

# Structural Characteristics of Polycyclic Aromatic Hydrocarbon Isomers in Coal Tars and Combustion Products

Masaharu Nishioka, Huey-Ching Chang, and Milton L. Lee\*

Department of Chemistry, Brigham Young University, Provo, Utah 84602

■ Isomeric polycyclic aromatic hydrocarbons (PAH) with two to six rings in coal-derived products and in a carbon black were separated, identified, and quantified by using capillary column gas chromatography and gas chromatography-mass spectrometry. A newly synthesized smectic liquid-crystalline polysiloxane and a conventional polymethylsiloxane were utilized as stationary phases. Many previously difficult to separate isomeric PAH (i.e., methylphenanthrenes/methylanthracenes, triphenylene/chrysene, methylchrysenes, benzofluoranthenes, and pentaphene/benzo[b]chrysene) were identified. The relative abundances of the PAH in these samples were compared and correlated to the reaction conditions during their production. The relationship between abundance and structure for the identified PAH was also discussed.

## Introduction

Coal-derived products and thermally cracked petroleum oils are highly aromatic in nature and contain polycyclic aromatic hydrocarbons (PAH) as major components. Although average descriptive parameters are usually obtained for such materials (i.e., distillation curve, molecular weight range, aromaticity, etc.), it is oftentimes very important to obtain detailed compositional and structural information.

Many of the PAH are toxic and/or mutagenic in various biological test systems. The toxicities of various PAH are related to specific structures and positions of ring substitution. The methylphenanthrene and methylchrysene isomers are typical examples. The 1- and 9-methylphenanthrenes are mutagenic, while the other isomers are inactive (1), and 5-methylchrysene is one of the strongest carcinogens, while the other isomers are only moderately carcinogenic (2). Isomeric parent PAH may differ markedly in their activities; benzo[a]pyrene has significantly greater carcinogenicity than benzo[e]pyrene, the relative carcinogenicity varies within the series of dibenzanthracenes, and benzo[g]chrysene appears to be more active than benzo[c]chrysene (3, 4).

A number of components of the process oils play important roles in the upgrading processes. Hydrogenated compounds such as tetralin are hydrogen donor solvents for coal liquefaction (5). Cracked gas oils containing highly aromatic compounds are often composed of discontinuous fractions in discrete boiling point ranges. For example, alkylated PAH with boiling points between acenaphthylene and phenanthrene, or phenanthrene and pyrene, are relatively less abundant. It is very important to identify components and to recycle specific product oils when these oils must be used in the processes (6).

Finally, the PAH in the upgraded products may be related to the compositions of the feedstocks. The detailed characterization of such products is essential to obtain information about the complex structure of fossil fuels such as coal, oil shale, and petroleum.

It is, however, difficult to identify these PAH isomers even by using high-resolution chromatographic and mass spectrometric methods because of their similar retention behavior and fragmentation patterns. In many cases,

