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Novel aryl polycyclic aromatic hydrocarbons: Phenylphenanthrene and phenylanthracene identification, occurrence and distribution in sedimentary rocks

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ABSTRACT

Numerous reports have recognised the presence of compounds with molecular weight 254 a.m.u. in aromatic fractions. However, their unequivocal identification has not been achieved due to a lack of reference substances. In geological samples, such m/z 254 compounds could potentially be represented by a number of structural isomers of binaphthyl, phenylphenanthrene, phenylanthracene and indenofluorene with each compound type possessing several positional isomers. In this work, all these m/z 254 compounds, with the exception of the tentatively recognised indenofluorenes, have been unequivocally identified in sedimentary rocks for the first time. Comparison of the mass spectra and the gas chromatography (GC) retention times of synthesised standards with the natural compounds in rocks shows that the major components of aromatic fractions are phenylphenanthrene isomers and, to a lesser extent, binaphthyls and 9-phenylanthracene. The elution sequence expressed as standard retention indices of all these m/z254 isomers were determined by using high resolution capillary GC with three stationary phases: 5%, 35% and 50% (mole fraction) phenyl substituted methylpolysiloxane on HP-5MS, DB-35MS and DB-17MS columns, respectively. A survey of more than 350 sedimentary rock samples of varying origins and maturity (R_r 0.3–1.4%) reveals that relative abundances of the m/z 254 isomers depend on the maturity of the organic matter. The isomers initially appear at the onset of oil generation ($R_r > 0.5\%$) exclusively in diagenetically/catagenetically oxidised samples containing varying proportions of Types II and III kerogen. Interestingly, all five possible positional phenylphenanthrene isomers (including the most sterically hindered isomer 4-phenylphenanthrene) are present from the beginning of the oil generation window. Such a distribution suggests that low-regioselectivity reactions are likely to be involved in the formation. Interaction, during maturation, of phenyl radicals from primary cracking with aromatic moieties of more resistant terrigenic components of kerogen in an oxidising diagenetic realm is postulated to be responsible for the neoformation of phenylated aromatics in geological samples. Up to the final stages of oil generation, the evolution of the phenyl PAH distributions presumably involve 1,2-phenyl shift reactions and cyclisation, if allowed by the molecular geometry. A near thermodynamically-controlled distribution, with only 3- and 2-phenylphenanthrene and minor 2,2'-binaphthyl remaining, is approached when vitrinite reflectance reaches 1.2% (R_r). The three compounds seem to be persistent beyond the oil window as is suggested by their presence in hydrothermal oil formed at T > 300 °C.

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1. Introduction

Naturally occurring polycyclic aromatic hydrocarbons (PAHs), together with their heterocyclic counterparts (polycyclic aromatic compounds, PACs) are a large group of structurally diverse compounds. Some PAHs are extremely pervasive constituents of oils and extracts of sediments, source rocks, coals, asphalts, meteorites and anthropogenic products, whereas occurrences of the others are limited to particular samples (e.g., Yunker et al., 1999, 2002). Specific classes of PAHs are applied as biomarkers (e.g., Püttmann and Villar, 1987; Strachan et al., 1988; Grimalt et al., 1988; de Las Heras et al., 1991; Clifford et al., 1998; Simoneit et al., 1986; Otto and Simoneit, 1999; Radke et al., 2000; Oldenburg et al., 2002; Marynowski et al., 2007a,b), and molecular maturity indicators (Radke and Welte, 1983; Radke and Willsch, 1991, 1994; Budzinski et al., 1995; Radke et al., 1986, 2000 and references therein; van Aarssen et al., 1999). PAHs are also used as markers of ancient wildfires (Jiang et al., 1998; Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Marynowski and Filipiak, 2007) and recent combustion of biomass and fossil fuels (Grimmer et al., 1985; Simoneit, 2002; Ré-Poppi and Santiago-Silva, 2005; Wang et al., 2007).

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Combustion residua typically contain adsorbed PAHs of which unsubstituted peri-condensed compounds such as pyrene, benzopyrenes, benzo[ghi]perylene and coronene accompanied by PAHs containing fused five membered rings such as fluoranthene, benzofluoranthenes and indeno[1,2,3-cd]pyrene (Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Kruge et al., 1994; Jiang et al., 1998) are characteristic. Additionally, some recent combustion and pyrolytic products contain aryl PAHs (Borwitzky and Schomburg, 1979; Tong and Karasek, 1984; Lauer et al., 1988; Blanco et al., 1991; Stock and Obeng, 1997; Meyer zu Reckendorf, 1997, 2000; Marynowski et al., 2004; Wang et al., 2007). Some of these have also been recognised in extracts of specific diagenetically/ catagenetically oxidised organic matter in sedimentary rocks (Püttmann and Goßel, 1990; Püttmann et al., 1990; Marynowski et al., 2001, 2002; Rospondek and Marynowski, 2004; Lewandowska et al., 2005; Rospondek et al., 2007, 2008, 2009).

In oxidised samples, the arylated PAHs are often constituents as important as are their alkyl counterparts in unoxidised rocks (Fig. 1). Examination of a diverse set of such sedimentary rock extracts and of a few bitumens has shown that the greatest number of arylated PAH isomers is observed in relatively immature samples ($R_r \sim 0.5\%$). In marine sulfur enriched rocks, aryl derivatives of polycyclic aromatic thiophenes are often abundant (Rospondek et al., 2007, 2008). Aryl thiophenes can be represented by phenylbenzo[b]thiophenes as well as phenyldibenzothiophenes accompanied by their structural isomers, i.e., phenylnaphtho[b]thiophenes and naphthylbenzo[b]thiophenes (Rospondek et al., 2007). The phenyldibenzothiophene isomer distribution resembles that obtained in experimental free radical phenylation of dibenzothiophene. Its isomers are formed during pyrolysis of dibenzothiophene (DBT) presumably resulting from the addition of phenyl radicals to the initial DBT (Dartiguelongue et al., 2006). As these arylated polycyclic aromatic thiophenes have been found exclusively in hydrothermally oxidised samples, such solutions, usually rich in benzene (e.g., Kissin, 1998; McCollom et al., 2001), have been proposed as a potential source of phenyl species (Rospondek et al., 2007).

Modelling of the relative thermodynamic stabilities of phenyldibenzothiophene isomers has led to the prediction of their equilibrium mixture composition, which shifts towards that obtained in maturation experiments and encountered in mature $(R_r \sim 1.2\%)$ geological samples. Systematic trends in relative phenyldibenzothiophene isomer abundances with increasing maturity give promise for their employment as sensitive molecular indicators of organic matter maturation for rocks formed in oxidising diagenetic facies (Marynowski et al., 2002; Rospondek et al., 2007), in contrast to the phenyldibenzofuran series (Marynowski et al., 2002). Apart from polyphenyls (Marynowski et al., 2001), the extent of other aryl PAH occurrence and diagenetic/catagenetic fate has not been fully explored yet.

This paper is a continuation of our previous research directed towards identification of aryl derivatives of PAHs and the factors controlling their distribution in sedimentary rocks (Marynowski et al., 2001, 2002, 2004; Rospondek and Marynowski, 2004; Rospondek et al., 2007, 2008). Here, the unequivocal identification of a series of m/z 254 isomeric compounds, including the not yet described phenylphenanthrene (PhP) and phenylanthracene (PhA) isomers, is reported from sedimentary rocks originating from different geological settings and varying in organic matter maturity. The isomer identification was achieved by comparison of gas chromatography (GC) retention times on three different capillary columns via co-elution experiments with synthesised standards, and the natural compound identifications were ascertained by comparison of their mass spectra with those of the standards.



Fig. 1. Partial chromatogram on a HP-5MS column showing (a) the aromatic fraction TIC and (b) aryl m/z 254 isomers of the oxidised Kupferschiefer facies; BBBF – benzobisbenzofurans (M^{*-} 258), MePhDBT – methylphenyldibenzothiophene or isomers (M^{*-} 274); M^{*-} 240 – cyclopentabenzochrysene or cyclopentatriphenylene or cyclopentabenzo[*a*]anthracene; * – impurity.

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2. Samples

All samples from our database that contain detectable amounts of isomeric m/z 254 compounds are discussed in the text (Table 1). Such rocks contain a mixture of various proportions of Types II and III kerogen affected by oxidation during maturation, and at least reached the threshold of oil generation. The compounds of interest have been not found by us in any samples that just contain either pure terrestrial or immature or unoxidised organic matter. Samples surveyed by us that do not contain m/z 254 compounds include more then 150 samples of the Oligocene shales from the Flysch Outer Carpathians, Southern Poland, characterised by mainly immature marine organic matter of $R_r < 0.5\%$ (Rospondek et al., 1997; Köster et al., 1998). They also include 48 samples of Middle Jurassic clays containing predominantly terrigenic organic matter and fossil wood of brown-coal rank (0.25–0.30% Rr; Marynowski et al., 2007a,b). Furthermore, the Miocene highly-immature $R_r < 0.35\%$ brown coals described by Fabiańska (2007) and Fabbri et al. (2008) do not contain the arylated PAHs. Surprisingly, the compounds of interest are absent from any of the Upper Carboniferous hard coals from the Upper Silesian Coal Basin, Poland (about one hundred samples of maturity up to $R_r < 0.7\%$). However, our database on the Polish Upper Carboniferous rocks lacks representative analyses of more mature coals and of the coal-associated black shales. The arylated PAHs are also absent from unoxidised facies of Kupferschiefer (Rospondek et al., 1994; Rospondek, 1998), whereas the oxidised "Rote Fäule" Kupferschiefer facies are strongly enriched in these PAHs (Marynowski et al., 2002; Rospondek et al., 2007). The samples with detectable arylated PAHs being discussed here are from the following sedimentary rock sequences:

- (1) Middle and Upper Devonian carbonates and shales from the Holy Cross Mountains (Góry Świętokrzyskie), Poland that vary in maturity $0.52\% < R_r < 1.2\%$ (Marynowski et al., 2000) and their equivalents from the Dębnik Anticline located in the Kraków–Silesia Monocline. In the case of the latter, their higher maturity ($R_r > ca 1.4\%$) is due to the thermal/hydrothermal influence of a large rhyodacite intrusion (Lewandowska, 1991, 2000) of Upper Carboniferous/Permian age (Nawrocki et al., 2007).
- (2) Upper Permian (Zechstein) dolomites, marls and shales (Kupferschiefer) from the Fore-Sudetic Monocline, Poland (Rospondek et al., 1993, 1994, 1998). The samples were collected from the Cu–Ag deposits in the Polkowice-Sieroszowice, Lubin and Rudna mines. The Rudna bitumen sample represents the expelled hydrocarbons hosted in quartz arenite (Rotliegende) underlying the Kupferschiefer. The sandstone is cemented by solid black bitumen occurring in place of common carbonate or anhydrite cements.
- (3) Upper Permian (Zechstein) shales and marls (Kupferschiefer) containing base metal sulfide mineralisation from the "Konrad" mine, North-Sudetic Syncline, Poland.

