.94	303.37
6-MeN12*b*T	317.11	322.85	317.19	323.15	304.14	307.25
7-MeN12*b*T	313.54	319.00	312.02	317.54	305.66	309.10
8-MeN12*b*T	312.90	318.31	311.46	316.93	300.85	303.26
9-MeN12*b*T	320.18	326.15	321.34	327.66	303.96	307.04
1-MeN21*b*T	320.76	326.78	322.19	328.58	303.15	306.05
2-MeN21*b*T	316.28	321.96	314.73	320.48	305.81	309.54
4-MeN21*b*T	315.73	321.36	315.36	321.17	302.83	305.67
5-MeN21*b*T	320.34	326.33	321.53	327.87	303.20	306.11
6-MeN21*b*T	321.26	327.32	322.26	328.66	307.84	311.99
7-MeN21*b*T	317.67	323.45	317.12	323.08	312.22	317.31
8-MeN21*b*T	317.18	322.92	315.92	321.78	304.59	308.05
9-MeN21*b*T	322.83	329.01	325.22	331.87	304.96	308.50

Table 4
GC retention indices (I_C and I_S) for the four-ring PASHs: benzo[*b*]naphthothiophenes (BNTs) and C_1-substituted BNTs on three stationary phases (DB-5MS, DB-17 SB-Smectic)

Compounds	DB-5MS		DB-17		SB-Smectic	
	I_C	I_S	I_C	I_S	I_C	I_S
BN12T	392.18	403.61	388.76	407.84	359.02	374.64
1-MeBN12T	400.83	413.02	403.52	423.26	349.31	362.86
2-MeBN12T	406.23	418.33	401.35	420.99	360.51	376.43
3-MeBN12T	409.99	422.05	408.37	428.32	385.73	405.01[a]
4-MeBN12T	414.04	426.04	419.02	439.45	384.60	404.22[a]
5-MeBN12T	413.36	425.38	418.44	438.85	375.10	394.12
6-MeBN12T	408.16	420.24	406.46	426.36	365.72	382.75
8-MeBN12T	407.73	419.88	406.95	426.86	378.39	398.11
9-MeBN12T	410.23	422.25	409.62	429.63	384.60	404.22[a]
10-MeBN12T	407.23	419.32	403.64	423.40	361.54	377.69
11-MeBN12T	402.67	414.81	405.29	425.10	354.73	369.43
BN21T	388.86	400.00	381.45	400.00	379.83	400.00
1-MeBN21T	413.97	425.94	418.78	439.21	395.51	413.82[a]
2-MeBN21T	405.62	417.71	399.89	419.48	386.71	405.60[a]
3-MeBN21T	406.53	418.61	401.62	421.29	407.02[a]	425.44[a]
4-MeBN21T	410.61	422.63	409.98	430.01	402.82[a]	420.75[a]
5-MeBN21T	409.35	421.38	407.17	427.09	379.69	399.65
6-MeBN21T	410.58	422.60	412.27	432.40	384.27	404.13[a]
7-MeBN21T	411.03	423.04	412.32	432.45	394.32	412.47[a]
8-MeBN21T	406.22	418.33	400.93	420.55	397.11	414.78[a]
9-MeBN21T	406.72	418.80	402.65	422.36	405.38[a]	423.61[a]
10-MeBN21T	403.12	415.25	397.29	416.75	381.70	401.50[a]
BN23T	395.69	407.45	391.14	410.35	385.26	404.49[a]
1-MeBN23T	414.47	426.45	417.19	437.54	388.91	407.69[a]
2-MeBN23T	413.67	425.66	410.76	430.81	388.91	407.69[a]
3-MeBN23T	414.21	426.12	414.04	434.26	411.46[a]	430.40[a]
4-MeBN23T	410.66	422.65	407.97	427.93	402.50[a]	420.39[a]
6-MeBN23T	414.01	425.96	415.75	436.05	392.10	410.72[a]
7-MeBN23T	415.57	427.54	418.32	438.72	393.55	411.72[a]
8-MeBN231T	413.75	425.77	411.47	431.58	409.03[a]	427.69[a]
9-MeBN23T	413.75	425.74	410.71	430.79	401.91[a]	419.73[a]
10-MeBN23T	413.13	425.13	411.80	431.92	381.30	401.52[a]
11-MeBN23T	421.93	433.80	436.43	457.62	405.76[a]	424.03[a]

[a] I_C/I_S data were calculated with the retention index markers benzo[*a*]pyrene and benzo[2,3]phenanthro[4,5-*bcd*]thiophene (see Section 2.3).

talline phase is significantly different from the other two phases. For the 5% phenyl and 50% phenyl methylpolysiloxane phases, solute retention is primarily attributed to differences in the vapor pressure of the solutes, and the elution order on these two phases is similar. This trend is observed for the alkyl-substituted DBT derivatives, because all the MeDBTs elute before the EtDBTs on both nonpolar columns. However, on the smectic liquid crystalline phase the elution of the MeDBTs and the EtDBT isomers is interspersed, and the elution order within each isomer group follows increasing length-to-breadth (L/B) ratios. Isomers substituted in the 3-position (see Table 1) have the largest L/B ratios within their alkylation group and elute last on the liquid crystalline phase (see Fig. 2). Solute thickness values for the MeDBTs are all similar whereas for the EtDBTs the values range from $T=4.22$ Å for 4-EtDBT to $T=5.13$ Å for 3-EtDBT (see Table 1).