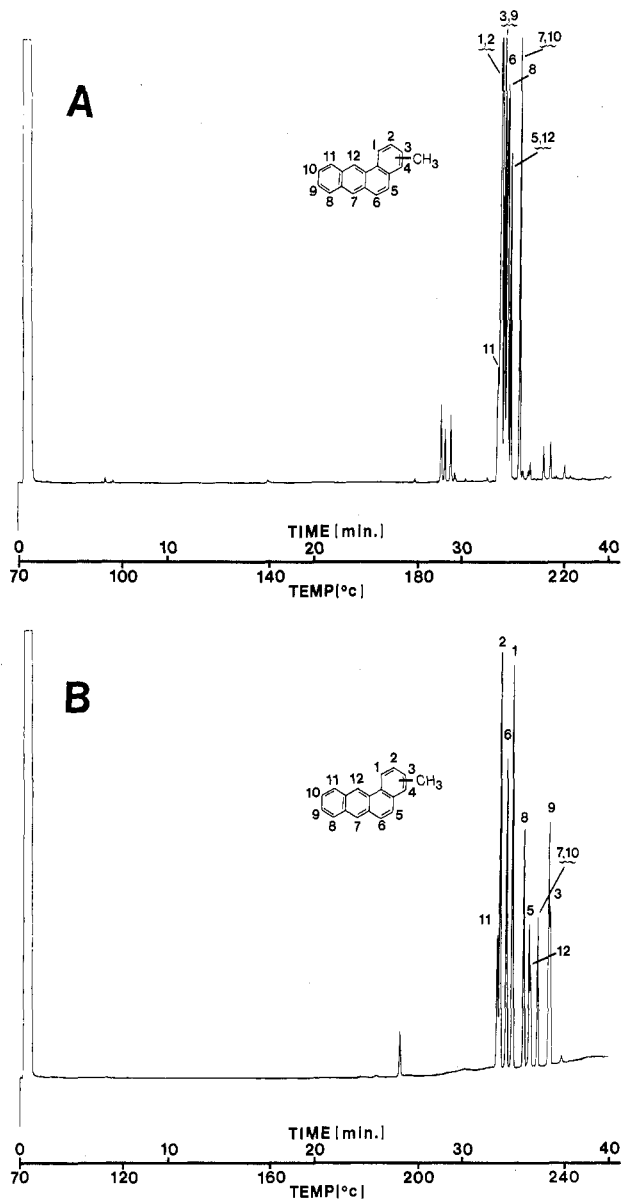
analytical methods for identification of isomeric PAH are complex and time consuming. For example, after relatively complex procedures employing several steps of solvent partition, liquid chromatography, and capillary gas chromatography, FT <sup>1</sup>H NMR was used to confirm the identities of each of the six methylated chrysene isomers (7). Because of the attendant sample complexity, open tubular column gas chromatography has accordingly become an indispensable technique for analysis of these species.

Capillary column gas chromatography using authentic standard compounds and selective stationary phases is one of the easiest and most reliable methods. Presently, the majority of PAH with up to five or six rings, including many alkylated compounds, are available (8, 9). Slightly polar gum phases such as SE-52 or SE-54 have been shown to offer high column efficiency, some selectivity, and high thermal stability for PAH (10); however, many compounds are not well resolved even with these phases (e.g., methylphenanthrenes/methylanthracenes, triphenylene/chrysene, methylchrysenes/methylbenz[a]anthracenes, benzo[e]pyrene/benzo[a]pyrene, benz[a]aceanthrylene/benzo[j]fluoranthene, and benzo[ghi]perylene/indeno[1,2,3-cd]pyrene/cata-condensed five-ring PAH). In contrast, mesomorphic (nematic or smectic liquid-crystalline) phases which provide separation on the basis of molecular geometry in addition to boiling point have been shown to be highly selective for PAH which coelute on other phases (11). Nematic polysiloxanes prepared by Laub and co-workers (12-14) and smectic polysiloxanes prepared by us (15-17) have unsurpassed resolution for PAH.

In this study, a newly synthesized smectic liquid-crystalline polysiloxane and a conventional SE-54 phase were utilized to identify the isomeric PAH with two to six rings in coal-derived products and in a carbon black produced in a combustion process. The relationship between abundance and structure for the identified PAH is discussed.

## Experimental Section

A solvent-refined coal heavy distillate (SRC II HD, 260-450 °C boiling point range) was collected during the processing of a West Virginia coal from the Pittsburgh Seam, and obtained from the Fort Lewis, WA, pilot plant which was operated by Pittsburg and Midway Coal Mining Co. This material is of pilot plant origin and should not necessarily be considered as representative of products that may eventually be produced on a commercial scale. A coal tar was obtained from the National Bureau of Standards (Washington, DC), which was a medium crude coke oven tar. A carbon black was obtained from Cabot Corp. (Boston, MA). A 10-g quantity of carbon black was extracted with 500 mL of methylene chloride for 24 h in a Soxhlet apparatus. The SRC II HD and the coal tar were fractionated into chemical classes by column adsorption chromatography on neutral alumina as previously described (18). The A-2 fractions (PAH) were selected for analysis in this study. A fraction containing five- and six-ring PAH from the coal tar was obtained by using a supercritical fluid fractionation method (19). The solute standards were dissolved in methylene chloride, except for

