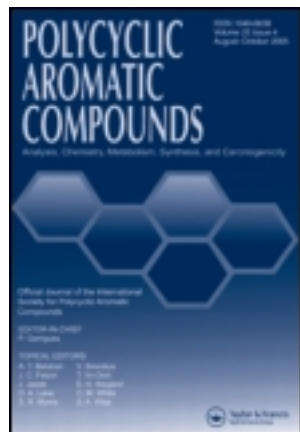


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## Polycyclic Aromatic Compounds

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# Mass Spectra and Retention Indexes for Polycyclic Aromatic Sulfur Heterocycles and Some Alkylated Analogs

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Polycyclic aromatic sulfur heterocycles (PASH) are ubiquitous in fossil fuels and pose risk to the environment due to their toxicity. Some PASH, resistant to degradation in the environment, are used to differentiate pollutant source and weathering. Although retention data exist for some PASH, few mass spectra are available, so misidentification often occurs between isomers in the same family. In this study, the retention behavior of 119 PASH on 14%-cyanopropyl/86%-polydimethylsiloxane (DB-1701ms), trifluoropropylmethylpolysiloxane (Rtx-200ms), 5%-phenyl/95%-dimethyl (Rxi-5ms), and 50%-diphenyl/50%-dimethyl (Rxi-17Sil-ms) are reported along with their mass spectra. This data is guiding on-going research aimed at identifying PASH in coal tar by multi-dimensional GC-GC/MS for compounds where standards are not available.

*Key Words:* Alkylated PASH, environmental forensics, fossil fuel samples, GC retention index, mass spectrometry

## INTRODUCTION

The dramatic explosion of British Petroleum's Deepwater Horizon drilling rig and resulting oil spill into the Gulf of Mexico has caused considerable debate

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Certain commercial equipment, instruments, or materials are identified in this article 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 necessarily the best available for the purpose.

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over potential ecosystem impacts (1–3). For example, immeasurable dispersion of potentially harmful organics from oil into ocean waters and widespread contamination of shorelines could pose long-term risks to flora and fauna. Investigators target polycyclic aromatic hydrocarbons (PAH) to assess risk because these compounds bioaccumulate (4,5), are toxic (6,7), mutagenic (8), and carcinogenic (9–14). Despite knowing many polycyclic aromatic sulfur heterocycles (PASH), condensed ring aromatic thiophenes, exhibit mutagenic (15,16) and carcinogenic (17–19) activity, they are generally ignored in risk assessments (20). A comprehensive study of their gas chromatographic retention times and mass spectral patterns is needed to accurately quantify them in the environment should these compounds become regulated.

In addition to parent PAHs, investigators use the C<sub>1</sub>–C<sub>4</sub> alkylated homologs to determine how much evaporation, dissolution, and degradation (weathering) fossil fuels and their by-products undergo in the environment (21–23). Similarly, some investigators use the alkylated homologs of dibenzothiophene to differentiate one fuel from another and to assess weathering processes (24–26). For example, Wang et. al. employed the ratios of isomeric methyl dibenzothiophenes to one another to elucidate the origin of fuel and the extent of weathering by microbial degradation (27). Based on previously published gas chromatographic retention time studies, the retention range of C<sub>1</sub> dibenzothiophenes overlaps with C<sub>1</sub> naphthothiophene compounds (28). In addition to these 3-ring PASH, the C<sub>5</sub> naphthalenes also elute in the same retention window and have the same molecular ion as the PASH (20). Analysis by selected ion monitoring (SIM) or extraction (SIE) of only the molecular ion leads to overestimation, since unambiguous peak identification is not possible. We were motivated, therefore, to learn if these compounds are identifiable based on their mass spectra or if selectivity provided by two different stationary phases would permit their separation. Moreover, little MS data exists for 4-ring and higher PASH that might serve as useful indicators of source and weathering (29). Toward this end, we produced mass spectra and retention time data for 119 PASH on 14% cyanopropyl, 86% dimethyl polysiloxane (DB-1701), and trifluoropropylmethylpolysiloxane (Rtx-200ms) columns. No retention data exists for PASH on these columns. Analysis of the same standards were performed on 50% dimethyl, 50% phenyl polysiloxane (DB-17), and 95% dimethyl, 5% diphenyl polysiloxane (DB-5) under retention time locked conditions. Our purpose was to obtain locked retention times so that each compound elutes at the same time independent of whether the analysis was accomplished by GC/MS or GC-GC/MS. To our knowledge, this work represents the most exhaustive collection of GC retention and mass spectral data for PASH.

Since authentic standards were not available for all isomers, the retention data provided a guide to column selection and elution times for detecting alkylated PASH in coal tar by automated sequential, multidimensional

gas chromatography/mass spectrometry (GC-GC/MS). We selected coal tar as the source of PASH because it is the richest source of these compounds in a single matrix. GC-GC/MS operates by transferring small sample portions at predetermined time intervals from the first column to the second column, a process called “heartcutting.” GC-GC/MS offers the best opportunity for separating coeluting compounds based on the efficiencies gained when the retention mechanisms on the two stationary phases are different (30). In an earlier publication, we used GC-GC/MS to build a library of retention times and mass spectra for the C<sub>1</sub>–C<sub>4</sub> naphthalenes and fluorenes found in diesel fuel (31). Based on the information provided in this report, research is in progress to develop a library of retention times and mass spectra for the 4-ring to 6-ring PASH found in coal tar and crude oil. This work should provide the foundation to catalog the aromatic content of fossil fuels. It will allow forensic investigators to more accurately identify and quantify PASH, which should lead to more robust fate and transport studies (20) and environmental impact statements. This will, in turn, improve the ability to address petroleum releases and coal tar contamination in a more scientific manner.

## EXPERIMENTAL

**Standards.** The majority of the 3–7 ring aromatic thiophenes were synthesized by Andersson (32) and Lee (33) and stored at the U.S. National Institute of Standards and Technology (NIST, Gaithersburg, MD). Dibenzothiophene-*d*<sub>8</sub>, 2-ethylthiophene, and 1-methylthiophene were obtained from Cambridge Isotopes Laboratory (Cambridge, MA, USA), Chiron Laboratory (Trondheim, Norway), and ASTEC GmbH (Münster, Germany), respectively. Naphthalene, phenanthrene, dibenzothiophene, chrysene, and benzo[*a*]pyrene were obtained from Fisher (Waltham, MA) while benzo[*ghi*]perylene was purchased from Restek Corporation (Bellefonte, PA). 5-acetyl-2,4-dimethylthiazole was purchased from Fisher Scientific (Waltham, MA). All standards were prepared and analyzed in toluene.

**Nomenclature.** Compound structures, names, and their corresponding abbreviations are shown in Figure 1. Fusion of thiophenes on the *c* side of the ring produces unstable isomers (34), therefore *b* side lettering was omitted when condensed rings were fused to one side of the thiophene ring (35–37). Also, certain compounds including acenaphtho[4,5-*a*]dibenzothiophene and the 7-ring PASH were named using “dibenzothiophene” nomenclature (38). Compounds that are both *ortho*- and *peri*-fused are termed “*peri*-condensed” (39,40) to differentiate them from compounds that have only *ortho*-fusion. We use the term “linear” to refer to compounds that are *ortho*-fused on at most two sides of a given ring and “nonlinear” to refer to compounds that contain an *ortho*-fused ring on more than two sides.