For the MeDBTs good correlations of retention on

Table 5
Correlation coefficients relating retention on the liquid crystalline phase with shape parameters

Compounds[a]	Length-to-breadth (L/B) correlation coefficient[b]	Thickness (T) correlation coefficient[c]
MeDBTs (4)	0.89	0.45
EtDBTs (3)	0.92	0.99
DiMeDBTs (15)	0.89	0.17
TriMeDBTs (6)	0.98	0.83
DBT/NTs (4)	0.82	0.29
MeN12*b*Ts (7)	0.68	0.27
MeN21*b*Ts (8)	0.87	0.11
MeBN12Ts (10)	0.73	0.72
MeBN21Ts (10)	0.81	0.13
MeBN23Ts (10)	0.81	0.25

[a] Numbers in parentheses give the number of isomers included in the regression calculations.
[b] Correlation coefficient for the following equation: $y\ [I_S\ (\text{SB-Smectic})] = m \cdot L/B + b$.
[c] Correlation coefficient for the following equation: $y\ [I_S\ (\text{SB-Smectic})] = m \cdot T + b$.

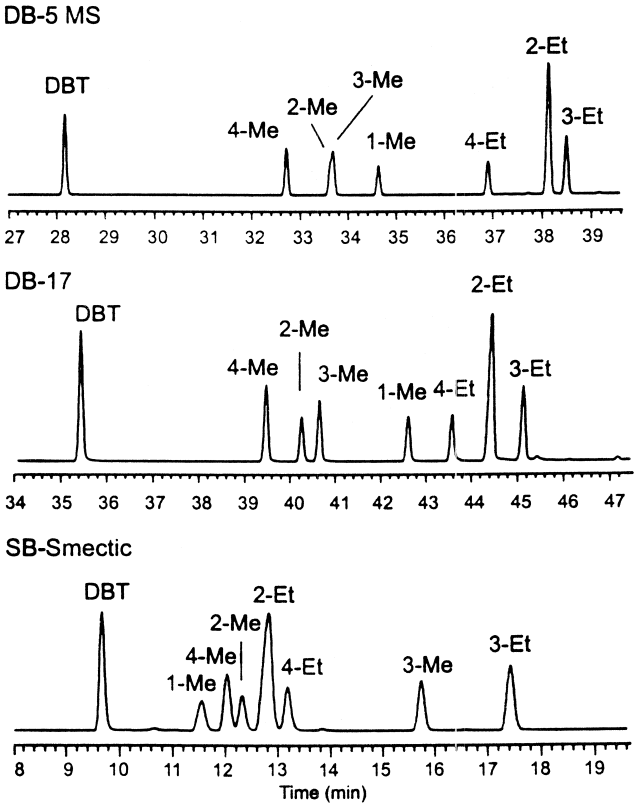

Fig. 2. GC–MS separation of dibenzothiophene (DBT) (m/z 184), four methyl-DBT (MeDBT) isomers (m/z 198), and three ethyl-DBT (EtDBT) isomers (m/z 212) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. The numbers identify the MeDBT and EtDBT isomers.

the liquid crystalline phase were observed with the L/B ratio ($r=0.89$) in contrast to the low correlation with the solute thickness ($r=0.45$), due to the fact that the T values are all very similar. The regression calculations for the three EtDBTs provided correlation coefficients of r (L/B ratio)$=0.92$ and r (T)$=$ 0.99 indicating that the solute parameters, L/B and T, have significant influence on their retention on the liquid crystalline column.

3.2. Dimethyldibenzothiophenes (DiMeDBTs)

The separations of 15 DiMeDBTs on the three GC stationary phases are shown in Fig. 3. Complete resolution of all components was not achieved on any of the columns; however, the best separation of the DiMeDBTs was obtained with the 50% phenyl methylpolysiloxane column. Two reference standards identified as 1,7- and 1,9-DiMeDBT coeluted on each of the columns studied, and therefore the identity of these reference compounds was suspect. A mixture containing 1,7- and 3,7-DiMeDBT from a different source (J. Andersson, University of Münster, Münster, Germany) was compared, and the results suggest that the 1,9-DiMeDBT standard was mislabeled as 1,7-DiMeDBT. Unfortunately, 1,9-DiMeDBT was not available from an alternate source, and thus retention data could be measured for only 15 of the 16 possible isomers.

The elution order of the isomers on the 5% phenyl phase is very similar to that observed for the 50% phenyl phase; however, better separation was achieved with the 50% phenyl column. A very different elution order for the DiMeDBTs was observed for the liquid crystalline phase. A plot of retention (I_S) on the liquid crystalline phase vs. L/B

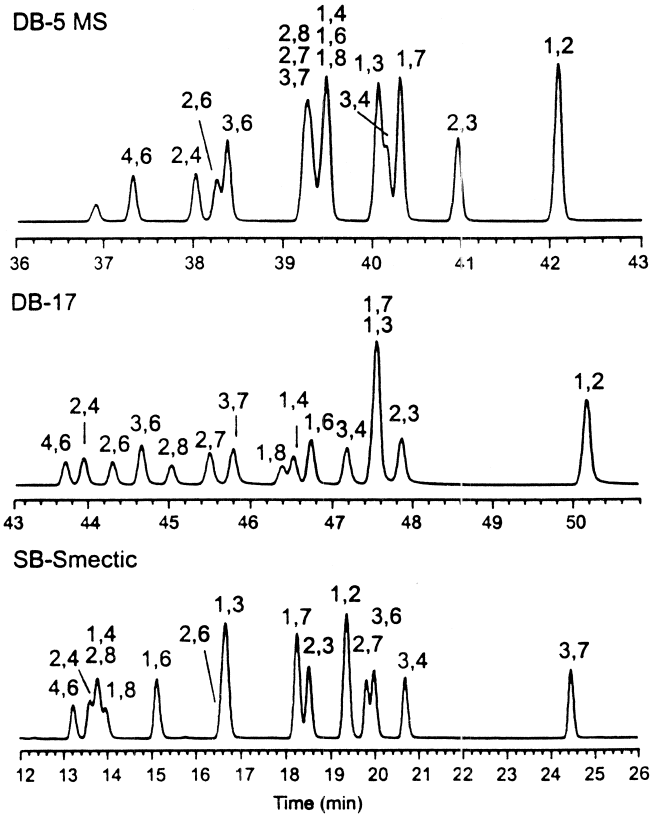

Fig. 3. GC–MS separation of 15 dimethyldibenzothiophene (DiMeDBT) isomers (m/z 212) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the DiMeDBT isomers.