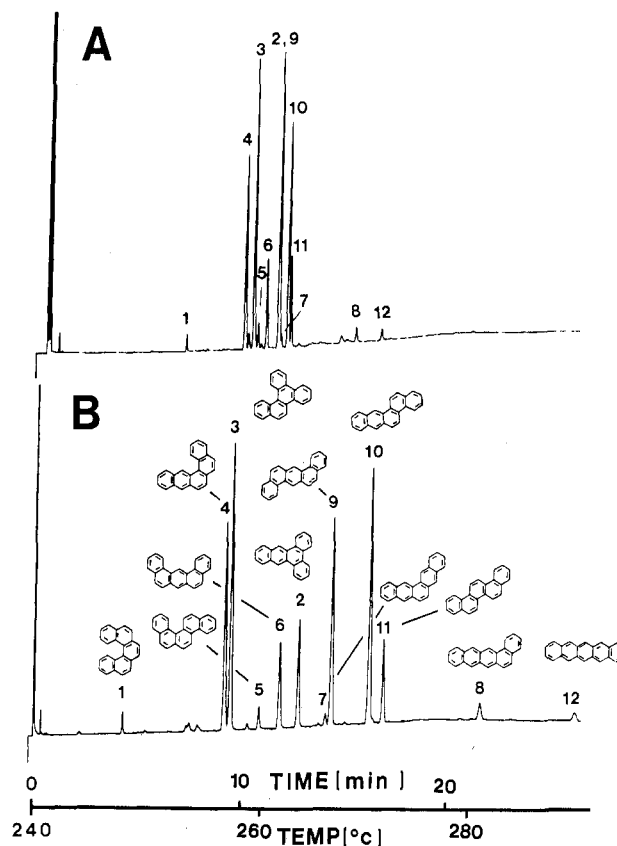


**Figure 1.** Chromatograms of isomeric methylbenz[*a*]anthracenes on (A) SE-54 (20 m × 0.3 mm i.d., 0.25- $\mu$ m film) and (B) a liquid-crystalline polysiloxane having 50% substitution with mesomorphic moieties (10 m × 0.3 mm i.d., 0.25- $\mu$ m film). Conditions: temperature program from 70 to 100 °C in (A) and to 120 °C in (B) at 10 °C min<sup>-1</sup> after an initial 2-min isothermal period and then at 4 °C min<sup>-1</sup>; hydrogen carrier gas at 100 cm s<sup>-1</sup> linear velocity.

pentacene which was dissolved in 1,2,4-trichlorobenzene.

A Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector was used. Sample injection was made in the splitless mode, and the hydrogen carrier gas was set at a linear velocity of 50–100 cm s<sup>-1</sup>. Capillary columns were prepared by statically coating fused silica capillary tubing (0.2 or 0.3 mm i.d., Hewlett-Packard, Avondale, PA) with SE-54 and smectic liquid-crystalline polysiloxanes having 25% and 50% substitution with mesomorphic moieties (16, 17). Both columns were cross-linked by using azo-*tert*-butane (20) and conditioned overnight at 280 °C under nitrogen gas flow.

Compounds were identified by comparison of sample component retention data with those of pure standards. Quantitation was accomplished by comparing peak areas of the resolved components with the peak areas resulting from a standard injection of phenanthrene, chrysene, and picene under the same chromatographic conditions. A Hewlett-Packard Model 5982A GC-MS system was used