**GC/MS Instrument Conditions.** Data were collected at NIST and Tufts University. The NIST GC/MS was an Agilent (Little Falls, DE, USA) model 6890/5973. On-column injections were made using an Agilent 7673A autosampler. A 1 m x 0.25 mm deactivated fused silica guard column preceded the analytical column. Two different instruments were used at the university: (1) an Agilent model 6890/5973 equipped with a CIS6 inlet (programmed at 20°C (0.50 min) then 12°C/s to 300°C (2 min)) and MPS2 autosampler from Gerstel (Linthicum, MD, USA) and (2) a Shimadzu (Columbia, MD, USA) QP2010 with an AOC-20i autoinjector with inlet held at 300°C. The ion source (70 eV), quadrupole, and transfer line temperatures were 230°C, 150°C, and 280°C, respectively. After spectrally tuning the MS, data were collected at 8 scans/s between 50 and 400 m/z. Table 1 lists the GC operating conditions for each column. The DB-1701 column was obtained from J&W Scientific (Folsom, CA); all other columns were from Restek. Ultra-high purity helium served as the carrier gas (Airgas, Salem, NH).

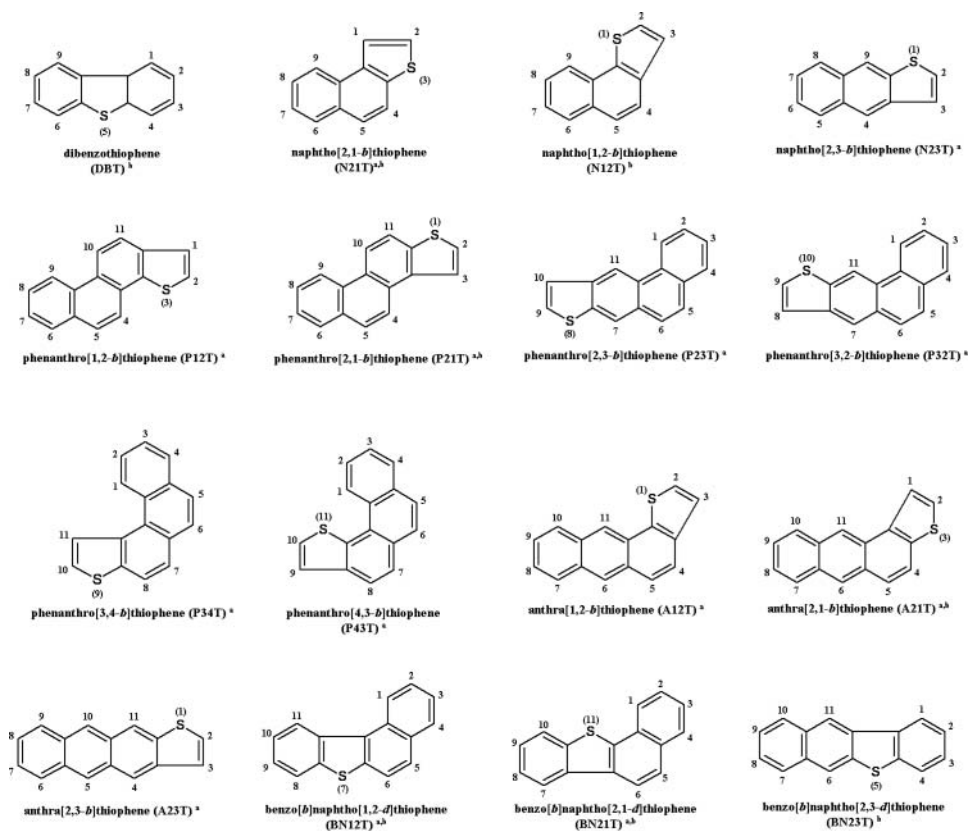


Figure 1: PASH name, numbering, structure, and abbreviation.

5-acetyl-2,4-dimethylthiazole was used to lock retention times on the Rtx-5 column by generating chromatograms using a constant head pressure. Retention times were regressed against the head pressures and a second-order polynomial fit to the data ( $r^2 = 0.99$ ). Based on these results, the head pressure was set so that 5-acetyl-2,4-dimethylthiazole eluted at 12.92 min.

**Multidimensional GC/MS Instrument Conditions.** Figure 2 depicts schematically the GC-GC/MS configuration. A Gerstel CIS6 inlet was used to inject sample onto the Rxi-17 column (C1) on one end and a crosspiece transferred sample onto the Rxi-5 column (C2) on the other end. About 10% of the first column eluant flowed continuously to the flame ionization detector (FID) through a 40 cm x 0.05 mm I.D. deactivated fused silica column. The Rxi-5 column was threaded through a Gerstel CTS1 cryotrap/thermal desorber, whose purpose was to concentrate and refocus the sample portion transferred to the second column. Two detectors were used

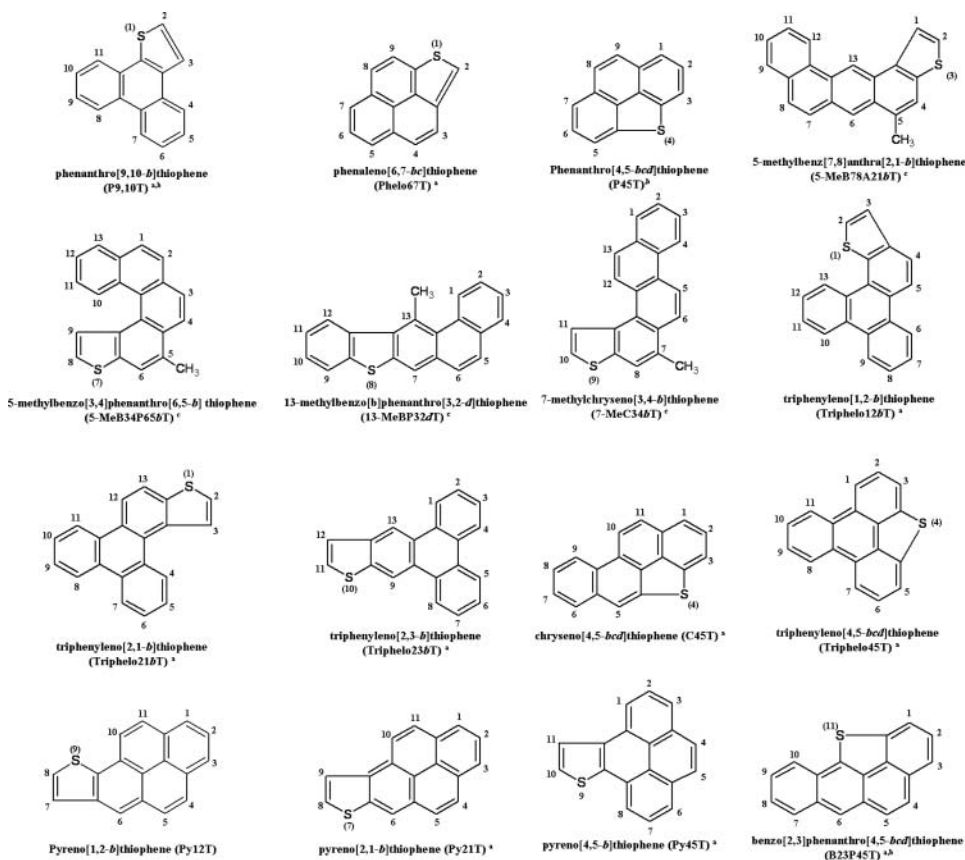
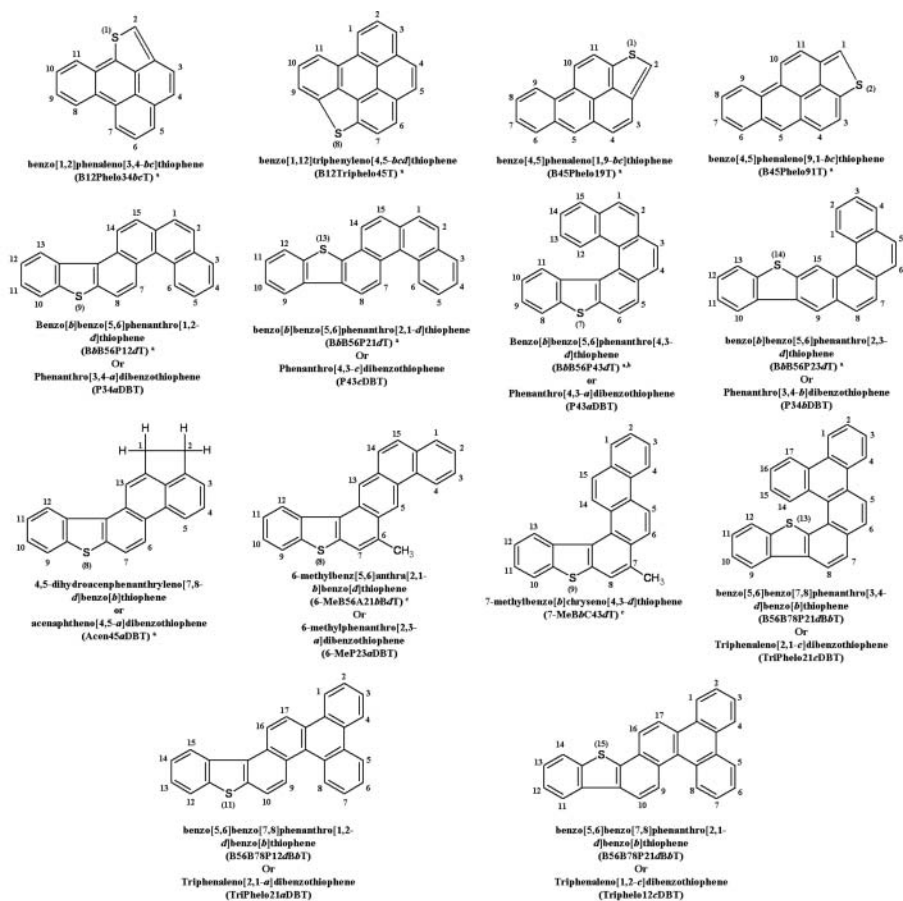


