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Novel arylated polyaromatic thiophenes: Phenylnaphtho[*b*]thiophenes and naphthylbenzo[*b*]thiophenes as markers of organic matter diagenesis buffered by oxidising solutions

Mariusz J. Rospondek [a,*], Leszek Marynowski [b], Maciej Góra [c]

[a] *Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland*
[b] *Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland*
[c] *Faculty of Chemistry, Department of Organic Chemistry, Jagiellonian University, ul. Ingardena 3, 30-063 Kraków, Poland*

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Abstract

Three naphtho[*b*]thiophenes (asymmetric dibenzothiophene isomers) are minor components relative to the prevailing dibenzothiophene constituents of aromatic fractions of diagenetically oxidised marine sedimentary rocks. Interestingly, the rocks containing naphtho[*b*]thiophenes often also contain their arylated derivatives, phenylnaphtho[*b*]thiophenes, as major components relative to phenyldibenzothiophenes. Both these series are accompanied by other structural isomers, i.e., naphthylbenzo[*b*]thiophenes. To our knowledge, phenylnaphtho[*b*]thiophenes and their naphthylbenzo[*b*]thiophene isomers have not been reported in geological samples and are unambiguously identified here using synthetic standards. The distribution of arylated thiophenic polycyclic aromatic compounds strongly depends on maturity. At low maturity, where kinetically controlled distribution of the arylated thiophenes is expected, the greatest number of isomers is observed, suggesting that low regioselectivity reactions are involved in their formation. At the beginning of the oil window, small amounts of unstable 3-phenylnaphtho[*b*]thiophenes, together with three 2-phenylnaphtho[*b*]thiophenes, naphthylbenzo[*b*]thiophenes, with major 2-(2-naphthyl)benzo[*b*]thiophene, and all four possible phenyldibenzothiophenes, with abundant kinetically favoured 1- and 4-substituted isomers, are present. Experimental free radical phenylation of dibenzothiophene yielded a phenyldibenzothiophene isomeric distribution very similar to that observed in natural samples, but different from that resulting from ionic phenylation. Since these arylated polycyclic aromatic thiophenes occur exclusively in samples in which sedimentary pyrite was hydrothermally transformed to hematite/goethite as a result of rock interaction with oxidising brines, such solutions, usually rich in benzene, can be considered as a potential source of phenyl species. At more advanced stages of maturity, 3-phenylnaphtho[2,1-*b*]thiophenes are transformed to 2-phenylnaphtho[2,1-*b*]thiophenes, as revealed by artificial maturation experiments. In turn, severe heating of 2-phenylnaphtho[2,1-*b*]thiophene leads to its complete disappearance and the formation of dibenzothiophene and phenyldibenzothiophenes. Under the same conditions, only phenyldibenzothiophenes isomerise, presumably by a 1,2-phenyl shift, and 1-phenyldibenzothiophene also cyclises to triphenyleno[1,12-*bcd*]thiophene. The thermodynamically controlled distribution of phenyldibenzothiophenes, dominated by 3- and 2-substituted isomers, is reached at about 1.2% R_r (vitrinite reflectance). The distribution is similar

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[*] Corresponding author.
E-mail address: m.rospondek@uj.edu.pl (M.J. Rospondek).

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to that encountered in hydrothermal petroleum generated above 300 °C in the rift system of the Guayamas Basin. Such a distribution can be experimentally obtained via prolonged heating a mixture of all possible phenyldibenzothiophene isomers at 330 °C in the presence of an acidic clay catalyst. The ratio between the sum of all phenyldibenzothiophenes and 2-phenylnaphtho[*b*]thiophene plus 2-(2-naphthyl)benzo[*b*]thiophene changes regularly with advancing maturity, suggesting a potential application of these newly identified compounds for maturity assessment.