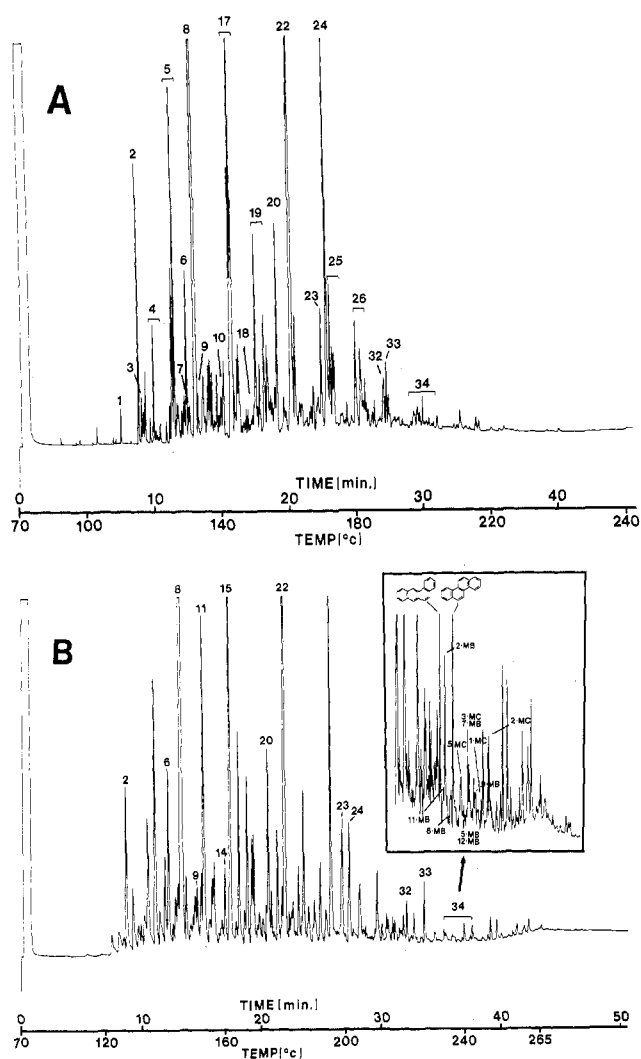
**Figure 2.** Chromatograms of all 12 isomers of the cata-condensed five-ring PAH in (A) SE-54 (12 m × 0.2 mm i.d., 0.25- $\mu$ m film) and (B) a liquid-crystalline polysiloxane having 25% substitution of mesomorphic moieties (13 m × 0.2 mm i.d., 0.10- $\mu$ m film). Conditions: temperature program from 240 to 280 °C at 2 °C min<sup>-1</sup> after an initial 1-min isothermal period; hydrogen carrier gas at (A) 70 and (B) 100 cm s<sup>-1</sup>. Key: (1) dibenzo[*c,g*]phenanthrene, (2) dibenz[*a,c*]anthracene, (3) benzo[*g*]chrysene, (4) benzo[*b,g*]phenanthrene, (5) benzo[*c*]chrysene, (6) dibenz[*a,j*]anthracene, (7) pentaphene, (8) benzo[*a*]naphthacene, (9) dibenz[*a,h*]anthracene, (10) benzo[*b*]chrysene, (11) picene, and (12) pentacene.

to obtain mass spectral confirmation of identified compounds. The same chromatographic columns were used, and the mass spectrometer was operated in the electron impact mode at 70-eV electron energy.

### Results and Discussion

The resolution of PAH in selected isomer groups including the methylphenanthrenes, cata-condensed four-ring PAH, and methylchrysenes using a smectic liquid-crystalline phase was described in a previous paper (16). The methylchrysenes and methylbenz[*a*]anthracenes have nearly identical relative retentions, and it is essential that these isomers be separated in order to identify them in real samples (4, 21). Figure 1 shows 11 isomers (4-methylbenz[*a*]anthracene missing) of the methylbenz[*a*]anthracenes on SE-54 (Figure 1A) and on the smectic phase (Figure 1B). The selectivity of the smectic phase was outstanding; a total of 17 isomers of the methylchrysenes and methylbenz[*a*]anthracenes could be separated, with only 3-methylchrysene, 7-methylbenz[*a*]anthracene, and 10-methylbenz[*a*]anthracene coeluting on this phase.

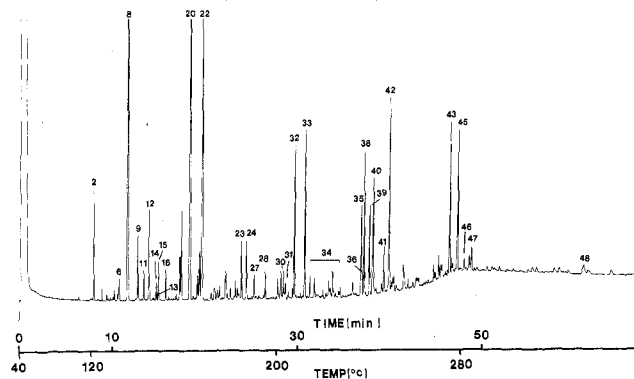
The cata-condensed five-ring PAH are also typically difficult to resolve. Again, it is necessary to fully separate these compounds for their exact identification. Figure 2 contrasts the separation of all 12 of the cata-condensed five-ring standard PAH on SE-54 (Figure 2A) and on the smectic phase (Figure 2B). The selectivity of the latter phase is clearly superior to that offered by the former.