Figure 1: (Continued).



Key: <sup>a</sup> The parent isomer of this compound is included in this study. <sup>b</sup> Alkylated analogs of this compound are included in this study. <sup>c</sup> Only this isomer is included in this study.

Figure 1: (Continued).

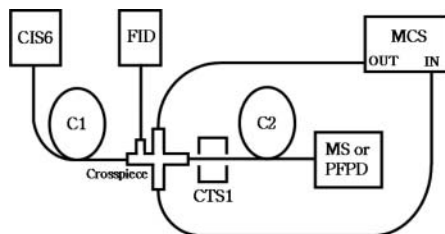


Figure 2: Schematic of GC-GC system used in this work. CIS6 = Cooled Injection System, FID = Flame Ionization Detector, C1, C2 = columns 1 and 2, respectively, MCS = Multi Column Switching system, CTS1 = Cryo Trapping System, MS = Mass Spectrometer, PFPD = Pulsed Flame Photometric Detector.

**Table 1:** GC temperature and pressure programs employed

	DB-1701ms "short run"	DB-1701ms "long run"	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms
Dimensions	60 m X 0.25 mm		60 m x 0.25 mm	30 m x 0.25 mm	30 m x 0.25 mm
Film Thickness	0.25 $\mu$ m		0.25 $\mu$ m	0.25 $\mu$ m	0.25 $\mu$ m
Oven Start temperature (hold time)	50°C (1 min)	90°C (2min)	90°C (2 min)	60°C (1 min)	60°C (1 min)
Ramp 1 Rate	40°C/min	40°C/min	40°C/min	5°C/min	5°C/min
Ramp 1 End Temperature (hold time)	200°C (2 min)	250°C (0 min)	200°C (2 min)	340°C (0 min)	320°C (0 min)
Ramp 2 Rate	2°C/min	0.5°C/min	2°C/min	n/a	n/a
Ramp 2 End Temperature	300°C	300°C	330°C	n/a	n/a
Flow or Pressure	1.2 mL/min constant flow	1.2 mL/min constant flow	1.2 mL/min constant flow	64.3 kPa constant head pressure	1.0 mL/min constant flow
Run Time (min)	56.75	106	71.75	57	55

n/a = not applicable.



to record data, an Agilent MS and an OI (Houston, TX) pulsed flame photometric detector (PFPD); these detectors were used separately. With the multi column switching device (MCS) countercurrent flow off, the pressure at the cross piece was 110 kPa when helium flowed through column 1 at 1 mL/min. In this pressure regime, all sample flowed from the first to the second column minus the 10% that went to the FID. In contrast, a 10 mL/min helium flow through the crosspiece at 110 kPa results in the sample going through the MCS to waste. Small portions of sample were transferred at specific time intervals by controlling carrier gas flow through the crosspiece. The Rxi-5 column was retention time locked so that 5-acetyl-2,4-dimethylthiazole eluted at 12.92 min. This ensured all PASH elution times were reproducible independent of detector.

Coal tar was obtained from a former manufactured gas plant in North Carolina. It was a fresh sample isolated from the environment that served as the source of PASH for the GC-GC/MS experiments. The sample was fractionated using the procedure developed by Wang (41). Briefly, silica gel (Grade 644, 150 Å pore size, 100–200 mesh, Sigma Aldrich, St. Louis, MO) was activated at 180°C overnight in an oven. After cooling, ~3 g of silica was dry packed into a 1 cm × 20 cm glass column with glass wool at the end of the column to prevent loss of silica. Prior to adding 30 mg of coal tar, 20 mL of hexane was passed through the column to condition the silica. 20 mL hexane was used to elute aliphatics followed by 20 mL of hexane/methylene chloride (50/50, v/v) to elute the aromatics.

**Calculation of Index Values.** When PASH eluted between the following standards, PASH retention indices were calculated using Eq. (1). For Lee (42) the PAH  $Index_{IS}$  was: phenanthrene (300), chrysene (400), benzo[*a*]pyrene (450), and benzo[*ghi*]perylene (500). For Andersson (43) the PASH  $Index_{IS}$  was: dibenzothiophene (300), benzo[*b*]naphtho[2,1-*d*]thiophene (400), benzo[2,3]phenanthro[4,5-*bcd*]thiophene (450), and acenaphtho[4,5-*a*]dibenzothiophene (550). Since acenaphtho[4,5-*a*]dibenzothiophene did not elute from the Rxi-17 column under the conditions used, triphenylene[1,2-*b*]thiophene was used as the last index standard and assigned the value 500. Variables  $t_{r_{IS}}$ ,  $t_{r_{IS+1}}$ , and  $t_{r_{compound}}$  are the retention times for the preceding and subsequent standards for the compound. For compounds that eluted before or after the internal standards, the  $Index_{IS}$  used is either the first or last standard, respectively (44). The indices for DB-1701 and Rtx-200 are based on triplicate analyses:

$$RI = Index_{IS} + \left[ \left( \frac{t_{r_{compound}} - t_{r_{IS}}}{t_{r_{IS+1}} - t_{r_{IS}}} \right) \times 100 \right]. \quad (1)$$

## RESULTS AND DISCUSSION

The purpose of this work was to accomplish the following three objectives. First, obtain mass spectra of PASH and their retention indices. Second, assess elution order variations as a function of stationary phase and determine which stationary phase results in the least number of coeluting critical pairs. Third, based on the first two objectives, determine if automated sequential 2-dimensional GC/MS provides the separation space needed to obtain MS and retention times of PASH from coal tar for which no standards exist. Toward this end, Table 2 lists the mass spectra for ions whose relative abundances (RA) are  $>7\%$  of the main ion. Like PAH, the majority of PASH produces fragment ions whose RA's are low compared to the molecular ion. Also, PASH produce "cluster" ions around the base and second largest ions. Doubly charged ions at one-half  $m/z$  of the molecular ion are also common. For example, both BN21T and BN21T-*d10* produce  $M^{2+}$  ions with RA of 24% and 29%, respectively. The mass spectra of PASH with more condensed rings vary less compared to those with fewer rings due to the increased aromatic character of the larger compounds.