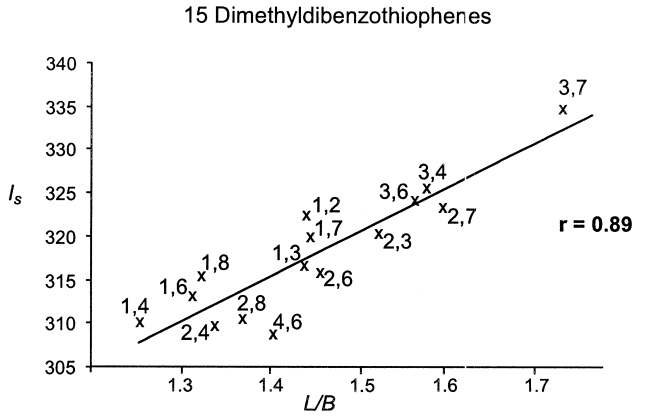

Fig. 4. Plot of retention (I_S values) on the liquid crystalline phase versus L/B value for the 15 dimethyldibenzothiophene (DiMeDBTs) isomers. Numbers identify the DiMeDBT isomers.

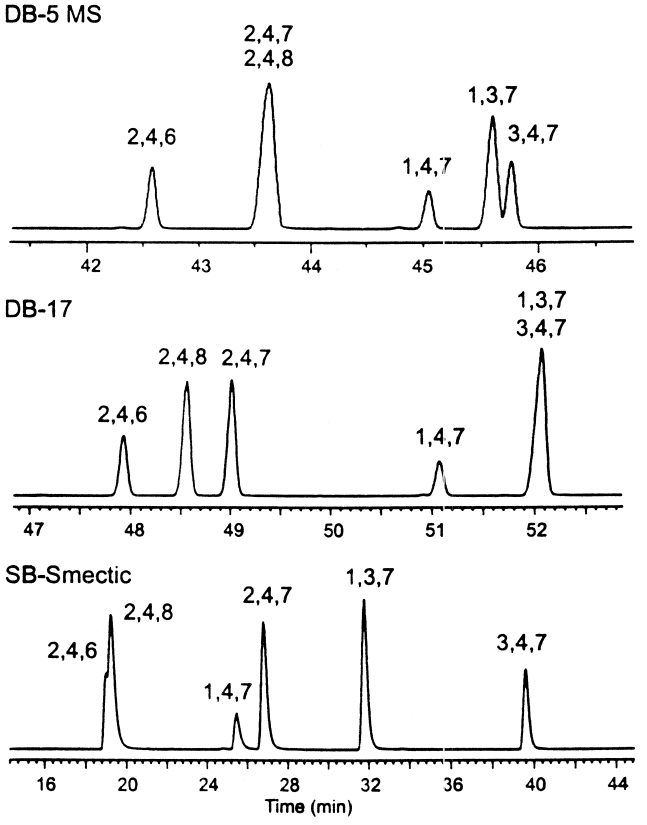

Fig. 5. GC–MS separation of six trimethyldibenzothiophene (TriMeDBT) isomers (m/z 226) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the TriMeDBT isomers.

for the 15 DiMeDBT isomers is shown in Fig. 4. The influence of the solute shape on the retention is significant with a correlation coefficient of $r=0.89$. The isomers with the largest L/B values, 3,6- (1.56); 3,4- (1.57); 2,7- (1.60); and 3,7-DiMeDBT (1.73), elute last. The two isomers with the largest deviation from the predicted elution order on the shape-selective liquid crystalline phase are the 4,6- and 1,2-DiMeDBT isomers. These two isomers are the first- and last-eluting components on the two nonpolar phases (see Fig. 3). Because the nonpolar phases provide separations based on the solute vapor pressure, 1,2-DiMeDBT may elute later than predicted on the smectic liquid crystalline column as a consequence of solute vapor pressure contribution. The 4,6-DiMeDBT elutes earlier than predicted for the same reason (this isomer elutes first on the two nonpolar columns). The influence of the solute thickness for the DiMeDBT isomers is minimal ($r=0.17$) because the T values for all of the isomers are similar (between 4.21 Å and 4.26 Å), with the only exception of $T=4.36$ Å for 1,2-DiMeDBT.

Budzinski et al. [22] studied the retention of the DiMeDBT isomers on the same smectic liquid crystalline phase. They reported a correlation coefficient of $r=0.74$ for the retention vs. L/B value. However, our method of calculation of the L/B values [40] accounts for the nonplanarity of the solute and for some isomers it provides different L/B values than those used by Budzinski et al. [22]. In addition, because Budzinski et al. [22] used 1,9-DiMeDBT from the same source as in our study (see discussion above), we eliminated this isomer from the data set. We then used our calculated L/B values for correlation with their retention data to obtain a correlation coefficient of $r=0.89$, which is the same