All of the Zechstein samples contain organic matter with TOC values ranging from 3.9–14.6 wt% (Table 1), which is within the range of 1–17 wt% previously reported for the mineralised Polish Kupferschiefer (Püttmann et al., 1989, 1990; Sawłowicz, 1993; Rospondek, 1998). The samples represent marine rocks containing predominantly Type II kerogen with minor Type III kerogen (Rospondek et al., 1993; Sawłowicz et al., 2000; Kotarba et al., 2006). Only rocks from the base of the Zechstein sections usually contain substantial amounts of Type III kerogen (e.g., Sun et al., 1995).

The Zechstein samples from the Cu–Ag deposits containing the m/z 254 isomers come from "Rote Fäule" facies – oxidised facies

resulting from diagenetic/catagenetic oxidation by hydrothermal solutions. The oxygen fugacity of these solutions was buffered at elevated values by equilibration with underlying red hematite-rich sandstones before entering the pyrite rich black shales. As a result sedimentary pyrite (often framboidal) was transformed into goe-thite/hematite or partly replaced by chalcocite and organic matter was oxidised. The process is well described by Oszczepalski (1989) and Püttmann et al. (1989, 1990). The phenomenon was presumably related to the main subsidence of the Kupferschiefer–Zechstein Limestone complex, which took place during the Late Permian–Late Triassic, with additional burial during the Jurassic and Late Cretaceous. Limited hydrocarbon generation from the Kupferschiefer source rocks occurring from Middle Triassic to Late Jurassic times reached maximum rates during the Jurassic (Kotarba et al., 2006).

- (4) Palaeogene dark grey shales of the Podhale Flysch sequence from the Polish part of the Podhale Trough in the Carpathians. The samples, collected from selected boreholes, contain substantial amounts of Type III with minor Type II kerogen (Rospondek and Marynowski, 2004; Środoń et al., 2006). The rock sequence yields thermal waters, which are a geothermal energy source for the Podhale region.
- (5) Hydrothermal petroleum from the Guaymas Basin, central part of the Gulf of California, Mexico (e.g., Simoneit, 1993). The oil is formed in active hydrothermal systems of the oceanic rift. Hot fluids penetrate a thick series of diatomaceous oozes and terrigenous silty muds filling tectonic graben (e.g., Kawka and Simoneit, 1990). In our sample database, there are no data on the abundance of the isomeric m/z 254 compounds in over-mature samples ($R_r > 1.2\%$). Thus, the hydro-thermal oil formed at ca 330 °C provides a good substitute for over-mature samples.

Basic information on the samples is given in Table 1.

3. Methods

3.1. Vitrinite reflectance (R_r)

Analysis were carried out using an AXIOPLAN II microscope adapted for reflected white light observation in oil immersion and a total magnification of $500 \times$. The reflectance standard used has R_r 0.62%. About one hundred vitrinite grains were measured for each sample.

3.2. Extraction and chromatography

Finely ground rock samples were Soxhlet extracted in pre-extracted thimbles with dichloromethane (DCM). The extracts were separated using preparative pre-washed thin layer chromatography (TLC) plates coated with silica gel (Merck 60, 20×20 cm, 0.250 µm) activated at $120 \degree$ C (1 h). The plates were loaded with DCM soluble extracts and developed with *n*-hexane. Bands comprising aliphatic ($R_{\rm f}$ 0.4–1.0), aromatic ($R_{\rm f}$ 0.05–0.4) and polar ($R_{\rm f}$ 0.0–0.05) fractions were collected for analysis.

3.3. Gas chromatography–mass spectrometry analyses

Gas chromatography–mass spectrometry (GC–MS) analyses were performed with an Agilent 6890 chromatograph equipped with an EPC Cool On-Column Inlet and fitted with one of the three fused silica capillary columns of different polarity used in this study (HP-5 MS or DB-35 MS, 60 m \times 0.32 mm, 0.25 µm film thickness, or DB-17 MS, 60 m \times 0.25 mm, 0.25 µm film thickness). Helium was used as the carrier gas.

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Table 1

Locality Lit	Lithology	Vitrinite reflectance <i>R</i> _r (%)	TOC (wt%)	EOM (mg/g TOC)	Phenylphenanthrenes (wt%)			9-Phenyanthracene/sum of phenylphenanthrenes (wt%)		
					4-PhP	9-PhP	1-PhP	3-PhP	2-PhP	9-PhA
Holy Cross Mountains, Poland (Devonian)										
Góra Łgawa M	larly limestone (Famennian)	0.52	0.73	27	23.9	19.8	15.1	18.6	22.6	17.0
Kowala DKX Bl	lack shale (Frasnian)	n.f. ^a	0.8	22	7.2	24.3	22.0	23.5	23.1	29.1
Kowala KWLF2 Bl	lack shale (Frasnian)	0.54	8.2	15	16.4	24.2	11.5	23.8	24.2	13.9
Kowala K3 Bl	lack shale (Frasnian)	0.55	4.00	30	19.6	42.4	10.4	14.2	13.3	n.d.
Kowala IG-1 (851 m) Do	olostone (Eifelian)	n.f.	n.d. ^b	n.d.	15.5	27.6	12.2	24.7	19.9	4.0
Kowala IG-1 (858 m) Do	olostone (Eifelian)	n.f.	n.d.	n.d.	5.7	23.9	11.9	30.9	27.6	2.9
Kowala IG-1 (873 m) Do	olostone (Eifelian)	n.f.	n.d.	n.d.	0.0	29.0	11.6	34.5	24.9	0.0
Panek (by Bolechowice) lir	mestone (Frasnian)	0.66	0.14	21	8.4	24.4	14.0	28.1	25.1	18.5
Radkowice Gi	reenish dolostone (Eifelian)	0.62	0.80	12	10.2	39.3	15.6	19.7	15.1	1.1
Radkowice Gr	reenish shale (Eifelian)	0.65	1.13	10	16.3	38.1	19.1	12.7	13.9	3.0
Besówka Lin	mestone (Famennian)	0.67	0.32	6	4.5	23.0	17.4	27.4	27.7	2.8
Piskrzyn do	olostone (Eifelian)	0.73	n.d.	n.d.	1.8	28.4	14.3	27.0	28.5	0.0
Piskrzyn Sh	hale (Eifelian)	0.76	n.d.	n.d.	0.0	25.9	14.5	32.3	27.4	0.0
Skały Lii	mestone (Givetian)	0.84	0.89	14	0.0	13.1	9.1	32.8	45.0	0.0
Janczyce IG-1 (depth 943 m) Do	olostone (Givetian?)	n.f.	0.03	20	0.0	16.1	9.1	32.4	42.4	0.0
Janczyce IG-1 (depth 1239 m) Do	olostone (Eifelian)	1.15	0.30	30	0.0	3.6	2.5	39.6	54.3	0.0
Miedziana Góra Bl	lack shale (Frasnian)	1.18	n.d.	n.d.	0.0	2.7	3.1	38.8	55.4	0.0
Kostomłoty, Małe Górki KMG13 bl.	lack shale (Frasnian)	1.20	n.d.	n.d.	0.0	3.6	3.9	36.3	56.3	0.0
Kostomłoty, Małe Górki KMG31 Bl	lack shale (Frasnian)	1.20	n.d.	n.d.	0.0	3.0	3.1	37.0	56.8	0.0
Kostomłoty, Małe Górki KMG33 Bl	lack shale (Frasnian)	1.20	n.d.	n.d.	0.0	3.2	3.2	39.6	54.0	0.0
Laskowa Góra Do	olostone (Eifelian?)	1.20	0.37	11	0.0	4.2	2.3	41.3	52.2	0.0
Laskowa Góra SHA Gi	reenish shale (Eifelian?/ Givetian?)	1.15	n.d.	n.d.	0.0	5.8	3.1	40.9	50.2	0.0
Holy Cross Mountains Poland (Parmian)										
Nowy Kościół 1	deritic limestone	0.71	nd	nd	0.0	37.6	14.9	20.1	27.4	0.0
Nowy Kościół 2	ideritic limestone	0.71	n.d.	n.d.	0.0	33.8	13.8	30.1	27.4	0.0
Kajatanów 1	mestone	0.90	0.40	50	0.0	11.0	76	373	44.1	0.0
Kajetanów 2	mestone	0.88	0.40 n.d	nd	0.0	183	14.8	28.2	38.6	0.0
Kajetanów 3	mestone	0.86	n.d.	n.d.	0.0	22.2	10.4	28.2	38.5	0.0
Ślichowice Li	mestone	0.96	0.97	94	0.0	9.2	6.0	413	43.5	0.0
Shehowice	mestone	0.50	0.57	54	0.0	5.2	0.0	41.5	45.5	0.0
Kraków–Silesian Monocline, Dębnik Antyclin	ne, Southern Poland (Devonian)									
Dębnik M	larly shale (Frasnian)	1.4	1.45	13	0.0	11.1	2.4	53.1	33.4	0.0
Fore-Sudetic Monocline, South-Western Pola	nd (Zechstein)									
Lubin LE-I/O "B	Basal" dolostone	n.f.	0.4	4	1.4	44.9	11.2	21.0	21.5	n.d.
Polkowice PW-II/1	aminated reddish dolostone	n.f.	1.00	6	2.1	32.3	14.0	24.2	27.3	0.9
Polkowice PW-III/1 Re	eddish/black marly shale	n.f.	n.d.	n.d.	3.9	42.1	11.6	20.7	21.7	1.3
(5)	pots of hematite)				5.5	.2	11.0	20.7	21.7	115
Polkowice PW-III/2 Re	eddish limestone (spots of hematite)	0.68	n.d.	n.d.	2.3	40.5	12.3	21.4	23.6	0.2
Sieroszowice S1	eddish/black shale (spots of hematite)	0.72	6.1	4	3.6	34.7	18.3	21.4	22.0	n.d.
Sieroszowice S3 Re	eddish limestone (spots of hematite)	nf	0.7	6	24	33.6	16.5	24.5	23.1	nd
Rudna Bi	itumen cementing sandstone	1	0.7	0	3.8	56.7	11.6	14.5	13.3	0.3
	······································				5.0	50.7	11.0		.5.5	015
North-Sudetic Trough, South-Western Poland	d (Zechstein)	_								
Konrad Cu M	larly limestone	n.t.	7.59	n.d.	7.1	41.1	21.5	17.7	12.5	n.d.
Konrad Pb M	larly limestone	0.68	3.70	n.d.	6.0	28.7	12.8	29.6	22.8	n.d.
Konrad "Rote Fäule" Re	eddish/black marly shale	0.70	5.26	n.d.	4.6	28.8	17.5	24.6	24.5	n.d.
(s)	pots of hematite)									
Podhale Trough. the Carpathians, Southern P	Poland									
Biały Dunajec PAN-1 (depth 2177 m) Lin	mestone (Mesozoic)	1.03	0.7	n.d.	0.0	12.8	9.1	37.1	41.1	0.0
Chochołów PIG-1 (depth 2410 m) Fly	ysch shale (Paleogene)	0.95	n.d.	n.d.	0.0	12.3	8.5	30.7	48.6	0.0
Chochołów PIG-1 (depth 2900 m) Fly	ysch shale (Paleogene)	1.02	n.d.	n.d.	0.0	5.7	7.7	33.7	52.9	0.0