The base ion produced from the ionization of the monomethylated PASH is the molecular ion. The second most abundant ion is due to the loss of hydrogen, which produces the PASH analog of the benzylium ion in equilibrium with the tropylium ion; see Figure 3a. Resonance delocalization of the cations in equilibria imparts thermodynamic stability to the kinetically controlled fragmentation products (45,46). For example, the average RA and standard deviation for the monomethylated 3-ring PASH ( $M-1$ )<sup>+</sup> ion is  $65\% \pm 14\%$  based on  $n = 17$  isomers. The fragmentation pathways with the next largest ions result in either  $m/z$  at 165 or 152, which are about 10% RA. The first ion stems from the loss of sulfur from benzylium/tropylium species ( $m/z$  197) to produce the methyl biphenylene cation ( $m/z$  165). The second ion is due to the loss of either thioformaldehyde or  $H_2$  and  $C = S$  (47) from the molecular ion to yield the biphenylene cation ( $m/z$  152).

For the dimethylated PASH the second most abundant ion is due to loss of hydrogen ( $M-1$ ) or methyl ( $M-15$ ) and appears to be location dependent; see Figure 3b. Although spectra for all isomers are not available, fragmentation patterns found in the literature (32,48,49), in the NIST database, and in Table 2 suggest substitution on both rings results in the ( $M-1$ )<sup>+</sup> ion as the dominant fragmentation product. In contrast, when two methyls are on the same ring, one  $\bullet CH_3$  cleaves and hydrogen shifts to produce the benzylium/tropylium cation at  $m/z$  197 that has a much higher relative abundance than when the groups are on both rings, viz., 60% vs. 20% RA; see Figure 3 for illustration.

Figure 3c shows the loss of  $\bullet CH_3$  creates the benzylium/tropylium species for ethylated  $C_2$  PASH without rearrangement. In this case, the ( $M-15$ )<sup>+</sup> ion is the base ion; see Table 2. The fragmentation product resulting from the loss of

**Table 2:** PASH mass spectra

Compound	Main Ion	Confirmation Ion (% Relative Abundance)				
<b>3-RING PASHs</b>						
<i>linear, ortho-fused</i>						
DBT-d8	192 (100)	146 (12)	160 (9)	96 (9)		
DBT	184 (100)	185 (14)	152 (8)	92 (8)		
N21T	184 (100)	185 (14)	152 (9)	92 (7)	183 (6)	
N23T	184 (100)	185 (13)	92 (10)	152 (9)		
<b>DBTs</b>						
<b>C1</b>						
1-MeDBT	197 (64)	199 (17)	165 (14)	152 (9)		
2-MeDBT	197 (68)	199 (18)	165 (10)	152 (9)		
3-MeDBT	197 (65)	199 (17)	165 (9)	152 (8)		
4-MeDBT	197 (65)	199 (17)	165 (10)	152 (8)		
<b>C2</b>						
2-EtDBT	212 (53)	198 (14)	152 (8)	213 (8)		
3-EtDBT	212 (57)	198 (15)	152 (8)	165 (8)		
4-EtDBT	212 (68)	198 (15)	213 (11)	165 (8)		
1,2-DiMeDBT	197 (78)	211 (24)	213 (17)	152 (16)	208 (10)	
1,3-DiMeDBT	197 (51)	211 (25)	213 (17)	178 (8)	178 (12)	
1,4-DiMeDBT	197 (55)	211 (25)	213 (16)	165 (9)		
2,3-DiMeDBT	197 (63)	211 (33)	213 (16)	152 (16)	198 (9)	
2,4-DiMeDBT	197 (56)	211 (31)	213 (18)	152 (12)	178 (10)	
2,8-DiMeDBT	211 (58)	105 (23)	197 (22)	213 (20)	106 (8)	
4,6-DiMeDBT	211 (52)	197 (19)	213 (18)	165 (10)	178 (10)	
<b>C3</b>						
1,3,7-TriMeDBT	211 (48)	225 (26)	227 (17)	208 (11)	209 (10)	
1,4,7-TriMeDBT	211 (51)	225 (22)	227 (18)	112 (13)	178 (10)	
2,4,6-TriMeDBT	211 (40)	225 (28)	227 (18)	112 (10)	208 (11)	
2,4,7-TriMeDBT	211 (43)	225 (35)	112 (12)	208 (7)	227 (8)	
2,4,8-TriMeDBT	211 (39)	225 (31)	227 (19)	113 (10)	208 (11)	
3,4,7-TriMeDBT	211 (50)	225 (29)	227 (16)	208 (11)	210 (8)	
<b>N12T</b>						
<b>C1</b>						
2-MeN12T	197 (93)	165 (25)	199 (24)	152 (22)	153 (8)	
5-MeN12T	197 (83)	199 (16)	152 (14)	99 (13)	85 (7)	
6-MeN12T	197 (67)	171 (18)	199 (17)	152 (11)	98 (9)	
7-MeN12T	197 (63)	171 (17)	199 (17)	152 (10)	151 (6)	
8-MeN12T	197 (64)	171 (18)	199 (17)	152 (11)	85 (7)	
				99 (8)	98 (7)	
				99 (8)	200 (5)	

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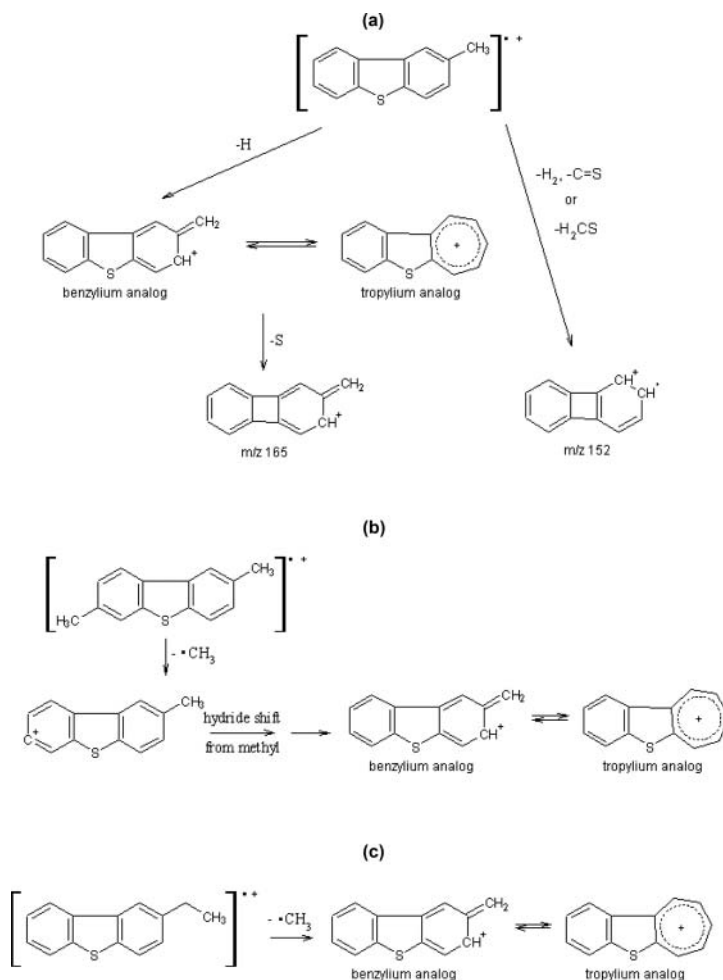
Table 2: PASH mass spectra (Continued)