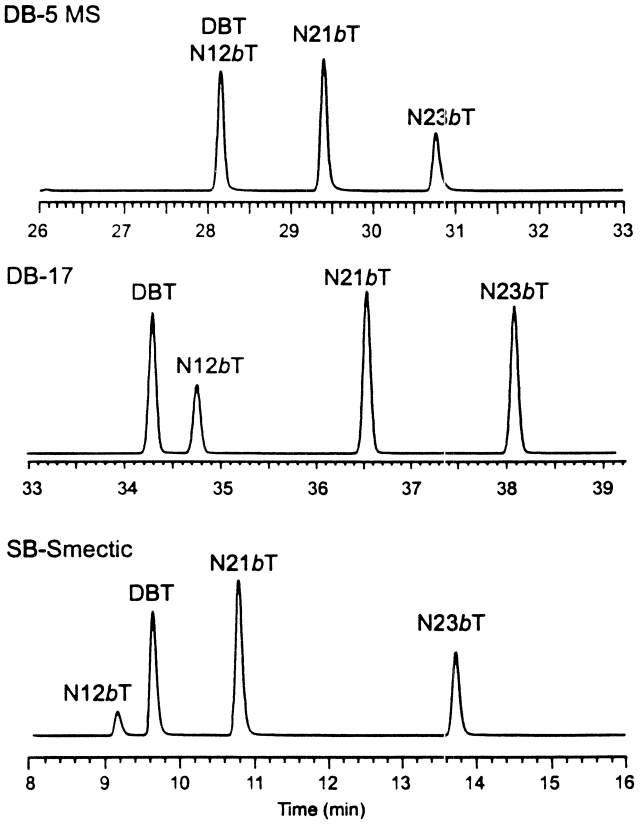

Fig. 6. GC–MS separation of dibenzothiophene (DBT), naphtho[1,2-*b*]thiophene (N12*b*T), naphtho[2,1-*b*]thiophene (N21*b*T), and naphtho[2,3-*b*]thiophene (N23*b*T) (m/z 184) on different stationary phases: DB-5MS, DB-17 and SB-Smectic.

as for our data (see Table 5). In a similar study of 25 dimethylphenanthrene isomers, three-ring PAH isomers with a similar arc-like structure, Budzinski et al. [27] observed a correlation coefficient of $r = 0.83$ for retention vs. L/B.

3.3. Trimethyldibenzothiophenes (TriMeDBTs)

Even though only six of 28 possible TriMeDBTs isomers were available for this study, they illustrate selectivity differences for the three stationary phases. To our knowledge, the retention indices in Table 3 represent the only retention data for the TriMeDBTs reported to date. In Fig. 5 the separations of the six TriMeDBT isomers on the three stationary phases are shown. Isomer coelutions occurred with each column: 2,4,7- and 2,4,8-TriMeDBT on the 5% phenyl phase, 1,3,7- and 3,4,7-TriMeDBT on the 50% phenyl phase, and 2,4,6- and 2,4,8-TriMeDBT on the liquid crystalline phase. There is a strong correlation of the retention on the liquid crystalline phase with the solute L/B ratio ($r = 0.98$).

3.4. Dibenzothiophene (DBT), naphtho[1,2-b]thiophene (N12bT), naphtho[2,1-b]thiophene (N21bT), and naphtho[2,3-b]thiophene (N23bT)

GC separations of the four structural isomers DBT, N12*b*T, N21*b*T, and N23*b*T are shown in Fig. 6. Good separations were obtained with all of the columns with the exception of the coelution of DBT and N12*b*T on the 5% phenyl methylpolysiloxane column. On the 50% phenyl methylpolysiloxane column N12*b*T eluted shortly after DBT, and on the smectic liquid crystalline phase N12*b*T elutes prior to DBT as predicted by the smaller L/B ratio of

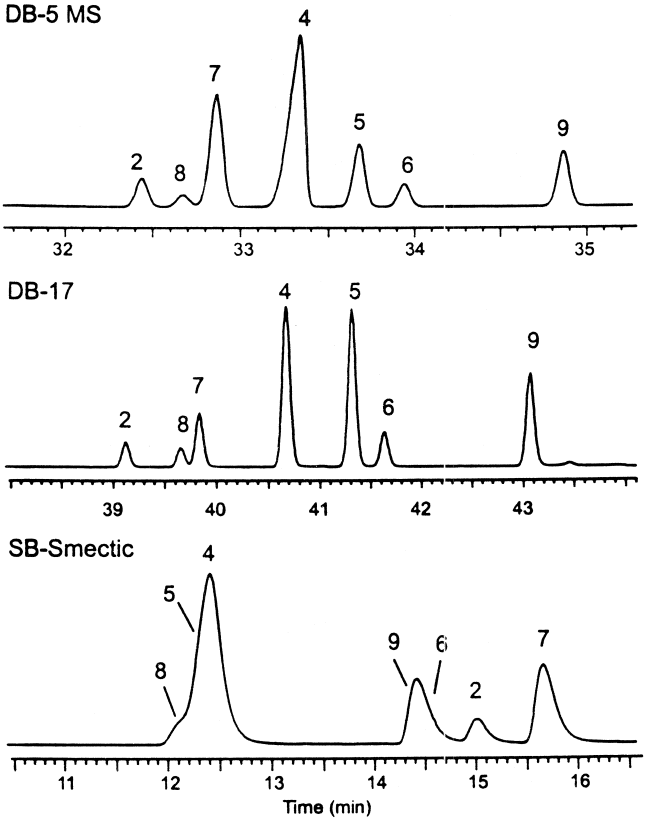

Fig. 7. GC–MS separation of seven methylnaphtho[1,2-*b*]thiophene (MeN12*b*T) isomers (m/z 198) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the MeN12*b*T isomers.

N12*b*T ($L/B=1.40$) compared to DBT ($L/B=1.45$). On all three columns studied, N23*b*T, the isomer with the largest L/B ratio, elutes last. Correlation of retention on the liquid crystalline column vs. L/B (see Table 5) resulted in a correlation coefficient of $r=0.82$.