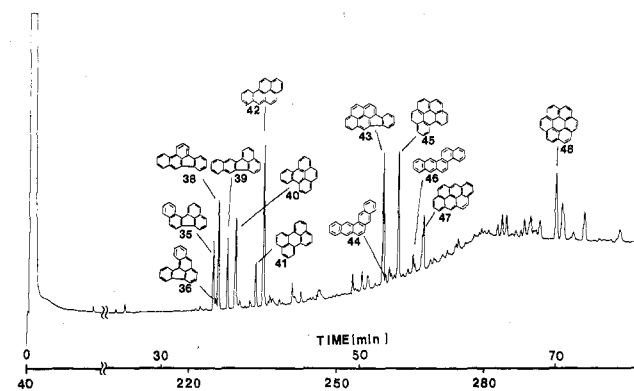
**Figure 3.** Chromatograms of an SRC II HD PAH fraction on (A) SE-54 (12 m  $\times$  0.2 mm i.d., 0.25- $\mu$ m film) and (B) a liquid-crystalline polysiloxane having 50% substitution of mesomorphic moieties (10 m  $\times$  0.3 mm i.d., 0.25- $\mu$ m film). Conditions as in Figure 1. Peak assignments are listed in Table 1. Key: MC = methylchrysene; MB = methylbenz[a]anthracene.

The PAH in the SRC II HD were identified by using retention data from columns coated with SE-54 and the smectic phase. Figure 3 shows chromatograms of the SRC II HD PAH fraction on SE-54 (Figure 3A) and on the smectic phase (Figure 3B). All methylphenanthrene and methylanthracene isomers were separated on the smectic phase, and 2- and 3-methylphenanthrenes were found as major components. The separation of chrysene and triphenylene was also accomplished by using this phase. Of the five cata-condensed four-ring PAH isomers, only chrysene and benz[a]anthracene were present in significant concentrations in the SRC II HD. Although the methylchrysene isomers were minor components in the SRC II HD, the 2- and 3-methylchrysenes were the most abundant of the isomers.

A chromatogram of the PAH in the coal tar on the liquid-crystalline phase is shown in Figure 4. The PAH in this sample were identified in the same manner as previously described for the SRC II HD. Unsubstituted PAH predominated in the coal tar as well as several polycyclic aromatic sulfur heterocycles (PASH) (22, 23). Fluorene and its benzologues such as 4*H*-cyclopenta[*def*]phenanthrene, benzo[*a*]fluorene, and benzo[*b*]fluorene were more abundant in the coal tar than in the SRC II HD. Also, nonalternant PAH such as fluoranthene, benzo[*ghi*]fluoranthene, and cyclopenta[*cd*]pyrene were rela-



**Figure 4.** Chromatogram of a coal tar PAH fraction on a liquid-crystalline polysiloxane having 25% substitution of mesomorphic moieties (13 m  $\times$  0.2 mm i.d., 0.10- $\mu$ m film). Conditions: temperature program from 40 to 120  $^{\circ}$ C  $\text{min}^{-1}$  after an initial 2-min isothermal period and then to 280  $^{\circ}$ C at 4  $^{\circ}$ C  $\text{min}^{-1}$ ; hydrogen carrier gas at 100  $\text{cm s}^{-1}$ . Peak assignments are listed in Table I.