Compound	Main Ion	Confirmation Ion (% Relative Abundance)									
<b>N21T</b>											
<b>C1</b>											
1-MeN21T	198 (100)	197 (68)	152 (29)	165 (26)	153 (18)	199 (17)	151 (10)	99 (8)	199 (17)	98 (8)	
2-MeN21T	198 (100)	197 (84)	199 (18)	165 (17)	152 (14)	99 (8)					
4-MeN21T	198 (100)	197 (66)	199 (17)	152 (9)	165 (8)						
5-MeN21T	198 (100)	197 (74)	199 (17)	152 (11)	171 (8)	165 (8)					
6-MeN21T	198 (100)	197 (60)	199 (17)	165 (12)	152 (12)	171 (8)	153 (9)				
7-MeN21T	198 (100)	197 (49)	199 (17)	165 (11)	152 (11)	153 (9)					
8-MeN21T	198 (100)	197 (44)	199 (16)	165 (14)	152 (12)	153 (11)					
9-MeN21T	198 (100)	165 (40)	197 (37)	152 (18)	153 (17)	199 (16)	151 (7)				
<b>4-RING PASHS</b>											
<b>linear, ortho-fused</b>											
P12T	234 (100)	235 (19)	189 (10)	232 (9)	117 (9)						
P21T	234 (100)	235 (18)	189 (10)	117 (9)	232 (9)						
P23T	234 (100)	235 (18)	189 (10)	117 (10)	232 (8)						
P32T	234 (100)	235 (18)	117 (10)	232 (9)	189 (9)						
P34T	234 (100)	189 (23)	235 (18)	202 (12)	232 (9)						
P43T	234 (100)	235 (18)	232 (16)	233 (11)	104 (8)	189 (8)	117 (8)				
A12T	234 (100)	235 (18)	117 (10)	189 (9)	232 (9)						
A21T	234 (100)	235 (18)	117 (12)	189 (11)	232 (8)						
A23T	234 (100)	235 (18)	117 (12)	189 (9)	232 (7)						
BN12T	234 (100)	235 (18)	117 (16)	232 (14)	104 (12)	189 (11)	116 (10)	233 (8)		187 (7)	
BN21T	234 (100)	117 (24)	235 (18)	189 (10)	232 (9)	104 (8)	202 (8)	116 (7)			
BN21T-d10	244 (100)	243 (46)	122 (29)	245 (20)	242 (12)	240 (10)	108 (9)	212 (8)			
BN23T	234 (100)	117 (25)	235 (18)	189 (10)	232 (8)	104 (7)	116 (7)	94 (6)			
<b>non-linear, ortho-fused</b>											
P9,10bT	234 (100)	235 (18)	189 (11)	232 (9)	117 (8)						
<b>peri-condensed</b>											
Phelo67T	208 (100)	163 (24)	164 (19)	209 (16)	104 (13)	162 (8)	103 (7)				
<b>linear, ortho-fused</b>											
<b>C1</b>											
2-MeBN12T	248 (100)	247 (29)	245 (22)	249 (20)	122 (8)	124 (7)					
3-MeBN12T	248 (100)	247 (33)	245 (21)	249 (20)	124 (7)						
4-MeBN12T	248 (100)	247 (33)	249 (20)	245 (19)	122 (7)						
5-MeBN12T	248 (100)	247 (46)	249 (20)	245 (15)	122 (7)	215 (7)					
6-MeBN12T	248 (100)	247 (38)	249 (20)	245 (13)	124 (7)	215 (7)					
8-MeBN12T	248 (100)	247 (33)	249 (20)	245 (17)	124 (8)						
9-MeBN12T	248 (100)	247 (39)	249 (20)	245 (18)	122 (7)						
10-MeBN12T	248 (100)	247 (37)	249 (20)	245 (20)	124 (8)	122 (8)					
11-MeBN12T	248 (100)	247 (64)	245 (40)	249 (21)	246 (16)	122 (14)	221 (12)				

1-MeBN21T	248 (100)	247 (43)	249 (20)	245 (12)	221 (7)	110 (8)	221 (8)		
2-MeBN21T	248 (100)	247 (37)	249 (20)	245 (12)	124 (8)	221 (8)	124 (8)		
3-MeBN21T	248 (100)	247 (37)	249 (20)	245 (12)	110 (8)	221 (8)	221 (8)		
4-MeBN21T	248 (100)	247 (37)	249 (19)	245 (12)	124 (8)	110 (8)			
5-MeBN21T	248 (100)	247 (53)	249 (21)	215 (12)	245 (11)	124 (9)			
6-MeBN21T	248 (100)	247 (45)	249 (20)	215 (14)	245 (10)				
7-MeBN21T	248 (100)	247 (39)	249 (20)	215 (13)	245 (10)				
8-MeBN21T	248 (100)	247 (39)	249 (20)	124 (10)	245 (9)	215 (9)			
9-MeBN21T	248 (100)	247 (42)	249 (20)	245 (10)	124 (9)				
10-MeBN21T	248 (100)	247 (37)	249 (20)	124 (10)	245 (9)	215 (8)			
1-MeBN23T	248 (100)	247 (30)	249 (20)	215 (15)	124 (10)	245 (9)			
2-MeBN23T	248 (100)	247 (40)	249 (20)	124 (10)	245 (9)	215 (9)			
3-MeBN23T	248 (100)	247 (35)	249 (20)	245 (8)	124 (8)				
6-MeBN23T	248 (100)	247 (51)	124 (19)	249 (19)	122 (13)	245 (12)	215 (8)	202 (6)	
7-MeBN23T	248 (100)	247 (36)	110 (18)	249 (18)	124 (15)	245 (13)	110 (11)	202 (6)	
8-MeBN23T	248 (100)	247 (37)	249 (22)	245 (14)	124 (12)	110 (12)	123 (7)	96 (5)	
9-MeBN23T	248 (100)	247 (37)	249 (20)	245 (13)	110 (8)	124 (8)	122 (9)		
10-MeBN23T	248 (100)	247 (39)	249 (20)	245 (14)	110 (8)	221 (8)	124 (8)		
11-MeBN23T	248 (100)	247 (55)	249 (21)	215 (14)	245 (10)	202 (10)	124 (9)		
3-MeP21T	248 (100)	247 (34)	249 (20)	215 (18)	202 (16)	203 (9)			
10-MeP21T	248 (100)	247 (58)	245 (26)	249 (20)	246 (15)	122 (11)	221 (10)		
3-MeP9_10T	248 (100)	247 (37)	249 (20)	202 (16)	215 (15)	203 (9)			
1-MeA21T	248 (100)	247 (22)	249 (20)	202 (16)	215 (12)	245 (8)			
<b>C1</b>									
1-MeP45T	222 (100)	221 (90)	223 (20)	111 (16)	219 (9)	189 (8)			
2-MeP45T	222 (100)	221 (72)	111 (34)	223 (18)	110 (12)	97 (12)	189 (12)	176 (8)	
<b>5-RING PASHS</b>									
<b>linear, ortho-fused</b>									
<b>C1</b>									
5-MeB78A21bT	298 (100)	299 (24)	297 (23)	295 (15)	149 (9)				
5-MeB34P65bT	297 (100)	282 (85)	298 (81)	283 (55)	141 (51)	295 (22)	299 (20)	296 (13)	147 (12)
13-MeB32cdT	298 (100)	297 (50)	295 (28)	299 (24)	296 (14)	148 (13)			
7-MeC34bT	298 (100)	299 (23)	297 (23)	295 (14)	300 (7)	149 (7)			
<b>nonlinear, ortho-fused</b>									
Triphelo23bT	284 (100)	285 (23)	282 (16)	142 (12)	141 (8)				
Triphelo21bT	284 (100)	285 (22)	239 (16)	282 (15)	237 (8)	141 (8)			
Triphelo12bT	284 (100)	285 (23)	282 (22)	141 (13)	142 (11)	283 (8)			