9-Phenyanthracene/sum of phenylphenanthrenes (wt%) 9-PhA 95.2 96.7 n.d. 0.0 2-PhP 4.2 9.3 0.0 38.8 52.4 3-PhP 41.7 5.6 12.4 0.0 13.1 1-PhP 30.4 40.9 0.0 1.2 EOM (mg/g TOC) Phenylphenanthrenes (wt%) 2.2 9-PhP 32.4 16.2 100.0 46.9 3.7 4-PhP 27.4 21.2 0.0 0.0 0.0 Vitrinite reflectance Rr (%) TOC (wt%) Hydrothermal oil Temperature (°C) and 330 Lithology 40 150 90 250 Gulf of California, Mexico (Holocene) Results of laboratory experiments Not determined (n.d.). ree radical phenylation ree radical phenylation Artificial maturation ^a Not found (n.f.). able 1 (continued onic phenylation **Guaymas Basin** Experiment Locality

Samples were injected on column at 40 °C. The oven temperature was kept constant for 3 min, increased to 120 °C at 20 °C min⁻¹, subsequently to 300 °C at 3 °C min⁻¹ and kept there for 35 min. The chromatograph was coupled to an Agilent 5973 Network with mass selective detector (MSD). The spectrometer was operated with an ion source temperature set at 200 °C, ionisation energy 70 eV and a cycle time of 1 s in the range m/z 50– 700. Spectra from the Wiley Registry of Mass Spectral Data (7th ed.) were used for MS data comparison (Table 2).

3.3.1. GC retention data

In order to compare a given compound retention on different columns or simply to numerically characterise its behaviour on a column, the retention index system is used (Kováts, 1958). These retention indices (I) are usually 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 (1963) extended this retention index system for use with temperature programmed GC techniques. As retention index markers should closely resemble the analysed compounds (Lee et al., 1979; revalued by Vassilaros et al., 1982), naphthalene, phenanthrene, chrysene and picene were chosen for the PAH analyses. These compounds were assigned retention index values related to their ring number multiplied by one hundred giving *I* = 200, 300, 400 and 500, respectively. In this paper, the retention indices of the m/z 254 isomeric series were calculated according to the equation given by Lee et al. (1979) for HP-5MS ($I_{\text{HP-5MS}}$), DB-35MS (I_{DB-35MS}) and DB-17MS (I_{DB-17MS}) columns.

3.4. NMR spectroscopy

NMR spectra of the synthesised and purified reference compounds (Table 2) were recorded with a Bruker AMX500 or a Bruker 300 spectrometer in $CDCl_3$ operating at 500 MHz (¹H NMR) and 125 MHz (¹³C NMR) or 300 MHz (¹H NMR) and 75 MHz (¹³C NMR), respectively. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard.

4. Reference compounds

Reference standards of phenylphenanthrene, phenylanthracene and binaphthyl isomers were used to identify structural isomers of the $C_{20}H_{14}$ compounds present in aromatic factions of the rock extracts.

Phenylphenanthrenes: None of the phenylphenanthrene isomers were commercially available. All five possible positional isomers were synthesised as pure reference substances. In addition to pure standards, isomer mixtures of all phenylphenanthrenes were obtained using free radical phenylation of phenanthrene as described in Section 4.2.1.

Phenylanthracene: The only commercially available isomer was 9-phenylanthracene (purchased from Aldrich). The remaining isomers were synthesised using free radical phenylation of anthracene as described in Section 4.2.1.

Binaphthyls: All three binaphthyl isomers were synthesised during an earlier study (Marynowski et al., 2001).

Other PAH standards used in this study are reported elsewhere (Marynowski et al., 2001, 2002; Rospondek et al., 2007).

4.1. Synthesis of phenylphenanthrenes

4.1.1. Suzuki cross-coupling

Three phenyl isomers of phenanthrene (9-, 3- and 2-phenylphenanthrene) were synthesised via Suzuki cross-coupling with Pd(PPh₃)₄ as catalyst (Table 2) according to the protocol described

 Table 2

 Summary of the synthesised phenylphenanthrene and phenylanthracene isometers
 s physical properties spectral data method of synthesis and sub-