**Figure 5.** Chromatogram of PAH containing five and six rings in a coal tar fraction on a liquid-crystalline polysiloxane having 25% substitution of mesomorphic moieties (13 m  $\times$  0.2 mm i.d., 0.10- $\mu$ m film). Conditions: temperature program from 40 to 120  $^{\circ}$ C at 12  $^{\circ}$ C  $\text{min}^{-1}$  after an initial 2-min isothermal period and then to 280  $^{\circ}$ C at 2  $^{\circ}$ C  $\text{min}^{-1}$ ; hydrogen carrier gas at 100  $\text{cm s}^{-1}$ .

tively high in concentration. Benzo[*c*]phenanthrene and triphenylene were also found in this coal tar in contrast to the SRC II HD. The five- and six-ring PAH in the coal tar were easily identified after supercritical fluid fractionation (19) of the sample. Figure 5 shows the chromatogram of this fraction on the smectic phase with a temperature program rate of 2  $^{\circ}$ C  $\text{min}^{-1}$ . All isomers of the benzofluoranthenes, pentaphene, and benzo[*b*]chrysene were identified for the first time. The structures and relative abundances of these five- and six-ring PAH identified in this study were previously compared to the major PASH in the same sample (23).

The PAH in the carbon black were separated and identified as shown in Figure 6. Peri-condensed nonalternant PAH such as 4*H*-cyclopenta[*def*]phenanthrene, benzo[*ghi*]fluoranthene, and cyclopenta[*cd*]pyrene were significant. Table I lists the PAH identified and their approximate concentrations in the three samples analyzed in this study.

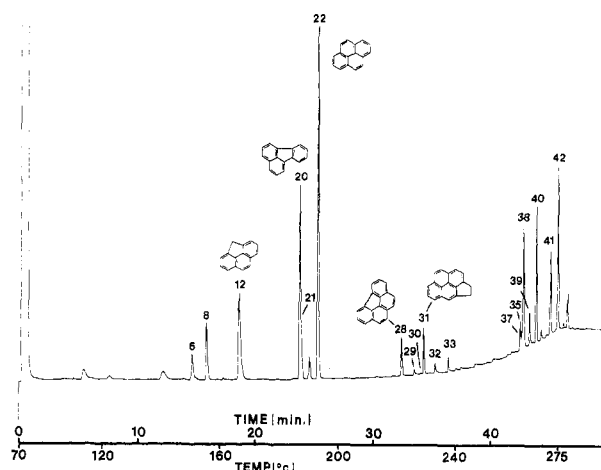
It was recently shown that the structures and relative abundances of the major sulfur heterocycles in mixtures of polycyclic aromatic compounds were analogous to those of the major PAH (23). By replacement of one of the aromatic rings in the most abundant PAH with a thiophene ring, the most abundant PASH were generally described. Major cyclopenta-containing PAH such as fluorene and benzofluorene also are structurally analogous to the most abundant alternant PAH. Benzo[*c*]phenanthrene was less abundant than chrysene and benz[*a*]anthracene in the coal-derived products, and ben-