(Continued on next page)





**Figure 3:** MS fragmentation pathways and mechanisms, using dibenzothiophene as the model PASH, of (a) monomethylated PASH, and (b) and (c) of  $C_2$  PASH, illustrating the difference in fragmentation between dimethyl (b) and ethyl (c) PASH.

methyl from the ethyl side chain is also the base ion for the  $C_3$  and  $C_4$  homologs (32), and the benzylium/tropylium ion is created by cleavage of ethyl, propyl, and butyl groups on propyl, butyl, and pentyl dibenzothiophenes, respectively, as well (49). Since there are so few synthesized  $C_2$ – $C_4$  alkylated PASH, work is in progress to detect these compounds in coal tar and crude oil by automated sequential GC-GC/MS.

Table 3 presents the retention indices for the Rxi-5, Rxi-17, Rtx-200, and DB-1701 columns using both the Lee (42) and Andersson (43) systems. The percent relative standard deviation (% RSD) for the DB-1701 and Rtx-200 columns was 0.002% and 0.013%, respectively,  $n = 3$ . Since precision was excellent, we

**Table 3:** PASH retention indices

Compound	Lee Index				Andersson Index			
	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms
<b>3-RING PASHs</b>								
<b>linear, ortho-fused</b>								
DBT- <i>d8</i>	296.46	296.20	295.49	295.59	299.66	300.08	299.45	298.93
DBT	296.88	296.24	295.47	295.44	15.767 <sup>a</sup>	10.189	25.863	29.846
(time)	297.72				10.714 <sup>b</sup>			
N21T	300.72	298.54	300.00	302.49	304.34	302.78	302.98	307.81
N23T	304.15	300.83	304.56	307.49	308.22	305.41	309.73	312.93
Phenanthrene	16.482 <sup>a</sup>	10.670	26.455	30.482				
(time)	11.037 <sup>b</sup>							
<b>DBTs</b>								
<b>C1</b>								
1-MeDBT	312.35	309.56	319.35	317.47	317.46	315.67	325.42	323.71
2-MeDBT	309.23	307.94	315.31	311.14	313.91	313.75	321.37	316.87
3-MeDBT	309.91	308.14	315.68	312.47	314.71	314.01	321.54	318.31
4-MeDBT	306.72	305.47	312.22	308.53	311.12	310.87	317.85	314.07
<b>C2</b>								
2-EtDBT	320.65	319.76	331.01	323.07	326.81	327.56	336.21	329.73
3-EtDBT	322.21	320.58	332.46	325.41	328.52	328.54	339.59	332.20
4-EtDBT	316.79	315.61	327.10	320.56	322.43	322.74	333.69	327.01
1,2-DiMeDBT	333.89	329.70	344.40	340.06	341.72	339.23	352.04	348.03
1,3-DiMeDBT	326.91	324.20	337.74	332.81	333.84	332.76	344.97	340.22
1,4-DiMeDBT	323.94	320.77	335.39	329.70	330.48	328.77	342.45	336.87
2,3-DiMeDBT	330.50	327.89	340.27	334.03	337.88	337.11	347.63	341.57
2,4-DiMeDBT	320.11	318.64	330.54	322.84	326.21	326.27	337.32	329.53
2,8-DiMeDBT	324.07	322.78	334.19	325.96	330.62	331.11	341.20	332.82
4,6-DiMeDBT	317.98	316.82	328.30	321.72	323.76	324.15	334.93	328.32
<b>C3</b>								
1,3,7-TriMeDBT	342.99	342.96	355.51	347.21	351.92	354.75	363.85	355.71
1,4,7-TriMeDBT	339.99	338.31	353.62	344.32	348.56	349.28	362.26	352.59
2,4,6-TriMeDBT	331.89	332.56	345.76	335.18	339.43	342.57	353.49	342.75
2,4,7-TriMeDBT	335.96	336.26	349.02	338.44	344.03	346.90	356.95	346.27
2,4,8-TriMeDBT	334.98	336.46	348.50	337.11	342.89	347.15	356.41	344.83
3,4,7-TriMeDBT	343.59	343.55	355.85	347.01	352.60	355.43	364.61	355.51
<b>N12bTs</b>								
<b>C1</b>								
2-MeN12T	ND	307.09	313.72	310.90	ND	312.55	319.44	316.67
5-MeN12T	311.80	309.51	318.41	317.20	316.75	315.52	324.41	323.39
6-MeN12T	313.28	310.21	319.35	318.14	318.48	316.43	325.42	324.39
7-MeN12T	309.81	308.43	315.31	312.89	314.57	314.31	321.12	318.75
8-MeN12T	309.35	307.85	314.66	312.28	314.08	313.67	320.52	318.10
<b>N21bTs</b>								
<b>C1</b>								
1-MeN21T	316.67	312.40	323.40	322.75	322.30	318.97	329.72	329.39
2-MeN21T	312.74	309.89	318.27	316.04	317.90	316.07	324.29	322.20
4-MeN21T	311.82	309.02	317.78	316.38	316.87	315.04	323.73	322.49
5-MeN21T	316.64	312.28	322.74	322.75	322.27	318.84	329.03	329.39
6-MeN21T	317.53	312.67	323.66	323.47	323.25	319.28	330.00	330.15
7-MeN21T	313.58	310.71	319.73	318.30	318.79	316.99	325.81	324.55
8-MeN21T	313.59	310.54	319.19	317.01	318.84	316.82	325.25	323.20
9-MeN21T	318.44	313.40	325.40	326.36	324.26	320.14	331.83	333.25
<b>4-RING PASHs</b>								
<b>linear, ortho-fused</b>								
P12T	395.22	391.15	396.29	397.45	407.74	406.51	406.97	409.20
P21T	401.76	397.51	400.75	403.20	413.27	410.80	411.57	414.89
P23T	403.32	399.94	402.08	403.95	414.84	412.37	412.80	415.60
P32T	402.72	399.17	401.60	403.32	414.30	411.89	412.38	414.99
P34T	395.69	390.29	396.70	398.85	408.12	405.89	407.38	410.64
P43T	394.15	390.10	395.34	396.89	406.88	405.76	406.04	408.66



Table 3: PASH retention indices (Continued)