Synthesised PAC	Solvent for crystallisation (substance appearance); purity, melting point (reference m.p.)	Spectral data ^a	Substrate and synthesis
1-Phenylphenanthrene (1-PhP)	Methanol/acetone (white needles); purity > 79%; m.p. 73–77 °C (m.p. 79.5–80.5 °C, Beckwith and Thompson (1961); m.p. 78–79 °C, Hayward and Leznoff (1971); m.p. 73–77 °C, m.p. 74–76 °C, Tinnemans and Laarhoven (1976))	¹ H NMR (300 MHz; CDCl ₃) 7.38–7.68 (m, 10H); 7.79 (dd, 1H, $J = 9.2$ Hz, $J = 0.6$ Hz); 7.68 (dd, 1H, $J = 7.7$ Hz, $J = 1.6$ Hz); 8.68– 8.72 (m, 2H) ¹³ C NMR (75 MHz; CDCl ₃) 122.1; 122.9; 124.6; 125.9; 126.6; 126.7; 126.8; 127.2; 127.9; 128.2 (2C); 128.4; 129.0; 130.2 (2C); 130.4; 130.7; 131.7; 140.9; 141.1	Modified synthesis according to Haworth (1932): reaction of phenylmagnesium bromide with 1,2,3,4- tetrahydrophenanthren-1-one followed by dehydration with KHSO ₄ and aromatisation with DDQ
2-Phenylphenanthrene (2-PhP)	Methanol/acetone (white plates); purity > 97%;m.p. 195–197 °C (m.p. 196–197 °C, Newman (1944); m.p. 194 °C Beckwith and Thompson (1961); m.p. 196–197 °C, Rao et al. (1991))	¹ H NMR (300 MHz; CDCl ₃) 7.37–7.42 (m, 1H); 7.48–7.54 (m, 2H); 7.58–7.70 (m, 2H); 7.75–7.82 (m, 4H); 7.89–7.93 (m, 2H); 8.10 (d, 1H, <i>J</i> = 1.9 Hz); 8.69–8.72 (m, 1H); 8.73–8.76 (m, 1H) ¹³ C NMR (75 MHz; CDCl ₃) 122.7; 123.2; 125.8; 126.6 (2C); 126.7; 127.1; 127.3; 127.4 (2C); 127.5; 128.6; 128.9 (2C); 129.4; 130.1; 132.1; 132.4; 139.2; 140.8 According to Rao et al. (1991) ¹ H NMR (90 MHz; CDCl ₃) 7.18–8.97 (m, 11H, ArH); 8.14 (d, <i>J</i> = 2.5 Hz, 1H, H-1); 8.60–8.70 (m, 2H, ArH) MS spectrum no. #193262	Suzuki cross-coupling of 2- bromophenanthrene with phenylboronic acid (Heynderickx et al., 2002)
3-Phenylphenanthrene (3-PhP)	Methanol (white fine needles); purity > 99.3%; m.p. 75-76 °C (m.p. 76 °C, Beckwith and Thompson (1961); m.p. 71-72 °C, Rao et al. (1991))	¹ H NMR (300 MHz; CDCl ₃) 7.37–7.43 (m, 1H); 7.48–7.55 (m, 2H); 7.57–7.71 (m, 2H); 7.74–7.80 (m, 4H); 7.82–7.85 (m, 1H); 7.88–7.91 (m, 1H); 7.93–7.96 (m, 1H); 8.75–8.78 (m, 1H); 8.87–8.88 (m, 1H) ¹³ C NMR (75 MHz; CDCl ₃) 121.1; 122.6; 126.0; 126.5; 126.6; 126.7; 127.0; 127.4; 127.6 (2C); 128.7; 128.9 (2C); 129.0; 130.4; 130.5; 131.2; 132.3; 139.4; 141.5 According to Rao et al. (1991) ¹ H NMR (90 MHz; CDCl ₃) 7.19–8.95 (m, 11H, ArH); 8.12 (d, <i>J</i> = 2.5 Hz, 1H, H-4); 8.59–8.76 (m, 2H, ArH)	 Five step synthesis from commercially available 3-acetylphenanthrene: Reaction with hydroxylamine to corresponding oxime, Bachmann and Boatner (1936a) Rearrangement of the oxime with the aid of PCIs to N-acetyl-3-aminophenanthrene, Bachmann and Boatner (1936a) HCl catalysed hydrolysis of N-acetyl-3-aminophenanthrene Diazotization of 3-aminophenanthrene followed by reaction with Kl to 3-iod-ophenanthrene, Bachmann and Boatner (1936b) Suzuki cross-coupling of 3-iodophenanthrene with phenylboronic acid, Heynderickx et al. (2002)
4-phenylphenanthrene (4-PhP)	Methanol/acetone (white fine needles); purity > 99.0%; m.p. 80– 81 °C (m.p. 80.5–81.5 °C, Beckwith and Thompson (1961); m.p. 81–82 °C, Hayward and Leznoff (1971))	¹ H NMR (300 MHz; CDCl ₃) 7.06–7.11 (m, 1H); 7.37–7.48 (m, 7H); 7.56 (dd, 1H, J = 7.8 Hz, $J = 7.3$ Hz); 7.69–7.76 (m, 3H); 7.79 (dd, 1H, $J = 7.8$ Hz, $J = 1.5$ Hz); 7.85 (dd, 1H, $J = 7.8$ Hz, $J = 1.5$ Hz) ¹³ C NMR (75 MHz; CDCl ₃) 124.8; 125.6; 125.9; 127.0; 127.4; 127.5; 128.2; 128.3; 128.4; 128.5; 128.9 (2C); 130.0 (2C); 130.4; 130.8; 133.4; 133.6; 140.5; 145.3 MS spectrum no. #193265	Haworth's synthesis, Haworth (1932): Reaction of phenylmagnesium bromide with 1,2,3,4-tetrahydrophenanthren-4-one followed by dehydration with $KHSO_4$ and aromatisation with DDQ
9-Phenylphenanthrene (9-PhP)	Methanol/acetone (white plates); purity > 99.7%; m.p. 105–106 °C (m.p. 106 °C, Beckwith and Thompson (1961); m.p. 105–106 °C, Cadogan et al. (1977); m.p. 86–87 °C, Kanno et al. (2005))	¹ H NMR (300 MHz; CDCl ₃) 7.44–7.56 (m, 6H); 7.59–7.67 (m, 4H); 7.86–7.93 (m, 2H); 8.70 (d, 1H, <i>J</i> = 8.1 Hz); 8.76 (d, 1H, <i>J</i> = 8.2 Hz) ¹³ C NMR (75 MHz; CDCl ₃) 122.5; 122.9; 126.4; 126.5; 126.6; 126.8; 126.9; 127.3; 127.5; 128.3 (2C); 128.6; 129.9; 130.0 (2C); 130.6; 131.1; 131.5; 138.7; 140.8 According to Kanno et al. (2005) ¹ H NMR (300 MHz, CDCl ₃): δ7.28–7.55 (m, 10 H), 7.73–7.82 (m, 2 H), 8.55 (dd, <i>J</i> = 8.08 Hz, 1 H), 8.61 (d, <i>J</i> = 8.26 Hz, 2 H) ¹³ C NMR (75 MHz, CDCl ₃): δ 122.50, 122.87, 126.41, 126.47, 126.54, 126.63, 126.89, 127.32, 127.49, 128.27, 128.63, 129.93, 130.04, 130.60, 131.10, 131.53, 138.74 140.77	Suzuki cross-coupling of 9- bromophenanthrene with phenylboronic acid, Heynderickx et al. (2002)

(continued on next page)

Table 2 (continued) Solvent for crystallisation (substance appearance); purity, melting point (reference m.p.) Spectral data^a Substrate and synthesis 9-Phenylanthracene (9-PhA) 9-Phenylanthracene; purity ≥ 98% MS spectrum nos. #193234 and #193235 Commercially available

^a NMR spectra obtained in this work; #MS spectra from Wiley MS database.

by Heynderickx et al. (2002). In brief, a solution of either 2-, 3- or 9-halogenophenanthrene (2 mmol), Na₂CO₃ (0.53 g; 5.0 mmol) and benzeneboronic acid (0.27 g; 2.25 mmol) in dimethoxyethane/ water (1:1, v:v; 9 ml) was refluxed with stirring for 3 h. After the usual work-up procedure, pure 2-, 3- and 9-phenylphenanthrene (Table 2) were isolated with yields of 73, 81 and 78%, respectively. Commercially available 9-bromophenanthrene was used without further purification, and 2-bromophenanthrene was synthesised via the Pschorr reaction according to the literature protocol (Nodiff et al., 1975). In turn, 3-iodophenanthrene was obtained in a four step synthesis from 3-acetylphenanthrene (technical, Aldrich, 90%) via 3-aminophenanthrene (Bachmann and Boatner, 1936a, 1936b; Table 2). In these reactions, 2-iodophenanthrene was also formed from 2-acetylphenanthrene, which was the major impurity in technical 3-acetylphenanthrene. 2-Iodophenanthrene remained in the liquor at the stage of crystallisation of 3-iodophenanthrene after the amine-iodide exchange reaction.

4.1.2. Haworth procedure

4-Phenylphenanthrene and 1-phenylphenanthrene were synthesised from 1,2,3,4-tetrahydrophenanthren-4-one and 1,2,3,4tetrahydrophenanthren-1-one, respectively, following the classic Haworth (1932) protocol. A solution of phenylmagnesium bromide, prepared under argon atmosphere from magnesium (0.24 g, 10.0 mmol) and bromobenzene (1.57 g, 10.0 mmol) in 30 ml of anhydrous diethyl ether, was added drop by drop to a stirred solution of 1,2,3,4-tetrahydrophenanthren-4-one or 1,2,3,4tetrahydrophenanthren-1-one (1.77 g, 9 mmol) in a mixture of 20 ml anhydrous benzene and 10 ml of anhydrous diethyl ether. After stirring the mixture overnight at room temperature, the solvents were removed in a vacuum yielding the crude carbinol which was dissolved in 30 ml of benzene and refluxed for 1 h with 0.5 g of KHSO₄. Removal of benzene and flash chromatography provided an alkene, which was subsequently aromatised by refluxing with 2,3dichloro-5,6-dicyanoquinone (DDQ). By refluxing the appropriate alkene (0.13 g, 0.51 mmol) with DDQ (0.12 g, 0.53 mmol) in 20 ml of anhydrous benzene for 1 h, the 1- and 4-phenylphenanthrenes were obtained with yields of 41% and 52%, respectively.

4.2. Syntheses of phenylphenanthrene and phenylanthracene isomer mixtures

Free radical and ionic phenylations of phenanthrene and anthracene were performed to evaluate differences in the phenyl PAH isomer distributions governed by different hypothetical reaction mechanisms as a rough approximation of hypothetical natural processes. The isomer mixtures obtained in the free radical phenylation were also used as the substrate in a maturation experiment evaluating the changes in the isomer abundance resulting from prolonged heating.

4.2.1. Free radical phenylation

Low temperature homolitic phenylations of phenanthrene and anthracene were carried out in two different ways. These experiments differed in the temperature and source of phenyl radicals, which were produced either by thermal decomposition of diazoaminobenzene or in reaction of aniline with pentyl nitrite. Positional isomer ratios in the resulting mixtures were determined and compared with those from the rock samples (Table 2).

- (i) 40 °C *phenylation*: Freshly distilled aniline (0.01 mol equiv. 0.09 ml) and pentyl nitrite (0.1875 ml) (Merck) were added to either phenanthrene or anthracene (0.001 mol equiv. 178 mg) in glass ampoules and the mixtures were homogenised by dissolution in DCM. After evaporation to dryness at room temperature, the ampoules were sealed and kept at 40 °C for two days as in Spagnolo et al. (1972).
- (ii) 150 °C phenylation: The mixtures of 1,3-diphenyltriazene (diazoaminobenzene) (0.08 mol equiv. 16 mg; Aldrich) with either phenanthrene or anthracene (0.001 mol equiv. 178 mg) were homogenised by dissolving in DCM, dried as described before and kept at 152 °C for 24 h as in Beckwith and Thompson (1961). Thermal decomposition of diazoaminobenzene yields phenyl and aniline radicals. The aniline radicals act as hydrogen acceptors and minimise the formation of tar products. PAHs were used in excess to reduce the formation of biphenyl derivatives.

After cooling, a DCM solution of an external standard was added to the reaction mixtures obtained in both experiments. The solvent was allowed to evaporate at room temperature. The content of the ampoules was extracted with DCM, separated on TLC plates and analysed using GC–MS according the procedure described in Section 3.3. Relative abundances of phenylphenanthrenes were determined as described in Section 4.4.

4.2.2. Ionic phenylation

The procedure, related to the Scholl reaction, was adopted from Clark and McKinnon (1981). A solution of phenanthrene (0.001 mol, ca 178 mg; Fluka, 90%) in benzene (80 ml) or benzene/chlorobenzene (80 ml, 1:1, v:v) was treated with 0.002 mol phenanthrene equivalent of anhydrous AlCl₃ (ca 256 mg; Merck) and the mixture was stirred and heated under reflux (4 h). An intense reddish-brown colour developed after addition of AlCl₃, which subsequently disappeared after addition of 20% ice cold HCl (100 ml) terminated the reaction. The organic fraction was

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isolated from the reaction mixture by ethyl acetate extraction, repeated three times. The combined extracts were washed with aqueous saturated NaCl, dried over MgSO₄ and fractionated (TLC) to give an aromatic fraction. The detected coupling products were 9-phenylphenanthrene and partly-hydrogenated counterparts in <10% yields of the 9-isomer (m/z 256 and 258). The observed formation of 9-phenylanthracene is due to substrate impurity.