**Table I. Polycyclic Aromatic Hydrocarbons Identified and Quantified in an SRC II HD, a Coal Tar, and a Carbon Black**

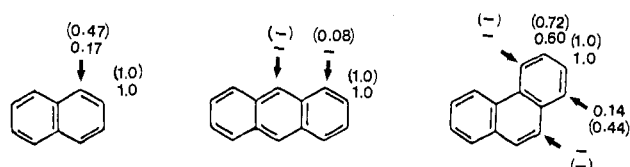
peak no.	compound	conc <sup>a</sup>		
		SRC II HD, mg/g	coal tar, mg/g	carbon black, µg/g
1	dibenzofuran	1.4		
2	fluorene	13	13	
3	C <sub>1</sub> -biphenyl isomer	2.1		
4	C <sub>2</sub> -biphenyl isomers	b		
5	C <sub>1</sub> -fluorene/C <sub>2</sub> -biphenyl isomers	b		
6	dibenzothiophene	11	1.6	50
7	tetrahydroanthracene isomer	1.7		
8	phenanthrene	95	53	110
9	anthracene	2.5	12	
10	1-phenylnaphthalene	2.2		
11	3-methylphenanthrene	18	1.8	
12	4 <i>H</i> -cyclopenta[def]-phenanthrene		6.3	270
13	1-methylanthracene		0.15	
14	1-methylphenanthrene	4.2	1.1	
15	2-methylphenanthrene	30	2.5	
16	2-methylanthracene		1.9	
17	C <sub>1</sub> -phenanthrene isomers	b		
18	2-phenylnaphthalene	1.0		
19	C <sub>2</sub> -phenanthrene isomers	b		
20	fluoranthene	12	40	310
21	phenanthro[4,5- <i>bcd</i> ]-thiophene			90
22	pyrene	61	31	570
23	benzo[ <i>a</i> ]fluorene	8.9	3.7	
24	benzo[ <i>b</i> ]fluorene	7.7	3.6	
25	C <sub>1</sub> -pyrene isomers	b		
26	C <sub>2</sub> -pyrene isomers	b		
27	benzo[ <i>c</i> ]phenanthrene		1.7	
28	benzo[ <i>ghi</i> ]fluoranthene		1.5	60
29	benzo[ <i>b</i> ]naphtho[2,1- <i>d</i> ]-thiophene			5
30	triphenylene		2.0	1
31	cyclopenta[ <i>cd</i> ]pyrene		0.63	70
32	benz[ <i>a</i> ]anthracene	2.0	8.0	10
33	chrysene	3.6	8.6	20
34	C <sub>1</sub> -chrysene isomers	b	b	
35	benzo[ <i>j</i> ]fluoranthene		5.7	20
36	benz[ <i>a</i> ]aceanthrylene		7.9	190
37	triphenyleno[4,5- <i>bcd</i> ]-thiophene			30
38	benz[ <i>c</i> ]-acephenanthrylene		0.4	
39	benzo[ <i>k</i> ]fluoranthene		4.9	40
40	benzo[ <i>e</i> ]pyrene		6.1	190
41	perylene		4.2	120
42	benzo[ <i>a</i> ]pyrene		9.7	250
43	indeno[1,2,3- <i>cd</i> ]pyrene		8.0	c
44	pentaphene		0.4	c
45	benzo[ <i>ghi</i> ]perylene		7.0	c
46	benzo[ <i>b</i> ]chrysene		0.6	c
47	dibenzo[ <i>def,mno</i> ]-chrysene		2.0	c
48	coronene		2.0	c

<sup>a</sup> Approximate concentration in mg/g or µg/g of original material. <sup>b</sup> These compounds were detected but were not quantified. <sup>c</sup> These compounds are known to be present but were not eluted under the chromatographic conditions used for the carbon black analysis.

zo[*c*]fluorene which is structurally analogous to benzo[*c*]phenanthrene was not found, while benzo[*a*]fluorene and benzo[*b*]fluorene which are structurally analogous to chrysene and benz[*a*]anthracene were found at significant levels. Although benzoated 4*H*-cyclopenta[*def*]-phenanthrenes were not identified because of the lack of standard reference samples, these isomers are expected to be present in these coal-derived products. Suspected



**Figure 6.** Chromatogram of a carbon black extract on a liquid-crystalline polysiloxane having 50% substitution of mesomorphic moieties (12 m × 0.2 mm i.d., 0.25-µm film). Conditions as in Figure 1. Peak assignments are listed in Table I.



**Figure 7.** Relative abundances of methylphenanthrenes in the SRC II HD and in the coal tar (numbers in parentheses refer to the coal tar). Arrows indicate the sites of steric hindrance.

isomers of these compounds with *m/z* 240 were detected by GC-MS. They could be structurally derived from the major peri-condensed five-ring PAH, benzo[*a*]pyrene and benzo[*e*]pyrene.

Anthracene was less abundant in the SRC II HD than it was in the coal tar. Of the five cata-condensed four-ring PAH isomers, chrysene and benz[*a*]anthracene were the most abundant in all three samples studied. Triphenylene and benzo[*c*]phenanthrene were not found in the SRC II HD, and naphthacene was not identified in any of these samples. The order of increase in resonance energy for these compounds is anthracene < phenanthrene and naphthacene < benz[*a*]anthracene < chrysene ≈ benzo[*c*]phenanthrene < triphenylene (24). There is a possibility that triphenylene and benzo[*c*]phenanthrene could only be synthesized by the high-temperature processes used to produce coal tar and carbon black. These two compounds were not found in the SRC II HD which was a lower temperature product. These results can be explained on the basis of the resonance energy, i.e., the greater the resonance energy, the higher the necessary temperature for synthesis. The relative abundance of these isomeric PAH might also reflect the original skeletal structures of components in feedstocks. The relative abundances of the peri-condensed PAH with high resonance energy such as 4*H*-cyclopenta[*def*]phenanthrene, benzo[*ghi*]fluoranthene, and cyclopenta[*cd*]pyrene increased in order of the SRC II HD, the coal tar, and the carbon black. The PAH structures in the high-temperature products are substantially different from the original feedstocks. However, the more abundant PAH such as chrysene, benz[*a*]anthracene, and phenanthrene in the SRC II HD, products of low-temperature reaction, may reflect the fundamental structure of coal.