3.5. Methylnaphtho[1,2-b]thiophenes (MeN12bTs)

GC separations of seven of the eight possible MeN12*b*T isomers are shown in Fig. 7. On both nonpolar phases all seven available isomers are separated in the same order of elution with no coelutions occurring. However, separations on the smectic liquid crystalline phase are surprisingly poor with only two isomers baseline separated. The correlation of the retention on the liquid crystalline phase with L/B provided the lowest correlation coefficient ($r=0.68$) of all PASH isomer sets investigated. Compared to the isomeric MeDBTs, the poor overall separation of the MeN12bTs on the liquid crystalline phase is interesting to note because the L/B ratio and T ranges for both isomer sets are comparable (see Table 1). As expected on a shape-selective phase, the two longest isomers, 2-Me and 7-Me (both $L/B=1.54$) elute latest on the smectic phase in contrast to their early elution on the two nonpolar phases.

3.6. Methylnaphtho[2,1-b]thiophenes (MeN21bTs)

The separations of all eight MeN21*b*Ts on the three GC stationary phases are shown in Fig. 8. In this case the 5% phenyl methylpolysiloxane phase provided the best separation of the isomers. The 50% phenyl methylpolysiloxane phase provided a similar order of retention although two isomers (1-Me and 6-Me) coeluted on this column. The liquid crystalline

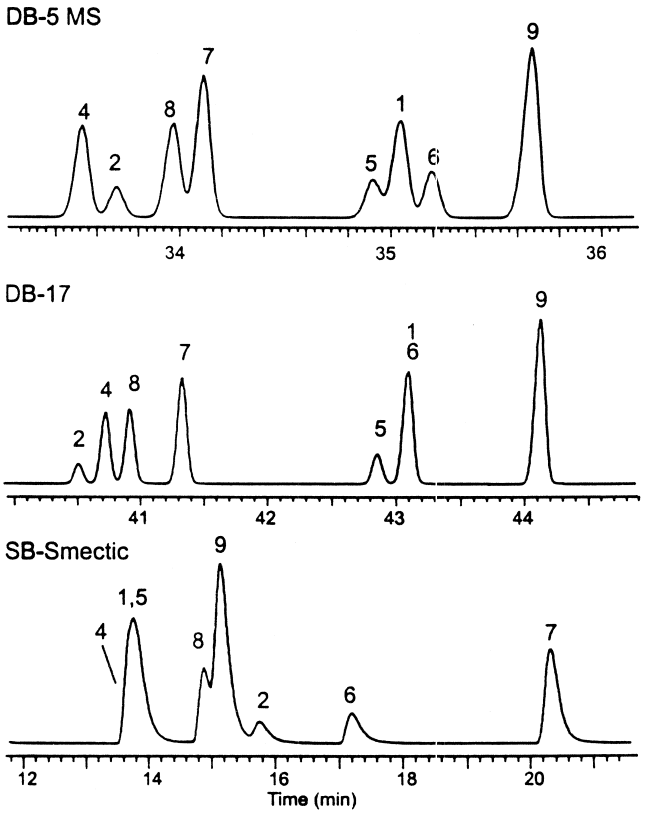

Fig. 8. GC–MS separation of eight methylnaphtho[2,1-*b*]thiophene (MeN21*b*T) isomers (m/z 198) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the MeN21*b*T isomers.

column provided a completely different elution order (7-Me has the largest L/B ratio and therefore elutes last), but with some coelutions and fewer baseline separations. Correlation of retention vs. L/B (see Table 5) resulted in a correlation coefficient of $r=0.87$.

3.7. Benzo[b]naphtho[1,2-d]thiophene (BN12T) and methyl-substituted isomers (MeBN12Ts)

Of the three stationary phases investigated, the smectic liquid crystalline phase provided the best separation of the MeBN12Ts (see Fig. 9), with only two isomers unresolved (9-Me and 4-Me). Of particular interest is the fact that on the liquid crystalline phase two methyl-substituted BN12T isomers (1-Me and 11-Me) elute prior to the unsubstituted parent PASH. Similar observations have been reported for the separation of selected methyl-substituted PAHs on a shape-selective polymeric C_{18} phase in LC, and this anomalous retention behavior has been attributed to the nonplanarity (related to the thickness) of the solute [38,41].

A plot of retention vs. L/B for the MeBN12T isomers is shown in Fig. 10A, which results in a correlation coefficient of $r=0.73$. This correlation coefficient is the lowest of the three MeBNT isomer sets. The 1-Me and 11-MeBN12T isomers eluted much earlier on the smectic liquid crystalline phase column than predicted by the L/B ratio. Early elution of nonplanar molecules has been reported in both LC and GC separations utilizing shape-selective columns [26,27,41]. Most of the methyl-substituted BNT isomers have planar molecular structures, as determined by molecular modeling and indicated by the similar thickness parameters (see Table 2). Com-