Compound	Lee Index				Andersson Index			
	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms
A12T	394.24	390.96	395.36	395.29	406.91	406.31	406.03	407.03
A21T	400.39	396.30	399.27	400.07	411.81	409.88	410.04	411.81
A23T	408.00	404.41	ND	ND	419.53	417.08	ND	ND
BN12T	389.81	385.12	392.94	392.46	403.38	402.39	403.50	404.23
BN21T	385.63 <sup>a</sup>	381.65	389.53	388.32	36.139 <sup>a</sup>	21.103	38.164	42.801
	378.30 <sup>b</sup>				22.138 <sup>b</sup>			
BN21T-d10	384.81	381.62	388.85	387.48	399.23	400.02	399.27	399.04
BN23T	394.42	390.45	395.76	395.01	407.03	405.99	406.44	406.75
<b>non-linear, ortho-fused</b>								
P9,10T	394.08	389.34	395.13	396.09	406.78	405.16	405.83	407.87
<b>peri-condensed</b>								
Phelo67T	348.32	336.83	354.83	358.57	357.98	347.56	363.20	367.96
Acen12T/P45T <sup>d</sup>	ND	ND	347.84	ND	ND	ND	356.08	ND
Acen12T/P45T <sup>d</sup>	ND	ND	349.65	ND	ND	ND	358.00	ND
Chrysene	39.437 <sup>a</sup>	23.449	39.533	44.430				
	25.216 <sup>b</sup>							
<b>linear, ortho-fused</b>								
<b>C1</b>								
2-MeBN12T	403.69	405.39	406.16	400.45	415.32	418.19	416.78	412.41
3-MeBN12T	406.74	407.72	409.54	404.87	418.31	420.58	420.05	416.50
4-MeBN12T	410.46	410.32	413.48	410.19	422.00	423.25	423.90	421.72
5-MeBN12T	410.24	410.22	413.01	409.94	421.84	423.14	423.45	421.48
6-MeBN12T	404.70	405.00	407.96	403.56	416.24	417.72	418.53	415.23
8-MeBN12T	404.29	405.10	407.55	403.64	415.87	417.82	418.12	415.30
9-MeBN12T	407.25	408.24	409.83	405.57	418.83	421.10	420.35	417.18
10-MeBN12T	404.50	406.17	407.02	401.62	416.06	418.94	417.61	413.30
11-MeBN12T	398.48	399.44	403.10	401.85	410.45	411.89	413.81	413.72
1-MeBN21T	409.43	409.04	412.97	410.56	421.04	421.94	423.44	422.05
2-MeBN21T	402.86	405.05	405.60	400.05	414.46	417.69	416.19	411.86
3-MeBN21T	403.67	405.95	406.20	401.46	415.14	418.72	416.82	412.97
4-MeBN21T	407.24	408.05	410.10	405.87	418.79	420.92	420.62	417.48
5-MeBN21T	406.26	407.16	408.94	404.23	417.77	419.98	419.49	415.85
6-MeBN21T	407.10	407.60	410.31	406.69	418.66	420.42	420.80	418.30
7-MeBN21T	407.27	407.88	410.59	406.86	418.84	420.71	421.08	418.48
8-MeBN21T	403.40	405.73	405.95	400.84	414.96	418.47	416.59	412.54
9-MeBN21T	404.00	406.14	406.48	401.95	415.57	418.90	417.09	413.70
10-MeBN21T	399.91	401.83	403.21	398.44	411.49	414.37	413.94	410.19
1-MeBN23T	411.52	411.61	413.62	409.77	423.06	424.53	424.04	421.29
2-MeBN23T	403.48	405.95	406.07	400.76	414.98	418.51	416.75	412.55
3-MeBN23T	411.33	412.42	412.84	408.83	422.90	425.43	423.30	420.34
6-MeBN23T	410.15	409.73	413.05	409.16	421.58	422.66	423.44	420.69
7-MeBN23T	412.28	412.33	414.72	410.39	423.90	425.36	425.12	421.91
8-MeBN23T	410.37	411.66	412.41	407.64	421.75	424.66	422.85	419.21
9-MeBN23T	410.45	411.33	412.42	407.32	421.99	424.31	422.85	418.92
10-MeBN23T	410.41	410.67	412.11	407.34	421.95	423.59	422.58	418.94
11-MeBN23T	418.19	416.73	420.71	419.50	429.76	429.92	430.91	430.73
3-MeP21T	419.40	417.83	420.69	420.10	430.90	431.07	431.04	431.36
10-MeP21T	417.98	415.94	ND	ND	429.54	429.13	ND	ND
3-MeP9,10T	413.63	412.86	415.83	413.70	425.15	425.89	426.15	425.11
1-MeA21T	414.90	414.51	416.04	413.58	426.40	427.59	426.39	424.98
Benzo(a)pyrene	53.788 <sup>a</sup>	33.255	45.784	51.141				
	45.907 <sup>b</sup>							
<b>peri-condensed</b>								
<b>C1</b>								
1-MeP45T	363.33	355.97	371.20	369.92	374.87	369.92	380.62	380.18
2-MeP45T	359.06	353.26	368.03	366.11	370.17	366.55	377.17	376.00

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**Table 3:** PASH retention indices (*Continued*)

Compound	Lee Index				Andersson Index			
	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms
<b>5-RING PASHS</b>								
<b>ortho-fused</b>								
<b>C1</b>								
5-MeB78A21bT	512.16	508.27	511.30		518.63	525.11	524.06	
5-MeB34P65bT (time)	473.38	476.49	481.56	475.65 54.574	481.77	492.43	493.64	490.34
13-MeBP32dT	509.36	505.21	509.88		515.91	522.21	522.60	
7-MeC34bT	512.68	510.52	511.41		519.17	527.89	524.12	
<b>nonlinear, unfused</b>								
Triphelo23bT	498.94	495.64	497.31		506.11	512.33	509.73	
Triphelo21bT	488.94	487.15	491.08		496.55	503.37	503.40	
Triphelo12bT (time)	490.20	488.70	491.93	485.05 55.743	497.74	505.06	504.24	500 <sup>c</sup>
<b>peri-condensed</b>								
C45T	444.68	442.41	447.08	447.40	456.27	456.68	457.96	458.83
Triphelo45T	443.76	440.01	445.10	444.82	453.05	454.38	455.58	456.23
Py12T	ND	443.42	446.18	447.59	ND	457.68	457.01	459.10
Py21T (time)	451.89	448.84	451.56	453.91 51.601	461.49	463.40	462.93	466.05
Py45T	441.23	439.91	443.68	444.60	453.87	454.37	453.85	456.02
B23P45T	442.19	436.18	440.50	439.34	50.467	30.523	44.596	49.710
	439.30				40.031			
B1,2Phelo34bcT	442.22	440.46	444.60	445.35	454.36	454.62	455.12	456.69
B1,12Triphelo45T	495.83	494.41	ND	ND	502.93	510.60	ND	ND
B45Phelo19T (time)	452.27	448.67	475.43	454.11 51.668	461.63	462.97	463.92	466.41
B45Phelo91T	ND	449.62	ND	ND	ND	464.12	ND	ND
<b>fused</b>								
<b>C1</b>								
1-MeB23P45T	448.19	450.36	452.67	446.87	458.51	464.91	464.13	458.47
3-MeB23P45T (time)	456.84	458.44	461.10	455.40 51.782	466.16	473.47	472.83	467.66
5-MeB23P45T (time)	454.18	455.93	458.80	451.78 51.369	463.73	470.69	470.45	463.87
7-MeB23P45T (time)	455.78	457.46	460.35	454.01 51.631	465.24	472.49	472.07	466.27
9-MeB23P45T (time)	452.74	455.15	456.63	450.36 51.097	462.19	470.02	468.34	461.99
Benzo(ghi)perylene <sup>a</sup> (time)		42.862	50.959					
	74.757 <sup>b</sup>							
<b>6-RING PASHS</b>								
<b>linear, ortho-fused</b>								
P34aDBT (time)		571.64	573.15			589.60	584.91	
		56.129					58.326	
P43cDBT (time)		567.82	569.99			585.97	583.54	
		55.521					58.184	
P43aDBT (time)	515.08	518.65	517.88		521.26	535.10	530.81	
		46.267					52.789	
BbbB56P23dT (time)		573.02	527.10			590.69	583.31	
		56.349					58.170	
Acen45aDBT (time)	<sup>a</sup>		536.75		<sup>a</sup>	48.565	54.758	
	100.951 <sup>b</sup>		54.758		550 <sup>b,c</sup>			
<b>C1</b>								
6-MeB56A21bBaT (time)		592.01				610.01		
		59.938						
7-MeBbcC43dT (time)		568.26				588.20		
		55.458						