1. Introduction

Benzo[*b*]thiophene and dibenzothiophene (for structures see Appendix), accompanied by their alkyl derivatives, are by far the most common aromatic sulfur compounds in crude oils and solvent extracts of many marine sedimentary rocks (e.g., Radke et al., 1986; Radke and Willsch, 1991, 1994; Rospondek et al., 1994). They have not been found in organisms and water column particulate matter and appear only in steadily increasing concentration with organic matter (OM) maturation, attesting to their formation upon diagenesis/catagenesis. The abundance of benzo[*b*]thiophenes decreases at more advanced maturity, as they are replaced by dibenzothiophene and its alkyl derivatives (Orr, 1974; Radke and Willsch, 1991, 1994; Santamaría-Orozco et al., 1998). The distribution of both alkylbenzo[*b*]thiophenes and alkyldibenzothiophenes is sensitive to maturation, although also influenced by lithology (e.g., Radke et al., 1986, 2000; Radke and Willsch, 1994). The distribution of methyldibenzothiophenes, as a result of large differences in thermal stability between isomers, is applicable to maturity assessment (Radke and Willsch, 1991, 1994; Radke et al., 1986, 2000 and citations therein). Similarly, the distribution of positional isomers of phenyldibenzothiophenes is controlled mainly by maturity, as shown for sedimentary rock extracts (Marynowski et al., 2002). At early maturity stages, the phenyldibenzothiophenes are accompanied by a series of unidentified compounds eluting closely after them and sometimes dominating the m/z 260 chromatograms. The unidentified compounds have the same molecular mass and very similar mass spectra, suggesting structural isomers with the formula $C_{18}H_{12}S$. It has been suggested that they could be phenylnaphtho[*b*]thiophenes or naphthylbenzo[*b*]thiophenes (Marynowski et al., 2002), though synthetic standards were not available for firm identification. To the best of our knowledge, such arylated, polycyclic aromatic thiophenes have not been identified in geological samples. This paper presents unequivocal assignment of these novel arylated series in a set of geological samples varying in maturity (Table 1), but having in common a hydrothermal diagenetic oxidation event. Identification was achieved by means of comparison of gas chromatography (GC) retention times on capillary columns with three different stationary phases via co-elution experiments with synthesized standards and comparison of mass spectra with those of the standards. None of the synthesized arylated thiophene isomers was available commercially.

2. Materials and methods

2.1. Samples

The samples are marine sedimentary rocks containing OM of a wide maturity range. They have in common oxidative diagenesis manifested in primary pyrite oxidation to hematite/goethite via enhanced circulation of oxidising aqueous solutions. The oxygen fugacity of such solutions was buffered at elevated values by equilibration with underlying red hematite-rich sandstones before entering the pyrite-rich black shales. The process is best described by Oszczepalski (1989) and Püttmann et al. (1988, 1990) for shales hosting hydrothermal copper–silver mineralisation (Kupferschiefer). Samples were collected from the following localities (Table 1):

1. Lower (Emsian) to Upper Devonian (Frasnian, Famenian) carbonate and shale of maturity from R_r 0.52% to 1.2% from the Holy Cross Mountains (for a detailed description see Marynowski et al., 2000). Analogous sediments (Frasnian/Famenian), though of higher maturity (reaching R_r 1.4% due to the thermal/hydrothermal influence of rhyodacite intrusion), came from the Kraków-Silesia Monocline, Dębnik Anticline (Southern Poland; Lewandowska, 1991, 1999).
2. Limestone, dolostone, marl and shale (Kupferschiefer) from the hydrothermal, copper–silver deposits in the Upper Permian (Zechstein) sedimentary sequence of the North-Sudetic Trough (the Konrad mine) and Fore-Sudetic Monocline

Table 1
Sample description and bulk organic geochemical data (n.f. = not found, n.d. = not determined)