Interest in the relative abundances of methylated PAH stems from the correlation between mutagenic activity and specific substituent positions, and from structural information relating to coal and coal products. Figure 7 gives the normalized relative abundances found for the me-

thlynaphthalenes, methylanthracenes, and methylphenanthrenes in the SRC II HD and in the coal tar.  $\beta$ -Substituted isomers such as 2-methylnaphthalene, 2-methylanthracene, and 2- and 3-methylphenanthrene were more abundant than  $\alpha$ -substituted isomers such as 1-methylnaphthalene, 1-methylanthracene, and 1- and 4-methylphenanthrene. It was shown by Garrigues and Ewald (21) that substituents on the 4- and 5-positions (4-methylphenanthrene, 4-methylchrysene, and 5-methylchrysene) were absent in examined crude oils, and they ascribed the low abundance of such compounds to steric hindrance (25). Another possibility is that bay region methylated PAH such as 4-methylphenanthrene cyclize to methylene-bridged PAH at elevated temperatures (26). Our results also show a similar tendency for the methylated PAH. Although the methylchrysenes were only minor components, the 2- and 3-methylchrysenes, which are  $\beta$ -substituted isomers, were more abundant.

#### Acknowledgments

We thank Stephen A. Wise and John C. Fetzer for supplying samples of cata-condensed five-ring PAH.

**Registry No.** Dibenzofuran, 132-64-9; fluorene, 86-73-7; methylbiphenyl, 28652-72-4; methylfluorene, 26914-17-0; dibenzothiophene, 132-65-0; tetrahydroanthracene, 30551-09-8; phenanthrene, 85-01-8; anthracene, 120-12-7; 1-phenylnaphthalene, 605-02-7; 3-methylphenanthrene, 832-71-3; 4*H*-cyclopenta[*def*]phenanthrene, 203-64-5; 1-methylanthracene, 610-48-0; 1-methylphenanthrene, 832-69-9; 2-methylphenanthrene, 2531-84-2; 2-methylanthracene, 613-12-7; methylphenanthrene, 31711-53-2; 2-phenylnaphthalene, 612-94-2; fluoranthene, 206-44-0; phenanthro[4,5-*bcd*]thiophene, 30796-92-0; pyrene, 129-00-0; benzo[*a*]fluorene, 30777-18-5; benzo[*b*]fluorene, 30777-19-6; methylpyrene, 27577-90-8; benz[*c*]phenanthrene, 195-19-7; benzo[*ghi*]fluoranthene, 203-12-3; benzo[*b*]naphtho[2,1-*d*]thiophene, 239-35-0; triphenylene, 217-59-4; cyclopenta[*cd*]pyrene, 27208-37-3; benz[*a*]anthracene, 56-55-3; chrysene, 218-01-9; methylchrysene, 41637-90-5; benzo[*j*]fluoranthene, 205-82-3; benz[*a*]aceanthrylene, 203-33-8; triphenyleno[4,5-*bcd*]thiophene, 68558-73-6; benz[*c*]acephenanthrylene, 205-99-2; benzo[*k*]fluoranthene, 207-08-9; benzo[*e*]pyrene, 192-97-2; perylene, 198-55-0; benzo[*a*]pyrene, 50-32-8; indeno[1,2,3-*cd*]pyrene, 193-39-5; pentaphene, 222-93-5; benzo[*ghi*]perylene, 191-24-2; benzo[*b*]chrysene, 214-17-5; di-benzo[*def,mno*]chrysene, 191-26-4; coronene, 191-07-1.

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