4.2.3. Heating experiments

The maturation experiment with a clay catalyst mimics natural acid-catalysed reactions (e.g., Wei et al., 2006). The heating experiment was conducted on a standard mixture (ca 25 mg) of all five phenylphenanthrene isomers produced by a free radical phenylation experiment, with the unstable 4-, 9- and 1-isomers prevailing (cf. Fig. 7a). The experiment aimed to establish whether the thermodynamic equilibrium mixture forms on heating.

The isomer mixture in DCM was adsorbed on to aluminium montmorillonite mixed with Cu powder (10:2; v:v) according to the procedure of Kagi et al. (1990) and Strachan et al. (1988). The solvent was evaporated and the mixture sealed at atmospheric pressure in glass ampoules, which were heated isothermally at 250 or 330 °C for one week. After cooling, the reaction mixture was extracted with DCM and the solvent then allowed to evaporate at room temperature to give a residue from which the fraction eluted with *n*-hexane/DCM (1:1; v:v) was analysed using GC–MS.

4.3. Confirmation of the synthesised standard identity

The synthesised compounds were identified based on comparison of their melting points, retention indices, NMR and mass spectra with those from the literature.

4.3.1. Melting points

The melting points of the synthesised phenylphenanthrenes are very similar to the literature values (Table 2). The single melting point (86–87 °C) reported for 9-phenylphenanthrene by Kanno et al. (2005) is much lower than obtained by others (106 °C, Beckwith and Thompson, 1961; 105–106 °C, Cadogan et al., 1977) and by us (105–106 °C). The Kanno et al. (2005) low value may result from measurements on non-recrystallised compound.

4.3.2. GC retention

4.3.2.1. Phenylphenanthrene isomers. The elution order of the phenylphenanthrene isomers on the HP-5MS capillary column is as follows: 4-PhP, 9-PhP, 1-PhP, 3-PhP and 2-PhP (Table 3 and cf.

Fig. 3a). All the positional isomers are well separated. The observed sequence is in agreement with the order of elution previously established for the limited number of phenylphenanthrene isomers (Lee et al., 1979). 9-Phenylphenanthrene was followed by the 1-substituted isomer on the SE-52 (methylpolysiloxane phase) fused-silica column, which is a similar to our nonpolar stationary phase (HP-5MS). Retention indices for 9-phenylphenanthrene of I_{SE-52} = 406.90 from Lee et al. (1979) and $I_{\text{HP-5MS}}$ = 405.63 in the present study show good agreement. However, the index for 1-phenylphenanthrene of I_{SE-52} = 421.66 from Lee et al. (1979) differs substantially from the I_{HP-5MS} = 407.82 retention observed here. The Lee et al. (1979) index is similar to the I_{HP-5MS} = 422.87 retention for 3phenylphenanthrene (Table 3), suggesting that 3-PhP was mistaken for 1-PhP in the cited work. Interestingly, in a critical evaluation of the retention indices for PACs (Vassilaros et al., 1982), the I values for the phenylphenanthrenes were not re-determined. Retention indices for both more polar stationary phases are shown in Table 3.

4.3.2.2. Phenylanthracene isomers. The two previously unidentified isomers following 9-PhA in the elution sequence of phenylanthracene isomers can now be identified as 1-PhA and 2-PhA (Table 3 and cf. Fig. 3b). This identification is based on interpretation of their mass spectra (see Section 4.3.4; Fig. 2g and h) and their position in the phenylanthracene isomer elution sequence. The agreement of retention indices for 9-phenylanthracene of I_{SE-52} = 396.38 from Lee et al. (1979) and the commercial compound retention of $I_{\text{HP-5MS}}$ = 395.45 confirms the identification. The retention indices on a different stationary phases are $I_{DB-35MS}$ = 391.37 and *I*_{DB-17MS} = 392.18 (Table 3). Though the next eluting 1-PhA coelutes $(I_{\text{HP-5MS}} = 404.25)$ with 1,2'-binaphthyl, both are separated on a different stationary phase: 1-PhA $I_{DB-35MS}$ = 398.85 is followed by 1,2'-binaphthyl $I_{DB-35MS}$ = 400.00 (Table 3). Finally, 2-PhA elutes as the last of the whole series with I_{HP-5MS} = 429.31 and *I*_{DB-35MS} = 421.65 (Table 3).

4.3.2.3. *Binaphthyls*. Comparison of the retention indices of the reference (Lee et al., 1979) and our synthesised compounds confirm the standard compounds identities (Table 3). In this table, the retention indices for both more polar stationary phases are also shown.

4.3.2.4. *Isomeric m/z 254 standard mixture*. The elution sequence based on the standard mixture of all positional isomers of phenylphenanthrene, phenylanthracene and binaphthyl is as follows: 1,1'-binaphthyl, 4-PhP, 9-PhA, 1-PhA, 1,2'-binaphthyl, 9-PhP, 1-

Table 3

Retention indices on HP-5MS, DB-35MS and DB-17MS capillary columns for the reference m/z 254 structural isomers.

Compound	Retention indices (I column TYPE)							
	$I_{\rm DB-17MS}$ (this work)	I _{DB-35MS} (this work)	<i>I</i> _{HP-5MS} (this work)	I _{SE-52} Lee et al. (1979)	I _{HP-5} Meyer zu Reckendorf (1997)	I _{HP-5} Wang et al. (2007)		
1,1'-Binaphthyl	385.98	384.00	386.65	388.38		402.77		
4-Phenylphenanthrene	386.07	385.44	389.05					
9-Phenylanthracene	392.18	391.37	395.45	396.38		406.47 ^c		
1-Phenylanthracene	398.51	398.85	404.25		402.43 ^b			
1,2'-Binaphthyl	400.39	400.00	404.25	405.35		404.58		
9-Phenylphenanthrene	400.39	400.49	405.63	406.90	404.02			
1-Phenylphenanthrene	401.91	402.10	407.82	421.66 ^a	406.09 ^b			
3-Phenylphenanthrene	414.13	415.30	422.87					
2,2'-Binaphthyl	416.86	418.20	425.52	423.91		421.55		
2-Phenylphenanthrene	419.29	420.48	427.64			424.19		
2-Phenylanthracene	420.16	421.65	429.31			426.54 428.29 ^d		

^a Misidentified by Lee et al. (1979).

^b Previously unidentified isomers.

^c The index of 9-phenylphenanthrene from Lee et al. (1979) was incorrectly ascribed to 9-phenylanthracene by Wang et al. (2007).

^d Two unidentified m/z 254 isomers eluting after 2-phenylphenanthrene according to Wang et al. (2007).

PhP, 3-PhP, 2,2'-binaphthyl, 2-PhP and 2-PhA (Table 3). The elution sequence is very similar on all three stationary phases (HP-5MS, DB-35MS and DB-17MS). The baseline separation of all isomers is achieved on DB-35MS, but 1-PhA and 1,2'-binaphthyl coelute on HP-5MS ($I_{HP-5MS} = 404.25$) and 1,2'-binaphthyl and 9-PhP coelute on DB-17MS ($I_{DB-17MS} = 400.39$). On the last column separation of 1,1'-binaphthyl ($I_{DB-17MS} = 385.98$) and 4-PhP ($I_{DB-17MS} = 386.07$) is poor, too. Nevertheless, HP-5MS is recommended for studying structural isomers in geological samples, because 1-PhA is unlikely to occur in the samples (see Section 5), and because chrysene/1,2'-binaphthyl coelute on DB-35MS (Table 3).

4.3.3. NMR spectra

The NMR spectra of the phenylphenanthrenes were also recorded and compared with the scarce data in the literature (Table 2). Kanno et al. (2005) reported the ¹H and ¹³C NMR spectrum of 9phenylphenanthrene. That cited spectrum and our ¹³C NMR are very similar to one to another, but our ¹H NMR seems to contain fewer bands originating from impurities (Table 2). Older published ¹H NMR spectra are of little comparative value due to their poor resolution caused by low NMR spectrometer operating frequencies. This is the case for the spectra of 2- and 3-phenylphenanthrene in Rao et al. (1991) and those of 1- and 4-phenylphenanthrene in Tinnemans and Laarhoven (1976). Due to the absence of ¹³C NMR data for a number of isomers and frequently incomparable ¹H chemical shifts (spectra recorded in CS₂ solutions: Tinnemans and Laarhoven, 1976), our ¹H and ¹³C NMR data on the synthesised phenanthrenes are reported in Table 2. It is worth noting that identification of phenylphenanthrene isomers can be achieved on the basis of our NMR datasets, especially when the chemical shifts of strongly deshielded H-4 nuclei (usually over 8.5 ppm) are considered. For all synthesised phenylphenanthrenes, the position of the phenyl substituent was additionally confirmed on the basis of 2D NMR experiments using HMBC, HSQC and COSY.



Fig. 2a-e. Mass spectra of reference phenylphenanthrene positional isomers ordered in their elution sequence on a HP-5MS column: (a) 4-phenylphenanthrene, (b) 9-phenylphenanthrene, (c) 1-phenylphenanthrene, (d) 3-phenylphenanthrene and (e) 2-phenylphenanthrene.

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Fig. 2f-h. Mass spectra of reference phenylanthracene positional isomers ordered in their elution sequence on a HP-5MS column: (f) 9-phenylanthracene, (g) 1-phenylanthracene and (h) 2-phenylanthracene.

4.3.4. Mass spectra

The identity of the synthesised phenylphenanthrenes was further confirmed by comparison of their mass spectra with those available from the 7th edition of Wiley Registry of Mass Spectral Data (Table 2). The database contains only the spectra of 2- and 4-phenylphenanthrene as well as that of isomeric 9-phenylanthracene. Background subtracted mass spectra of all the reference isomeric m/z 254 phenylphenanthrenes and phenylanthracenes are shown in Fig. 2.