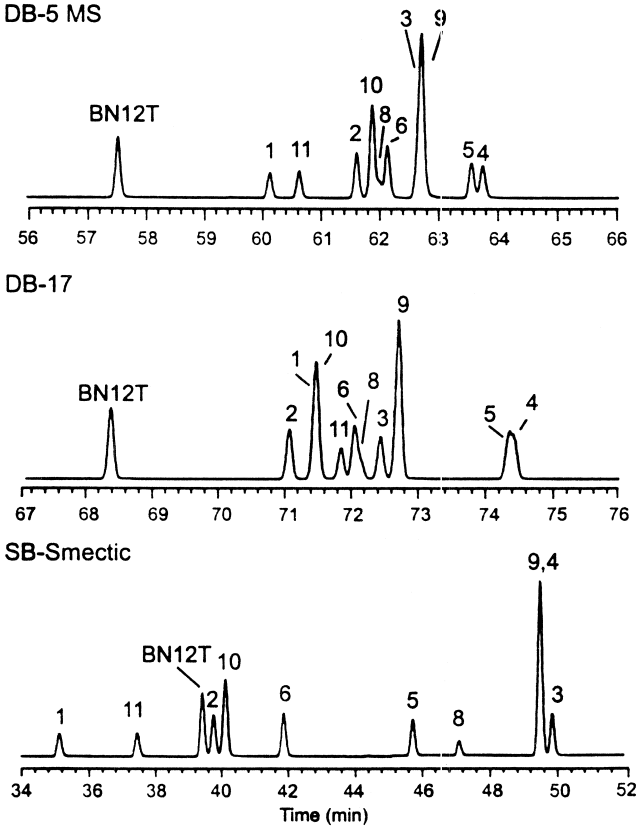

Fig. 9. GC–MS separation of benzo[*b*]naphtho[1,2-*d*]thiophene (BN12T) (*m*/*z* 234) and 10 methylbenzo[*b*]naphtho[1,2-*d*]thiophene (MeBN12T) isomers (*m*/*z* 248) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the MeBN12T isomers.

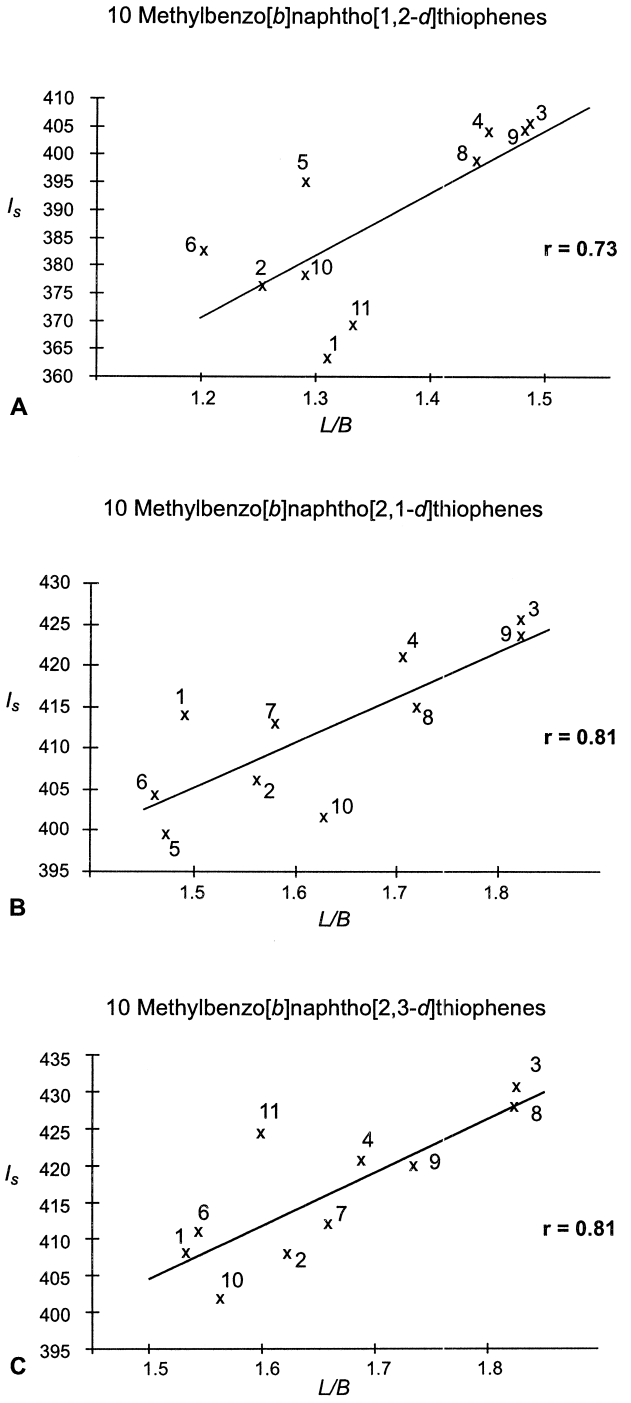

Fig. 10. Plot of retention (I_S values) on the liquid crystalline phase versus L/B values for the (A) methylbenzo[*b*]naphtho[1,2-*d*]thiophene isomers, (B) methylbenzo[*b*]naphtho[2,1-*d*]thiophene isomers, and (C) methylbenzo[*b*]naphtho[2,3-*d*]thiophene isomers. Numbers identify the specific methylbenzo[*b*]naphthothiophene isomers.

pared to the MeBN21Ts and MeBN23Ts, which are discussed below, the MeBN12Ts show the largest differences in solute thickness, ranging from 4.44 Å to 5.56 Å (see Table 2). The 1-Me and 11-MeBN12T isomers both have nonplanar structures due to steric hindrance effects of the methyl substitution as indicated by the two largest thickness values ($T=5.56$ Å and 5.24 Å, respectively). A correlation of the retention on the liquid crystalline phase with isomer thickness results in a correlation coefficient of $r=0.72$ (similar to the correlation with L/B).

3.8. Benzo[b]naphtho[2,1-d]thiophene (BN21T) and methyl-substituted isomers (MeBN21Ts)

GC separations of the MeBN21T isomers on the three different stationary phases are illustrated in Fig. 11. Dramatic differences are observed in the retention behavior of these isomers with the liquid crystalline phase compared with the two nonpolar phases. All 10 methyl-substituted BN21T isomers were separated on the liquid crystalline phase column, whereas only three isomers are well resolved with the 5% phenyl methylpolysiloxane phase column. The 50% phenyl methylpolysiloxane phase shows a similar separation (i.e., a similar elution order) as the 5% phenyl methylpolysiloxane phase, but with improved selectivity resulting in only one major coelution. On the liquid crystalline phase, 5-MeBN21T elutes prior to the parent compound BN21T. However, unlike the examples described above (i.e., 1-Me- and 11-MeBN12T), 5-MeBN21T appears to have planar geometry based on the thickness value of 4.22 Å as reported in Table 2. No explanation for this behavior is apparent.