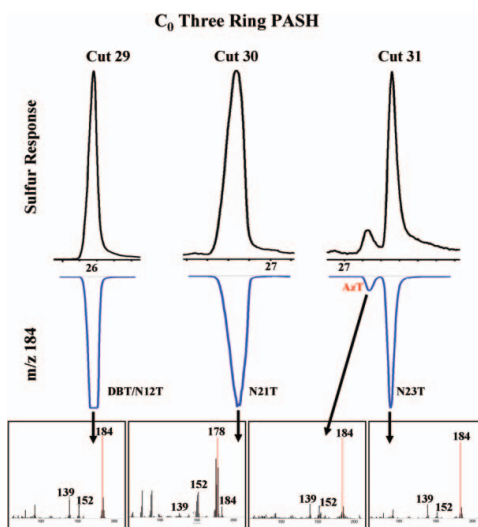
**Table 3:** PASH retention indices (*Continued*)

Compound	Lee Index				Andersson Index			
	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms	DB-1701ms	Rtx-200ms	Rxi-5ms	Rxi-17Sil-ms
5-MeBbB56P43aT (time)	536.18	532.64 <i>48.663</i>	534.53		541.22	551.03	547.74 <i>54.526</i>	
Triphelo21cDBT (time)		647.49 <i>70.350</i>				668.16		
Triphelo21aDBT (time)		647.63 <i>70.345</i>				668.11		
Triphelo12cDBT (time)		646.33 <i>70.112</i>				666.90		

analyzed 20% of the PASH to determine precision on the other two columns, which also was excellent ( $\%RSD = 0.01_2$  and  $0.01_0$  for Rxi-5 and Rxi-17, respectively, for  $n = 3$ ). Since Acen45aDBT did not elute from the Rxi-17 column under the conditions used, Triphelo12bT served as the last bracket, i.e.,  $RI = 500$ . This compound eluted at  $502.35 \pm 4.01$  Andersson units on the other three stationary phases. To compare elution of PASH with index values  $> 450$ , elution times can be calculated from the retention times of the internal standard provided in the table. In addition, some PASH did not elute using the 56.75 min run on DB-1701 (see Table 1 for conditions) and so were reanalyzed using a slower temperature program. In Table 3, 21 compounds with Andersson index  $> 450$  on DB-1701 were analyzed using the longer run time (106 min, see Table 1).

The most striking feature of the retention indices is the high correlation across all columns. The Pearson correlation coefficient is  $\sim 0.99$  when data for the four columns are regressed. Results demonstrate that for PASH the stationary phases are not dissimilar enough to produce orthogonal retention, i.e.,  $r^2 = 0$ . We calculated the number of coeluting compounds on each column based on the resolution ( $R_s$ ) criterion 1.0, which corresponds to  $4\sigma$  separation between peaks. The Rtx-200 did the best job of separation, with only 38% of compounds coeluting. The Rxi-5 and DB-1701 performed similarly to one another, with 44% and 48% of compounds coeluting, respectively, as opposed to 56% coelution on Rxi-17.

To determine if multidimensional GC provided the separation space needed to identify PASH in an aromatic fraction of coal tar, three 1-min sample portions were heartcut from Rxi-17 between 29 and 32 min. Figure 4 shows the portion of the chromatogram where PASH eluted on the Rtx-5 column. The retention index data guided our choice of heartcut windows. Consistent with the literature (28,50,51), DBT and N12T have the same mass spectra and coelute on both Rxi-17 and Rtx-5. In contrast, the other two isomers separate on both



**Figure 4:** Three heartcuts of a fresh coal tar sample. The chromatograms are selected ion extraction at  $m/z$  184 (molecular ion for three-ring thiophenes) and corresponding sulfur responses (color figure available online).

phases illustrated by the MS and PFPD response for the three cuts. The multi-dimensional separation removes matrix interferences on the analytical column so that pure mass spectra are obtained. The figure illustrates the mass spectrum at the peak maximum for each compound. As expected, N21T coelutes with phenanthrene (see Table 3), and so the mass spectrum is dominated by this higher concentration compound.

Since the retention times and spectra for all 3-ring PASH are known, we believe the peak at 27.15 min in Figure 4 is an azuleno thiophene. The molecular ion for this compound is the same as  $C_4$  naphthalene, which also elutes in the same retention window. Analysis by SIM could lead to misidentification. The PFPD, however, confirms the peak is due to a sulfur-containing organic. Moreover, the fragmentation pattern for the peak is the same as azuleno[2,1-*b*]thiophene, which is identical to 3-ring PASH except for minor differences in relative abundances. Similarly, heartcuts were made to obtain the identity of 4-ring *peri* condensed PASH. Three possible isomers exist, namely, Phelo67T, P45T, and acenaphtho[1,2-*b*]thiophene (Acen12T). No standards were available for the last two compounds. We made heartcuts based on the retention time of Phelo67T on Rxi-17 and found three peaks whose mass spectra match that of Phelo67T. Corresponding sulfur signals were observed at each retention time. We positively identified Phelo67T, but in the absence of retention times for standards, the order of elution cannot be assigned for the other two PASH. Table 3 includes the retention indices for these compounds. These examples illustrate the utility of using high sulfur content aromatic samples to

build retention time and mass spectral libraries of these compounds. Work is in progress to fully characterize crude oil and coal tars for this purpose.

*Peri* condensed isomers generally eluted earlier than their same-ring-number counterparts that are *ortho* fused. For example, Py45*b*T, B12Phelo45T, Py12T, Chry45T, Py21T, and B45Phelo19T all elute earlier than the Triphelo12*b*T, Triphelo21*b*T, and Triphelo23*b*T isomers. This trend is apparent in PAH as well, since pyrene elutes much earlier than chrysene, while benzo[*a*]pyrene elutes much earlier than picene. The primary reason for this observation is the higher carbon number for *ortho*-fused vs. *peri*-condensed; fewer carbons are required to reach the same number of rings when the rings are *peri*-condensed. Even on moderate or high polarity stationary phases, a major contribution to the partitioning coefficient of the isomer is the vapor pressure of the compound at a given temperature.

An interesting finding was the elution of the phenanthro-dibenzothiophenes. P43*a*DBT has a much smaller retention index than other phenanthro-dibenzothiophene isomers. P43*a*DBT has a shape which creates a *fjord* region in the isomer, whereas the other isomers have a more elongated shape without the pronounced *fjord* region in the molecule, see Figure 1. Therefore, the molecule has a smaller surface area for interaction with solvating stationary phase molecules, and therefore is less retained.

## CONCLUSION

Retention and mass spectra data have been reported for over 100 polycyclic aromatic sulfur heterocycles and some alkylated analogues. These data should prove useful for investigators attempting to determine the concentration of these compounds in fossil fuel and environmental samples. Forensic chemists routinely report the concentration of dibenzothiophene and its C<sub>1</sub> to C<sub>4</sub> alkylated homologs when tracing oil spills to their sources. Diagnostic ratios may be inaccurate since, e.g., the concentrations assigned to the C<sub>1</sub> dibenzothiophenes will include other 3-ring alkylated PASH in the sample due to coelution and identical mass spectra.

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