4.3.4.1. Phenylphenanthrene isomers. All isomers except 4-phenylphenanthrene have the molecular ion peak M⁺. 254 as a base peak (Fig. 2a-e). 4-Phenylphenanthrene has the base peak at m/z253 and the molecular ion peak M⁺. 254 is the second most intense (Fig. 2a). The very intense [M-1]⁺ and [M-2]⁺. ions in the spectrum of 4-phenylphenanthrene presumably originate from a cyclic benzo[*e*]pyrene-type species. Further dehydrogenation of such a *peri*condensed molecule would lead to the observed relatively intense m/z 251 [M-3]⁺ and 250 [M-4]⁺. ions. The spectrum has quite a number of low intensity ions, notably at m/z 248, 239 [M-15]⁺, 226/228, 213, 200, 189, 176, 150, and others that are unspecific, but characteristic for the whole family of polyaromatic compounds. The doubly-charged ion at m/2z 126 is relatively strong. The spectrum of our 4-phenylphenanthrene (Fig. 2a) is very similar to the Wiley reference spectrum #193265.

The spectra of the 9- and 1-isomers (Fig. 2b and c) are extremely similar. Relatively strong $[M-1]^+$ and $[M-2]^{+}$ ions arose from dehydrogenation, and subsequent cyclisation presumably leading to a benzo[*b*]fluoranthene-type of structure followed by $[M-4]^{+}$, from further dehydrogenation. Other low-intensity and doubly-charged ions are as in the spectrum of the 4-isomer.

The spectra of the 3- and 2-phenylphenanthrenes (Fig. 2d and e) seem indistinguishable. The only intense peak is the molecular ion peak M^* 254 (base peak). A fundamental difference between these two 2-, 3-isomers and the others (4-, 9- and 1-isomers) is in the intensity of [M-1]⁺ relative to [M-2]⁺. For both 2- and 3-isomers, these peaks are minor, and the ion [M-2]⁺ is more intense than

 $[M-1]^+$. Two peaks from the doubly-charged ions m/2z 126 and 127 are of similar intensity, the opposite of the spectra of the 4-, 1- and 9-isomers. The low intensity ions have lower abundances in comparison to the previous isomers and the ion at m/z 248 is not present. Given this, it is clear that these two molecules have little tendency to fragment indirectly – a reflection of their high thermodynamic stability. The spectrum of our 2-phenylphenanthrene (Fig. 2e) is similar to the reference spectrum #193262.

4.3.4.2. Phenylanthracene isomers. The spectra of the phenylanthracene isomers bear a great similarity to those of the phenylphenanthrene isomers (Fig. 2f–h). Though all have the molecular ion peak M^{+} 254 as a base peak, variations in the intensity of the $[M-1]^{+}$ and $[M-2]^{+}$ peaks relative to the ion peaks allows differentiation between them (Fig. 2f–h).

The spectrum of 9-phenylanthracene (Fig. 2f) is very similar to the Wiley MS reference spectra #193234 and #193235. The minor ions arising from fragmentation do not differ from those in the phenylphenanthrene isomers. The very intense $[M-1]^+$ and $[M-2]^+$ ions presumably originate from a cyclic benzo[a]fluoranthene-type structure. Subsequent dehydrogenation of such a cyclic molecule gives the observed relatively intense $[M-3]^+$ and $[M-4]^+$ ions at m/z 251 and 250, respectively.

The spectrum (Fig. 2g) of the next eluting phenylanthracene (Fig. 3b) can be assigned to 1-phenylanthracene based on its similarity to the spectrum of 9-phenylanthracene (Fig. 2f). The similarity in spectra results from the topological features of 1-phenylanthracene for which the formation, on electron impact, of a cyclic structure identical to that arising from 9-phenylanthracene can be anticipated. The generation of such a benzo[*a*]fluoranthene-type structure is suggested by the intense 251 [M-3]⁺ and 250 [M-4]⁺ ions in both spectra. These ions are not observed in the spectrum (Fig. 2h) of the last-eluting phenylanthracene (Fig. 3b). The fact that this isomer is extremely stable under the ionisation conditions in the mass spectrometer makes it similar to 3- and 2-phenylphenanthrene (Fig. 2h) has weak [M-1]⁺ and

 $[M-2]^{+}$ peaks accompanied by the characteristic doubly-charged ion pair m/2z at 126/127 as in 3- and 2-phenylphenanthrene. Hence, the compound can be identified as 2-phenylanthracene, the only possible β -substituted derivative of anthracene.

In summary, in all but one case the mass spectra of all the isomeric phenylphenanthrenes and phenylanthracenes are dominated by the intense molecular ions, and ions from the usual fragmentation are minor. The formation of [M-1]⁺ and [M-2]⁺. becomes significant if the molecular geometry allows cyclisation to accompany the fragmentation.

4.4. Relative response factors

Due to the significant variation in the MS fragmentation patterns within the isomeric series, response factors were calculated by relating peak area of the standards in the TIC (total ion current) chromatograms to those from the m/z 254 chromatograms (e.g., Yunker et al., 1999; Marynowski et al., 2002). The factors normalised to the most stable 3-PhP isomer are as follows: 4-PhP 2.00; 9-PhP 1.51; 1-PhP 1.65; 3-PhP 1.0; 2-PhP 1.05 and 9-PhA 1.50; 1-PhA 1.62; 2-PhA 1.39 (isomers follow elution sequence). Estimations of the relative abundances of the m/z 254 phenyl isomers (Table 1) were obtained by multiplying the peak areas measured in the m/z 254 chromatograms by the appropriate factor.

5. Identification of phenylphenanthrene and its structural isomers

To date, a number of aryl PAHs have been unequivocally identified in aromatic fractions of diagenetically oxidised sedimentary rocks (Fig. 1). They are, to mention the most important: biphenyl, terphenyls, polyphenyls, phenylnaphthalenes (Püttmann and Goßel, 1990; Marynowski et al., 2001; Rospondek and Marynowski, 2004; Lewandowska et al., 2005), all phenyldibenzofuran and



Fig. 3a. Comparison of the elution sequence on a HP-5MS column of the synthesised reference phenylphenanthrene positional isomers with the suspected *m*/*z* 254 isomers in the aromatic fraction of the Radkowice sample; PhP – phenylphenanthrene, PhA – phenylanthracene, BiN – binaphthyl.

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Fig. 3b. Comparison of the elution sequence on a HP-5MS column of 9-phenylanthracene and a mixture of all phenylanthracene positional isomers with the suspected *m*/*z* 254 isomers in the aromatic fraction of the Radkowice sample; PhP – phenylphenanthrene, PhA – phenylanthracene, BiN – binaphthyl.

phenyldibenzothiophene positional isomers (Marynowski et al., 2002), 2-phenylbenzo[*b*]thiophene (Püttmann et al., 1990; Rospondek et al., 2007), diphenylbenzo[*b*]thiophenes, phenylnaph-tho[*b*]thiophenes (Rospondek et al., 2007) and phenylfluorenes (Rospondek, 1998; Marynowski et al., 2001). Furthermore, naph-thyl PAHs have also been unambiguously recognised, including binaphthyls (Marynowski et al., 2001) and naphthylbenzo[*b*]thiophenes (Rospondek et al., 2007).

In aromatic fractions of the same and similar types of samples, a series of previously unidentified $C_{20}H_{14}$ compounds with the molecular ion M⁺ 254 have been encountered suggesting that they can be either phenylphenanthrene (Marynowski et al., 2001) or phenylanthracene isomers (compound L according to Bechtel et al., 2001). A hypothesis that the unknown series consists of phenylphenanthrene/anthracene isomers is based on the observation that the compounds have the molecular ion M⁺ 254 shifted by 76 Daltons from the molecular ion M⁺ 178 of phenanthrene, the major PAH present in the investigated samples (Marynowski et al., 2002; Rospondek et al., 1994, 2007). As in many Kupferschiefer extracts, the phenanthrene/anthracene ratio is >300, arylated anthracenes are less likely to occur as the major isomers. In geological samples, however, apart from five positional phenylphenanthrene isomers and three phenylanthracene isomers, the C₂₀H₁₄ substance can potentially reflect the presence of other m/z 254 structural isomers such as the binaphthyls (possessing three positional isomers) and the indenofluorenes (five positional isomers). In the investigated fractions, the major M⁺ 254 compounds are not binaphthyls, because their isomers have been firmly identified based on a comparison with authentic compounds. Comparisons of the mass spectra and GC retention times of the synthesised phenylphenanthrene standards (Fig. 3a and b and Table 3) with the natural compounds, confirms that the major compounds in geological samples are indeed phenylphenanthrene isomers (Figs. 1 and 3a).

Unequivocal identification of the novel compound series was initially performed using co-injection experiments of the reference compounds and the appropriate fractions of the rock extracts. All positional isomers of phenylphenanthrene were involved (Fig. 3a) as were all binaphthyls. However, of the three phenylanthracenes, the 1-PhA and the late eluting 2-PhA could not be detected, indicating the sole presence of the 9-PhA isomer (Fig. 3b). Thus, in geological samples, the elution sequence begins with 1,1'-binaphthyl followed by 4-PhP, 9-PhA, 1,2'-binaphthyl, 9-PhP, 1-PhP, 3-PhP, 2,2'-binaphthyl and 2-PhP (Figs 3a and 4a). Additionally, in some samples, indenofluorenes (InFl) terminate the whole series (Fig. 5d). Other previous m/z 254 isomer identifications, which were based exclusively on comparisons of the retention indices (e.g. Wang et al., 2007), should also be considered with due caution (Table 3). In our previous study (Fig. 3 in Marynowski et al., 2001), the early eluting 4-phenylphenanthrene was misidentified as indeno[2,3-*b*;3,4-*c*]fluorene.

The identification of the m/z 254 isomers was confirmed by comparison of the series retention times on three different, commonly used, stationary phases (Fig. 4). Most of the naturally occurring m/z 254 isomers are base-line separated on all columns. Exceptions are usually abundant 1,2'-binaphthyl and 9-PhP, which are poorly separated on the DB-35MS column (Fig. 4b and Table 3) and coelute on DB-17MS (Fig. 4c). On the third column, the separations of 1,1'-binaphthyl and 4-PhP are poor (Fig. 4c).