The correlation of retention and L/B value for the MeBN21T isomers is shown in Fig. 10B ($r=0.81$). The largest deviations occur for 1-Me and 10-

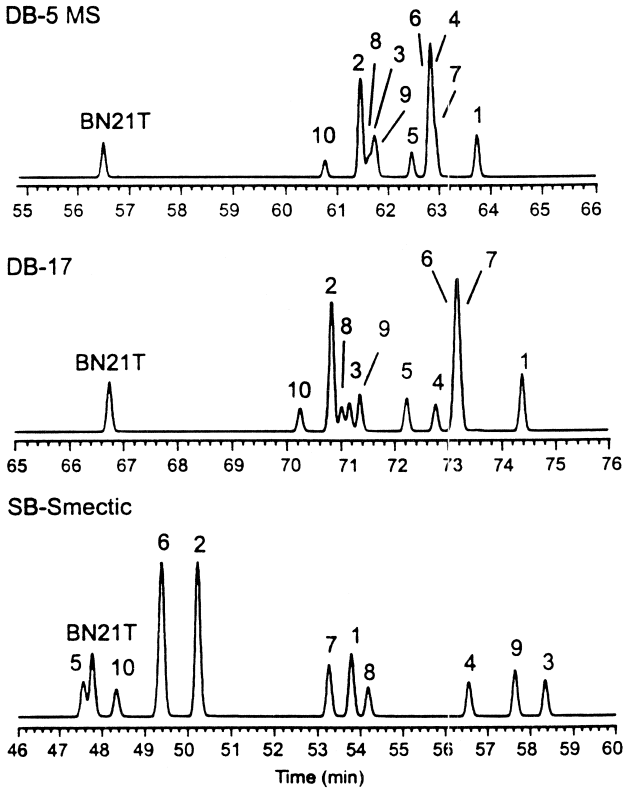

Fig. 11. GC–MS separation of benzo[*b*]naphtho[2,1-*d*]thiophene (BN21T) (*m*/*z* 234) and 10 methylbenzo[*b*]naphtho[2,1-*d*]thiophene (MeBN21T) isomers (*m*/*z* 248) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the MeBN21T isomers.

MeBN21T; 1-MeBN21T is retained more than predicted by the correlation equation, whereas 10-MeBN21T elutes before the expected retention time. Neither isomer is nonplanar based on the thickness parameter. In fact, none of the MeBN21T isomers are nonplanar and all have similar thickness (see Table 2). However, these two isomers have methyl group substitution adjacent to the sulfur atom. These deviations may be explained by the additional influence of the vapor pressure and/or polarity because 10-MeBN21T elutes first and 1-MeBN21T elutes last on both the nonpolar phases (see Fig. 11).

3.9. Benzo[b]naphtho[2,3-d]thiophene (BN23T) and methyl-substituted isomers (MeBN23Ts)

The GC separations of benzo[*b*]naphtho[2,3-*d*]thiophene and the 10 methyl-substituted isomers on the three stationary phases are shown in Fig. 12. Unfortunately, some of the reference compounds of the MeBN23Ts contained impurities of the MeBN21T isomers. The best separation of the MeBN23T isomers was obtained using the liquid crystalline phase with only one coelution (1-Me and 2-MeBN23T). Six of the ten possible isomers were resolved on the 50% phenyl phase, whereas on the 5% phenyl phase only three of the isomers were baseline resolved. The plot of liquid crystalline retention vs. L/B value is shown in Fig. 10C with a correlation coefficient of $r=0.81$, which is identical to the correlation coefficient for the MeBN21T isomers.

3.10. Complex mixture separation (MeBNTs)

The separations of the three benzo[*b*]-

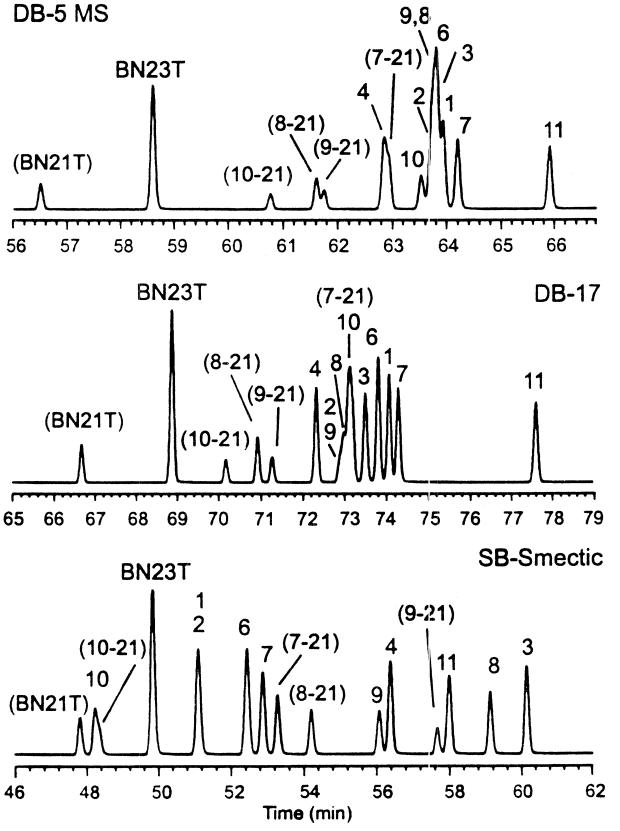

Fig. 12. GC–MS separation of benzo[*b*]naphtho[2,3-*d*]thiophene (BN23T) (*m*/*z* 234) and 10 methylbenzo[*b*]naphtho[2,1-*d*]thiophene (MeBN23T) isomers (*m*/*z* 248) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. Numbers identify the MeBN23T isomers.