Locality	Lithology (age)	R_{r} (%)	TOC (%)	EOM [mg/g TOC]
Holy Cross Mountains, Poland (Devonian)				
Bukowa Góra	Shale (Emsian)	1.15	n.d.	n.d.
Kowala-1 borehole (depth 851 m)	Dolostone (Eifelian)	0.64	n.d.	n.d.
Piskrzyn	Dolostone (Eifelian)	0.73	n.d.	n.d.
Piskrzyn	Shale (Eifelian)	0.76	n.d.	n.d.
Radkowice	Greenish shale (Eifelian)	0.65	1.13	10
Radkowice	Greenish dolostone (Eifelian)	0.62	0.80	12
Laskowa Góra	Dolostone (Eifelian?)	1.20	0.37	11
Laskowa Góra	Greenish shale (Eifelian?/Givetian?)	1.15	n.d.	n.d.
Janczyce-1 borehole (depth 943 m)	Dolostone (Givetian?)	n.f.	0.03	20
Sitkówa – Kowala	Limestone (Givetian)	0.63	0.25	68
Jaworznia	Limestone (Frasnian)	0.63	0.01	20
Kowala K1	Black shale (Frasnian)	0.57	3.68	18
Kowala K2	Black shale (Frasnian)	0.54	8.17	15
Kowala K3	Black shale (Frasnian)	0.55	4.00	30
Kowala K4	Black shale (Frasnian)	0.55	0.89	69
Kowala K5	Black shale (Frasnian)	0.57	4.14	43
Panek (by Bolechowice)	Limestone (Frasnian)	0.66	0.14	21
Góra Łgawa	Marly limestone (Famennian)	0.52	0.73	27
Fore-Sudetic Monocline, South-Western Poland (Permian, Zechstein)				
Lubin LE-I/0	“Basal” dolostone	n.f.	0.4	4
Lubin LE-I/1	Laminated black shale	0.67	4.6	n.d.
Lubin LE-I/2	Laminated shale	0.7	1.3	10
Polkowice PW-II/1	Laminated redish dolostone “Rote Fäule”	n.f.	1.00	6
Polkowice PW-III/1	Reddish/black marly shale “Rote Fäule”	n.f.	n.d.	n.d.
Polkowice PW-III/2	Limestone with hematite spots “Rote Fäule”	0.68	n.d.	n.d.
Sieroszowice S1	Reddish/black shale “Rote Fäule”	0.72	6.1	4
Sieroszowice S3	Limestone with hematite spots “Rote Fäule”	n.f.	0.7	6
Rudna	Bitumen cementing sandstone		n.d.	n.d.
North-Sudetic Trough, South-Western Poland (Permian, Zechstein)				
Konrad Cu	Marly limestone	n.f.	n.d.	n.d.
Konrad Pb	Marly limestone	0.68	n.d.	n.d.
Konrad “Rote Fäule”	Reddish/black shale “Rote Fäule”	0.70	n.d.	n.d.
Podhale Trough, the Carpathians, Southern Poland				
Zakopane	Flysch shale (Paleogene)	0.9	n.d.	n.d.
Poronin PAN-1 borehole (depth 1912 m)	Flysch shale (Cretaceous)	1.5	0.12	n.d.
Cracov-Silesian Monocline, Dębnik Antycline, Southern Poland (Devonian)				
Dębnik	Limestone (Givetian)	1.4	n.d.	n.d.
Dębnik	Marly shale (Frasnian)	1.4	1.45	13
Harz Mountains, Germany				
Winterberg	Bitumen		n.d.	n.d.
Gulf of California, Mexico (Holocene)				
Guaymas Basin	Hydrothermal oil		n.d.	n.d.

(the Polkowice-Sieroszowice mines, the Rudna and Lubin mine), South-Western Poland (for a description, see Oszczepalski, 1989; Püttmann et al., 1990; Rospondek et al., 1993, 1994). The mean vitrinite reflectance is generally lower in the Polkowice mining field (ca. 0.55–0.7% R_{r}, though reaching sporadically R_{r} 0.8%) and higher in the Rudna mining field (R_{r} 0.7–0.8%; Speczik, 1995). Within the ore grade areas, the mean vitrinite reflectance at the base of the sequence is generally higher than in the upper part, all within about 2–3 m thickness. This abrupt change is attributed to OM oxidation (Speczik, 1995). The sandstone sample from

Rudna is a quartz arenite cemented by black solid bitumen, which usually replaces common carbonate or anhydrite cements. The solid bitumen is completely soluble in organic solvents (Bogacz and Sawłowicz, 2001).
3. Cretaceous and Tertiary Flysch shales with a maturity range between R_r 0.9% and 1.5% from the Podhale Trough, Western Carpathians of Southern Poland (Rospondek and Marynowski, 2004). The rock sequence yields recent thermal waters, which are a geothermal energy source for the Podhale region.
4. Upper Devonian reef limestone with solid bitumen from the Winterberg quarry, Harz Mountains (Germany; Gischler, 1996).
5. Hydrothermal petroleum from the Guaymas Basin, central Gulf of California (Mexico), generated in the hydrothermally active oceanic rift zone in a tectonic graben filled with thick diatomaceous ooze and terrigenous silty mud (e.g., Kawka and Simoneit, 1990).