Fig. 4. Partial mass *m*/*z* 254 chromatograms of the Polkowice sample showing the elution sequence of all positional isomers of phenylphenanthrene and phenylanthracene and the binaphthyls on commonly used capillary columns: (a) HP-5MS, (b) DB-35MS and (c) DB-17MS. The additional peak marked as M⁺ 254 comes from isotopic bands of the molecular ion of benzofluoranthene; BiN – binaphthyls.

Although the separation among the individual m/z 254 isomers is good, there are a number of co-elutions with other common PACs. On the HP-5MS column, 1-PhP poorly separates from 4-phenyldibenzothiophene (Fig. 1), 9-PhA from benzo[b]naphtho[2,3-d]thiophene and 2-PhP co-elutes with 2-naphtho[2,1b]thiophene (for this compound identification, see Rospondek et al., 2007). On the HP-35MS column, 9-PhP poorly separates from 1,2'-binaphthyl which also co-elutes with chrysene (Table 3). The co-elutions mentioned made the measurement of isomer abundances in TIC chromatograms difficult and, therefore, the abundances were estimated from m/z 254 mass chromatograms (Table 1) as described in Section 4.4.

6. Effect of maturity on phenylphenanthrenes and its structural isomers

The relative abundance of the individual isomeric m/z 254 compounds in sedimentary rocks depends on the maturity of the organic matter (Figs. 5 and 6). The changes in the distribution of the m/z 254 isomers are well illustrated by partial mass m/z 254 chromatograms for a series of Devonian marine samples from the Holy Cross Mountains (Fig. 5). At the onset of the oil-generation window (R_r 0.5–0.65%; e.g., Radke et al., 2000), all isomeric m/z 254 compounds are present except for the indenofluorenes. Such distributions are exemplified by the m/z 254 mass chromatogram of the Kowala (ca R_r 0.55%) and Radkowice (ca R_r 0.65%) samples

(Fig. 5a and b). The least stable 4-, 9-, 1-PhP and 9-PhA isomers are present, interestingly with 9-phenylanthracene being quite abundant, e.g., in the Kowala DKX sample (Table 1). It is worth noting, however, that the 4-, 1- and 9-substituted phenanthrenes (Fig. 2a–c) and 9-phenylanthracene (Fig. 2f) have a fragmentation pattern with $[M-1]^+$, $[M-2]^+$; $[M-3]^+$ and $[M-4]^+$ ions in higher relative abundance when compared to the 3- and 2-isomers, and thus their apparent abundance is lower in the m/z 254 chromatograms (Figs. 1, 3-5). All three binaphthyl isomers are less abundant in comparison to the phenyl isomers. This is exemplified by the Piskrzyn sample (ca R_r 0.73%) in which the least stable 4-PhP, 9-PhA isomers also completely disappear along with 1,1'-binaphthyl. The most stable 3- and 2-substituted phenanthrenes begin to dominate over the 9-and 1-isomers at this stage (Fig. 5c). The binaphthyls present are the 1,2'- and 2,2'-isomers. At the final stage of oil generation, exemplified by the distribution of the Laskowa Góra sample (ca R_r 1.20%), 9- and 1-phenylphenanthrene are very minor compared to the thermodynamically most stable 2- and 3-isomers, and 2,2'-binaphthyl is the only binaphthyl present (Fig. 5d). 2-PhA, as the thermodynamically most stable phenylanthracene isomer, may be a minor constituent. The Laskowa Góra extract also contains indenofluorenes, although in small amounts. They are expected to form at advanced maturity by cyclisation of appropriate ortho-methylterphenyls according to the mechanism proposed by Kagi et al. (1990). The Laskowa Góra distribution is similar to the pattern encountered in the hydrothermal oil from



Fig. 5. Partial mass m/z 254 chromatograms on a HP-5MS column showing the changes in relative amounts of the phenylphenanthrene isomers with increasing maturity: (a and b) onset of oil generation, (c) oil generation peak and (d) final stage of oil generation. Note that the abundance of 4-, 9- and 1-phenylphenanthrene plus 4-phenylanthracene is higher than displayed in the m/z 254 mass chromatogram due to differences in the fragmentation patterns of the isomers. BiN – binaphthyls, InFl – indenofluorenes.

Guaymas Basin (Fig. 7d) suggesting that 2- and 3-phenylphenanthrene (together with 2,2'-binaphthyl) are stable beyond the oil window. The oil formation/evolution occurs in high temperature water at ca 300 °C and at least 200 bar (Simoneit, 1993).

The trends in the phenylphenanthrene distributions are similar to those resulting from laboratory heating of a mixture of all phenylphenanthrene isomers at 300 °C in an experiment designed to simulate maturation (Fig. 7a and c). The proportion of phenylphenanthrene isomers in the input mixture (Fig. 7a) was similar to that of immature samples (e.g., Fig. 5a). The mixture comprised 28.4% of 4-PhP, 34.9% of 9-PhP, 26.3% of 1-PhP, 6.0% of 3-PhP and 4.5% of 2-PhP (Table 1). When this mixture was heated, the proportions of phenylphenanthrene isomers changed (Fig. 7c) to roughly reflect the relative thermodynamic stabilities of the isomers.

The likely explanation is that acid-catalysed phenyl-shift reactions (Rospondek et al., 2007) around the stable aromatic ring system of phenanthrene are involved. The reactions are reversible. The more stable and less reactive isomers are, once formed, less likely to undergo the reverse reaction than are the less stable and more reactive isomers. Nonetheless, the relative concentration of 9-PhP was surprisingly high in the experimentally heated mixture (Fig. 7c). The phenomena can result from the higher energy barrier for phenyl shift beginning from the 9-position in contrast to the lower energy for 1,2-shift reactions, e.g., those proceeding from 1- to 2- and from 4- to 3-carbon positions. The 1,2-shift reaction barriers must be in a similar range as those for the phenyldibenzo-thiophene isomers, for which the energies have been estimated to range from $\Delta E_{(aq)}$ 20 to 30 kcal/mol (Rospondek et al., 2008), consistent with the onset of the isomerisation observed for phenylph-enanthrenes in our sample set (Fig. 6a). The relatively low temperature and short duration of our experiment may preclude the reaction from crossing the energy barrier from the 9- to 1-position. That such a reaction involves two discrete reactions further lowers its probability.

The maturity dependent distribution trends described can be clearly shown on a plot of individual phenylphenanthrene isomer abundances and organic-matter maturity expressed as random vitrinite reflectance R_r (Fig. 6a). In the samples investigated, the



Fig. 6. Comparison of (a) the abundances of individual phenylphenanthrene isomers and (b) the ratio of (2 - 4 - 3 - PhP)/[(2 - 4 - 3 - PhP)] vs. organic-matter maturity expressed as the random vitrinite reflectance (R_r). The abundances of phenylphenanthrene isomers are corrected for differences between isomers in MS fragmentation patterns.

proportions of the 3- and 2-isomers increase with maturity whereas those of 4-, 1- and 9-PhP decrease. Due to their decay, good correlations are obtained in an exponential regression model for the 4-, 1- and 9-isomers. The exponential regression equations are as follows: $Ab_{4-PhP} = 1534e^{-10.7R_r}$ with coefficient of determination $R^2 = 0.6$ and $Ab_{1-PhP} = 83e^{-2.6R_r}$ with $R^2 = 0.8$ and $Ab_{4-PhP} = 250e^{-3.3R_r}$ with $R^2 = 0.8$. The 4-isomer decays first to a concentration below detection limits at about 0.7% R_r whereas 1-PhP decays to a very minor concentration at about 1.2% R_r due, most likely, to reaching the energy threshold for 1,2-phenyl shifts or cyclisation. In turn, logarithmic regression equations can represent increasing trends for the 3- and 2-isomers. These are as follows: $Ab_{2-PhP} = 45 \ln(R_r) + 43$ with coefficients of determination $R^2 = 0.7$ and $Ab_{3-PhP} = 30\ln(R_r) + 36$ with $R^2 = 0.8$ (Fig. 6a).

It can be seen from the graph (Fig. 6a) that 3-PhP prevails over 2-PhP at early maturity stages. Such a feature could be explained by the formation of 3-PhP at the expense of 4-PhP via a 1,2-phenyl shift with a lower energy barrier than that for 1-PhP to 2-PhP isomerisation. The formation of 2-PhP eventually predominates due to the conversion of 4-PhP to 3-PhP. Some deviations from the trend lines (Fig. 6a) can be explained by lithological differences in the samples. High carbonate to clay ratios can hinder clay catalysed phenyl shift reactions. Furthermore, in the highly oxidised samples, where the arylated compounds are found in highest concen-

trations, the vitrinite reflectance values are clearly higher than those in corresponding less oxidised samples (e.g., Sun, 1998). Based on the evolution trends from the plot in Fig. 6a, the ratio y = (2 - + 3 - PhP)/[(2 - + 3 - PhP) + (4 - + 1 - + 9 - PhP)] can express the overall changes in the PhP distribution with advancing maturity (Fig. 6b). A logarithmic regression model equation y = 0.8 $\ln(R_r) + 0.8$ with a high R^2 of 0.9 represents this trend well. The ratio relies on the increased abundances of the stable isomers relative to the less stable ones, a phenomenon thought to be determined by mechanisms such as 1,2-phenyl shift and cyclisation if allowed by molecular geometry (1-, 4-, 9-PhP and 9-, 1-PhA), and varying generation rates of individual isomers with advancing maturity.