naphthothiophenes and all 30 methyl-substituted isomers on the three columns are shown in Fig. 13. The best overall separation of this isomer mixture was achieved on the smectic liquid crystalline phase. The three BNT isomers are separated on all three phases, but the elution order of the BN12T and the BN21T is reversed on the nonpolar phases compared to the liquid crystalline phase, on which they elute in the order of increasing L/B. It is interesting to note the different time ranges needed for the GC separations on the three stationary phases. For the 50% phenyl column (60 m length), the methyl-substituted BNTs elute within a period of 8 min, whereas these compounds elute over a period of 25 min on the

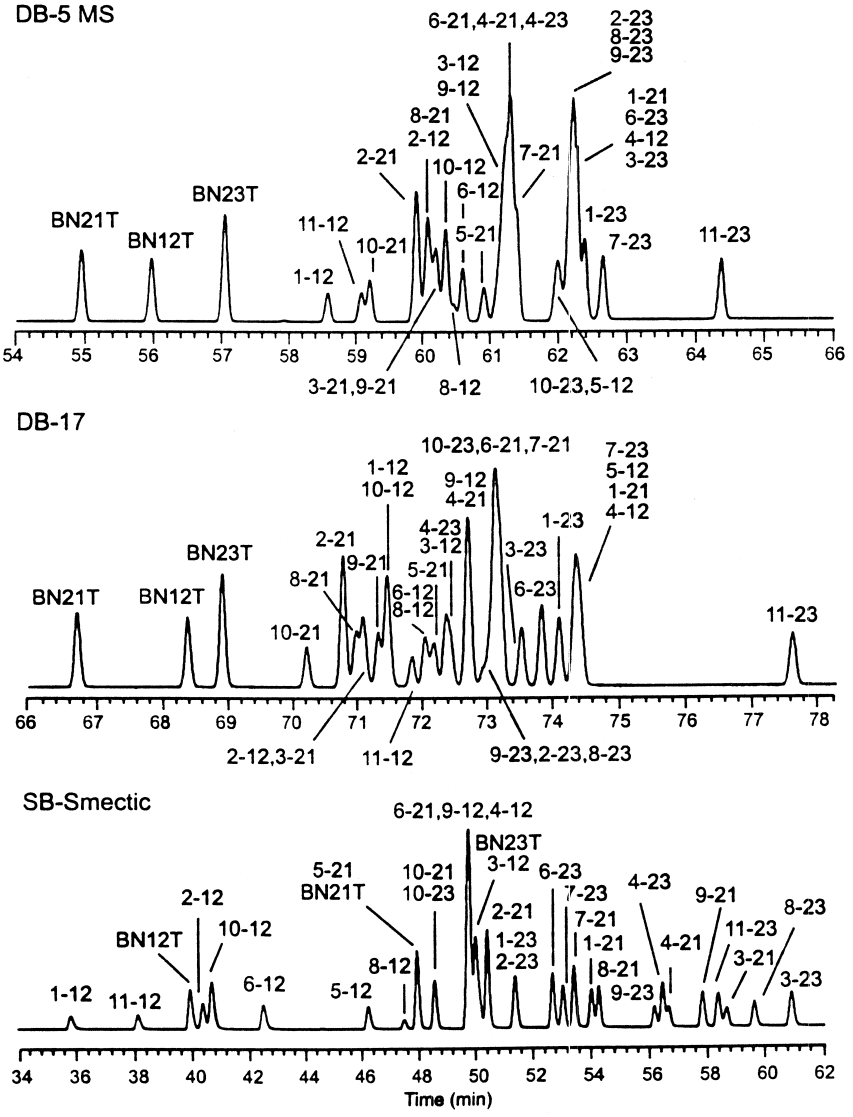

Fig. 13. GC–MS separation of 3 benzo[*b*]naphthothiophene (BNT) (*m*/*z* 234) isomers and 30 methylbenzo[*b*]naphthothiophene (MeBNT) isomers (*m*/*z* 248) on different stationary phases: DB-5MS, DB-17 and SB-Smectic. BN12T = benzo[*b*]naphtho[1,2-*d*]thiophene, BN21T = benzo[*b*]naphtho[2,1-*d*]thiophene, and BN23T = benzo[*b*]naphtho[2,3-*d*]thiophene. Numbers identify the specific methylbenzo[*b*]-naphthothiophene isomers, e.g., 1–12 = 1-methylbenzo[*b*]naphtho[1,2-*d*]thiophene, 8–21 = 8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene, 11–23 = 11-methylbenzo[*b*]naphtho[2,3-*d*]thiophene, etc.

smectic liquid crystalline phase column (25 m length) using a similar temperature program. Even though the liquid crystalline phase column provided the best overall separation of the isomers, specific isomers may be better resolved on one of the nonpolar columns. For example, 10-MeBN21T and 10-MeBN23T coelute on the smectic liquid crystalline phase, but they are well separated on the 5% phenyl methylpolysiloxane column. In addition, the three BNT isomers elute prior to all the methyl-substituted isomers on the two nonpolar phases (which may be an advantage in some applications), whereas they are interspersed among the methyl isomers on the liquid crystalline phase. It should also be noted that several important operational restrictions are imposed with the use of SB-Smectic liquid crystalline columns. The upper temperature limit for this column is 250°C isothermal, or 270°C when temperature programmed. Extensive use of the SB-Smectic column at these upper temperature limits significantly reduces the useful lifetime of the column, and column selectivity often changes dramatically with use [28]. Despite these disadvantages, the smectic liquid crystalline column offers unique selectivity that often provides separation of PASH isomer mixtures that are not possible with other columns.

Acknowledgements

S.G.M. acknowledges and thanks the Alexander von Humboldt-Foundation (Germany) for providing her with a postdoctoral grant.

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