2.2. 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×. The reflectance standard used has R_r 0.62%. About one hundred vitrinite grains were measured for each sample. Vitrinite was abundant except in the samples from Bukowa Góra and Jaworznia. In the samples from the Janczyce-1 borehole, Lubin LE-I/0, Polkowice PW-II/1, PW-III/1, Sieroszowice S3 and Konrad Cu vitrinite was not found (Table 1).

2.3. Extraction and chromatography

The finely ground 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, 20 × 20 × 0.25 cm) activated at 120 °C (1 h). The plates were loaded with DCM soluble fractions and developed with *n*-hexane. Bands comprising aliphatic (R_f 0.4–1.0), aromatic (R_f 0.05–0.4) and polar (R_f 0.0–0.05) fractions were collected.

Gas chromatography mass spectrometry (GC–MS) was carried out with an Agilent 6890 chromatograph equipped with an EPC Cool On-Column Inlet and fitted with three different fused silica columns (HP-5 ms and DB-35 ms, 60 m × 0.32 mm, 0.25 μm film thickness; DB-17 ms, 60 m × 0.25 mm, 0.25 μm film thickness). He was the carrier gas. Samples were injected on-column at 40 °C. The oven temperature was kept isothermally for 3 min, increased to 120 °C at 20 °C $\min^{-1}$, to 300 °C at 3 °C $\min^{-1}$ and kept there for 35 min. The chromatograph was coupled to an Agilent 5973 Network MSD (mass selective detector). 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). In addition, a gas chromatograph with a FPD (flame photometric detector) was used. Identification of individual compounds was performed by co-injection of reference compounds obtained as described by Marynowski et al. (2002) and synthesized as described in Section 2.5.

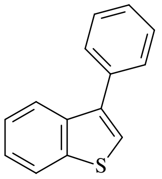
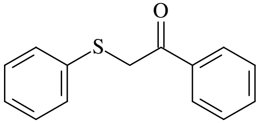
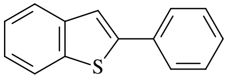
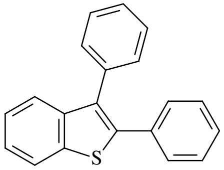
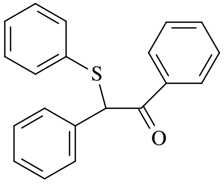
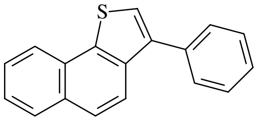
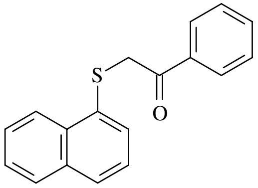
2.4. NMR spectroscopy

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

2.5. Synthesis of standards

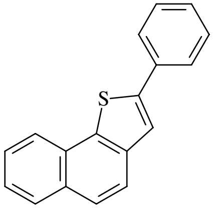
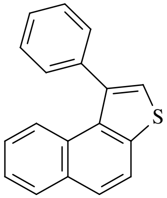
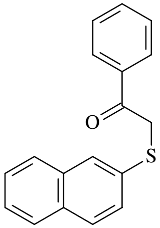
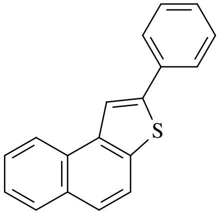
Aryl derivatives of benzo[*b*]thiophene and naphtho[*b*]thiophenes were synthesized following a classical method (e.g., Dann and Kokorudz, 1958) via cyclisation of appropriate 1-aryl-2-(arylthio)ethanones (Fig. 1; Table 2) or benzoylmethylphenylthiophene (Demerseman et al., 1954). When the method did not yield pure products, synthesis was independently repeated using regioselective Suzuki cross coupling reactions (Table 2). The classical method involves a two step procedure. In the first, 1-aryl-2-(arylthio)ethanones were obtained by reaction of thiophenol or thionaphthols with appropriate 2-bromo-1-arylethanones (Seshadri et al., 1981). Next, cyclisation of the appropriate 1-aryl-2-(aryl-