7. Formation of phenylphenanthrene and structural isomers

7.1. Combustion

Isomeric m/z 254 compounds have frequently been reported from incomplete combustion products including fine particulate matter (dust) and volatiles emitted from many sources such as domestic and industrial furnaces, and by other industrial pyrolytic processes (e.g., Borwitzky and Schomburg, 1979; Tong and Karasek, 1984; Lauer et al., 1988; Blanco et al., 1991; Aceves and Grimalt, 1992; Stock and Obeng, 1997; Meyer zu Reckendorf, 1997; Ricking et al., 2003; Marynowski et al., 2004; Ré-Poppi and Santiago-Silva, 2005; Wang et al., 2007). The authors have often suggested that the abundant m/z 254 compounds could be phenylphenanthrene isomers though a firm identification has never been achieved. In urban air particulate matter, a tentative identification of some phenylphenanthrene isomers was provided by Marynowski et al. (2004). To date, however, only a single isomer (9-phenylphenanthrene) has been unambiguously identified based on a comparison with a standard compound. This was in volatiles formed during pyrolytic carbonisation of coal tar pitches (Meyer zu Reckendorf, 1997). Two further isomers were suggested to be present. Comparison of their retention indices with the indices of our standards suggests that they may be 1-phenylphenanthrene and either co-eluting 1-phenylanthracene/1,2'-binaphthyl (Table 3).

During combustion, the aryl-substituted PACs (including heterocycles such as thiophenes, furans, etc.) are generated as a result of pyrolytic reactions involving homolytic cracking taking place in the oxidising furnace atmosphere (Meyer zu Reckendorf, 1997, 2000). Their origin is seen in the consecutive reactions of free radicals, mainly phenyl, with unsubstituted PACs in the gaseous phase. Phenyl, the key radical formed from benzene in such reactions, has been detected as a major radical in pyrolysates of many hydrocarbons (Hausmann and Homann, 1997). Although the hightemperature formation mechanism described is unlikely to proceed in a similar way under geological conditions, there is evidence that the reactions involving homolytic cracking taking place in both pyrolysis experiments and natural maturation are related (e.g., Schenk and Horsfield, 1998).

7.2. Maturation

While the major phase of primary organic matter cracking is separated from aromatisation/polycondensation processes during laboratory pyrolysis, extrapolation based on extended kinetic parameters illustrates an overlap between both reaction types when it comes to geological heating conditions. Type II kerogen is predominantly aliphatic and its thermal degradation involves a suite of cracking reactions, Type III kerogen is aromatic/phenolic (e.g., Tegelaar et al., 1989) and, therefore, its compositional evolution during maturation could involve more recombination reactions. Reactions between products of early cracking and the more resistant terrigenous, aromatic component of sedimentary organic matter seem to occur during the main phase of hydrocarbon generation (Dieckmann et al., 2006). The generation of alkyl/methyl moieties in a typical reducing source-rock realm (e.g., Smith et al. 1995) seems to be replaced by aryl in an oxidising realm. Indeed, all of the phenyl derivatives of the common PACs encountered so far (Marynowski et al., 2002; Rospondek and Marynowski, 2004; Rospondek et al., 2007) originate from samples containing organic matter composed of Types II and III kerogen that reached at least the onset of oil generation ($R_r > 0.5\%$), and are significantly diagenetically/catageneticaly oxidised. The importance of redox reactions in the diagenesis of organic matter is being recognised (e.g., Wilkes et al., 1998; McCollom et al., 2001; Oldenburg et al., 2002; Armstroff et al., 2007; Lewandowska et al., 2005; Rospondek et al., 2007). Aryl PAC derivatives can form as the oxidation capacity of dissolved oxidants exceeds the reduction capacity of sedimentary organic carbon and ferrous iron at high fluid/ rock mass ratios during diagenesis/catagenesis. Sulfur species are potentially the most important agents promoting the electron transfer at redox boundaries in many anoxic geological systems (e.g., McCollom et al., 2001). This seems to be the case with hydrothermally oxidised organic matter from the "Rote Fäule" facies of the Kupferschiefer with its abundance of aryl PACs (Fig. 1). In contrast, in coals the enormous total amount of sedimentary organic carbon and ferrous iron (e.g., in pyrite) buffers diagenetic fluids in strongly reducing conditions. Hypothetically, a deficiency in the Type II reactive component of kerogen can also play a role in delaying kerogen cracking and subsequent condensation reactions. Both of these phenomena are likely to be responsible for the absence of aryl PAHs in the investigated coals. If the postulated mechanism is correct, only coals of higher rank and, therefore, more oxidised are likely to contain aryl PAC derivatives. Unfortunately such samples are missing from our database.

Pyrolytic arylated PAC distributions show interesting similarities with those in geological samples affected by oxidising hydrothermal solutions during diagenesis/catagenesis (Marynowski et al., 2002; Rospondek and Marynowski, 2004; Rospondek et al., 1994, 2007, 2008). Such samples contain measurable concentrations of all phenylphenanthrene positional isomers and comparable distributions of all the previously identified phenyldibenzothiophene and phenyldibenzofuran isomers (Marynowski et al., 2002;

a free radical phenylation



Fig. 7. Partial m/z 254 mass chromatograms on HP-5MS comparing the distributions of phenylphenanthrene isomers resulting from laboratory experiments and natural processes: (a) free radical and (b) ionic phenylation of phenanthrene; (c) 300 °C heating of a phenylphenanthrene isomer mixture and (d) hydrothermal petroleum formed above 300 °C.

Rospondek et al., 2007, 2008), which may suggest their formation in a reaction involving a highly reactive species. The phenyl radical is a highly reactive species among those effecting aromatic substitution and benzene is abundant in nature (e.g., Kissin, 1998; McCollom et al., 2001). A high degree of reactivity is combined with a lack of selectivity. Thus, our samples of lower maturity (R_r ca 0.5%) contain phenylphenanthrene isomers in similar proportions to those resulting from free radical phenylation of phenanthrene (Dickerman et al., 1973). The similarities were confirmed by our free radical phenanthrene phenylation experiments (Fig. 7a). Both phenylating reagents used in the low temperature experiments yielded all the positional isomers, the most abundant being 1-, 9-, and 4-isomers followed by 3- and 2-isomers. This contrasts strongly with the distribution of the ionic phenylation (see Section 4.2.2) yielding only the 9-PhP isomer (Fig. 7b). This also agrees with the observed similarities between the natural abundance of 9-phenylanthracene (Figs. 3b and 5a) and the experimentally obtained isomer mixture (see free radical phenylation: Section 4.2.1), where both are dominated by the 9-isomer (95.2%) and other isomers are subordinate (1-PhA ca 4.3% and 2-PhA ca 0.5%; Fig. 3b). Therefore, it is tempting to propose that free radical phenylation of phenanthrene or anthracene moieties would account for the observed phenylphenanthrene and phenylanthracene distributions in our oxidised set of samples containing mixtures of Types II and III kerogen. Cyclisation/aromatisation of common linear precursors is not an attractive alternative to a phenylation hypothesis. Such a process would lead exclusively to the formation of 1-phenylphenanthrene/1,8-diphenylphenanthrene though most likely with extra and distinctive dialkyl substituents. However, such molecules were not detected. In addition, the formation of 9-phenylanthracene would be unlikely with this alternative mechanism.

8. Conclusions

Based on the comparison of the mass spectra and the gas chromatography retention times of the synthesised standards and the natural isomeric m/z 254 compounds, it is clear that the important components of the aromatic fractions of the analysed sedimentary rocks are phenylphenanthrene isomers along with binaphthyls and 9-phenylanthracene. To the best of our knowledge, phenylphenanthrene and phenylanthracene isomers have not been reported from geological samples apart from the tentative identification of Marynowski et al. (2001). In geological samples, a high-quality analysis of the m/z 254 isomers can be achieved on the most commonly used HP-5MS column as the likely absence of 1-PhA means that there is no need to discriminate between 1,2'-binaphthyl and 1-PhA. If necessary for non-geological samples, these latter compounds can be differentiated on DB-35MS.

In rocks, the natural occurrence of PhP and PhA isomers appears to be restricted to samples affected by diagenetic/catagenetic oxidation of organic matter comprising Type II with varying admixture of Type III kerogen and with maturity attaining at least the onset of oil window. Such a characteristic of the samples containing arylated PACs can be elucidated based on the analyses of our large database of 350 rocks containing varying types of organic matter at different maturities. The PhP and PhA isomer abundance is the highest in the samples coming form the base of the Zechstein (oxidised Kupferschiefer) overlaying the red beds (Rotliegende), where sedimentary pyrite was hydrothermally transformed to hematite/goethite by unoxic oxidising solutions. Similar samples have yielded all the previously identified aryl PAH derivatives such as phenylnaphthalenes, phenylbenzo[b]thiophenes, phenyldibenzofurans, phenyldibenzothiophenes and phenylnaphtho[b]thiophenes (Püttmann and Goßel, 1990; Püttmann et al., 1990; Marynowski et al., 2001, 2002; Rospondek and Marynowski, 2004; Rospondek et al., 2007, 2009). In such samples, the organic matter oxidation is also reflected by extensive dealkylation of PACs concomitant with the formation of unsubstituted, and presumably arylated PACs. The postulated origin of the phenyl PACs from phenyl radical phenylation of the corresponding unsubstituted aromatic moieties during maturation of oxidised kerogen arises from a distribution characterising all arylsubstituted PACs identified until now. The presence of all possible positional isomers (e.g., of phenylphenanthrene, phenyldibenzothiophene, phenyldibenzofuran) from the beginning of the oil generation window (R_r ca 0.5%), including abundant amounts of the most sterically hindered isomers, suggests the involvement of low-regioselectivity reactions in their formation. With increasing maturity the distributions of the m/z 254 compounds changes systematically. The isomerisation via 1,2-phenyl shifts, and at even more advanced maturity stages, cyclisation reactions, progressively lead to thermodynamically controlled distributions. The observed systematic trends in the relative abundances of the phenylphenanthrene isomers with increasing maturity give promise for their employment as sensitive molecular indicators of organic matter maturation, but at the same time pointing to a poor quality of the source rocks due to intense diagenetic/catagenetic oxidation of organic matter.

Future laboratory experiments and studies of geological samples are needed to determine in detail the mechanisms involved in the genesis and evolution of the phenyl PAHs derivatives in nature. It can be expected that phenylphenanthrene isomers are also the significant aryl PACs in many petrochemical and combustion products.

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