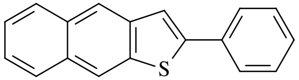
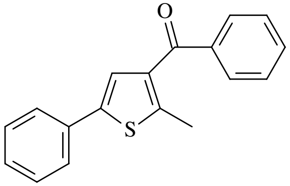
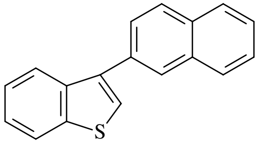
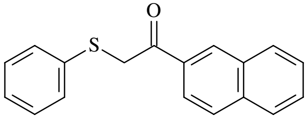
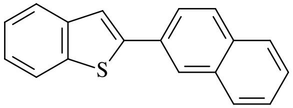
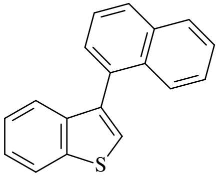
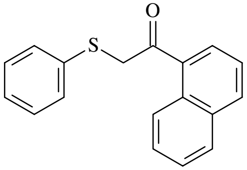
Table 2
Summary of data on synthesised arylated thiophenes, synthetic method and substrates

Thiophene (structure number)	Solvent, purity, melting point	Spectral data[a]	Reaction substrate
3-phenylbenzo[*b*]thiophene (I) 	*n*-Hexane/toluene (9:1, v:v) TLC Purity >90% Yellow oil (oil, Dann and Kokorudz, 1958)	^{1}H NMR (CDCl$_3$, 500 MHz): 7.36–7.40 (m, 4H); 7.45–7.48 (m, 2H); 7.56–758 (m, 2H); 7.89–7.91 (m, 2H) ^{13}C NMR (CDCl$_3$, 125 MHz): 122.90 (2C); 123.37; 124.31; 124.39; 127.53; 128.71 (4C); 136.04; 137.94; 138.12; 140.72 MS spectrum (Porter, 1967, 1985)	1-phenyl-2-(phenylthio)ethanone  cyclisation in polyphosphoric acid at 100 °C (Dann and Kokorudz, 1958)
2-phenylbenzo[*b*]thiophene (II) 	Methanol (white crystals) Purity >97% Mp 173–174 °C (mp 175–176 °C, Banfield et al., 1956)	^{1}H NMR (CDCl$_3$, 500 MHz): 7.28–7.36 (m, 3H); 7.42–7.43 (m, 2H); 7.54 (s, 1H); 7.70–7.72 (m, 2H); 7.76 (d, 1H, $J = 7.5$ Hz); 7.82 (d, 1H, $J = 8.3$ Hz) ^{13}C NMR (CDCl$_3$, 125 MHz): 119.46; 122.26; 123.56; 124.31; 124.51; 126.52 (2C); 128.25; 128.94 (2C); 134.35; 139.55; 140.72; 144.28 MS spectrum (Porter, 1967, 1985)	1-phenyl-2-(phenylthio)ethanone cyclisation in hot polyphosphoric acid at 180 °C (Banfield et al., 1956; Dann and Kokorudz, 1958)
2,3-diphenylbenzo[*b*]thiophene (III) 	Chloroform (white needles) Purity >92% Mp 111–112 °C (mp 109 °C, Heyndericks et al., 2002; mp 113–114 °C, Capozzi et al., 1970)	NMR (Heyndericks et al., 2002) ^{1}H NMR (CDCl$_3$, 300 MHz): 7.20–7.25 (m, 3H); 7.30–7.41 (m, 9H); 7.56–7.61 (m, 1H); 7.83–7.89 (m, 1H) ^{13}C NMR (CDCl$_3$, 75 MHz): 122.05; 123.34; 124.42; 124.51; 127.36; 127.68; 128.32 (2C); 128.63 (2C); 129.61 (2C); 130.44 (2C); 133.25; 134.25; 135.53; 138.85; 139.54; 140.89	1,2-diphenyl-2-(phenylthio)ethanone  cyclisation in hot polyphosphoric acid at 180 °C
3-phenylnaphtho[1,2-*b*]thiophene (IV) 	Ethanol Purity >96% Mp 56 °C (oil, Clark and McKinnon, 1981)	^{1}H NMR (CDCl$_3$, 500 MHz): 7.38–7.44 (m, 2H); 7.46–7.51 (m, 3H); 7.54–7.56 (m, 1H); 7.60–7.61 (m, 1H); 7.71 (d, 1H, $J = 8.8$ Hz); 7.87 (d, 1H, $J = 8.8$ Hz); 7.90 (d, 1H, $J = 8.1$ Hz); 8.15 (d, 1H, $J = 8.0$ Hz) ^{13}C NMR (CDCl$_3$, 125 MHz): 121.25; 122.10; 123.57; 125.43; 125.82; 126.60; 127.54; 128.72 (3C); 128.81 (2C); 129.19; 130.89; 135.53; 136.11; 138.39; 139.54	2-(1-naphthylthio)-1-phenylethanone  cyclisation in polyphosphoric acid at 100 °C

(*continued on next page*)

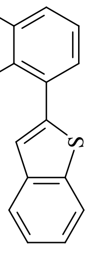
Table 2 (*continued*)

Thiophene (structure number)	Solvent, purity, melting point	Spectral data[a]	Reaction substrate
2-phenylnaphtho[1,2-*b*]thiophene (V) 	Toluene Purity >95% Mp 122 °C (no literature mp available)	^{1}H NMR (DMSO d_6, 300 MHz): 7.35–7.38 (m, 1H); 7.43–7.53 (m, 3H); 7.55–7.61 (m, 1H); 7.66 (s, 1H); 7.73 (d, 1H, $J = 8.7$ Hz); 7.77–7.81 (m, 3H); 7.90–7.93 (m, 1H); 8.11–8.14 (m, 1H) ^{13}C NMR (DMSO d_6, 75 MHz): 120.69; 121.99; 123.55; 125.59 (2C); 126.37 (2C); 126.70; 128.11; 128.89 (2C); 129.02 (2C); 130.79; 134.37; 136.89; 138.40; 143.45	2-(1-naphthylthio)-1-phenylethanone cyclisation in BF_3–CH_3COOH complex at 150 °C
3-phenylnaphtho[2,1-*b*]thiophene[b] (VI) 	Methanol Purity >99% Mp 82–83 °C (mp 86 °C, Dann and Kokorudz, 1958)	^{1}H NMR (CDCl$_3$, 500 MHz): 7.20–7.24 (m, 1H); 7.33 (s, 1H); 7.39–7.43 (m, 1H); 7.46–7.52 (m, 5H); 7.74 (d, 1H, $J = 8.7$ Hz); 7.78 (d, 1H, $J = 8.3$ Hz); 7.78–7.90 (m, 2H) ^{13}C NMR (CDCl$_3$, 125 MHz): 120.96; 123.89; 124.52; 124.97; 125.62; 125.76; 127.73; 128.55 (2C); 128.68; 129.62 (2C); 129.89; 131.91; 132.80; 138.75; 139.07; 140.31 Spectrum MS no. 1378 (Porter, 1985) and Wiley MS database #200609	2-(2-naphthylthio)-1-phenylethanone  cyclisation in polyphosphoric acid at 100 °C (Dann and Kokorudz, 1958)
2-phenylnaphtho[2,1-*b*]thiophene (VII) 	Ethanol Purity >99% Mp 106–108 °C (mp 106–108 °C, Dann and Kokorudz, 1958)	^{1}H NMR (CDCl$_3$, 500 MHz): 7.32–7.35 (m, 1H); 7.42–7.45 (m, 2H); 7.50–7.53 (m, 1H); 7.58–7.61 (m, 1H); 7.70 (d, 1H, $J = 8.8$ Hz); 7.77–7.79 (m, 2H); 7.82 (d, 1H, $J = 8.4$ Hz); 7.91 (d, 1H, $J = 8.0$ Hz); 8.17 (s, 1H); 8.33 (d, 1H, $J = 8.2$ Hz) ^{13}C NMR (CDCl$_3$, 125 MHz): 117.68; 120.46; 123.51; 125.08; 125.31; 126.40 (2C); 126.46; 128.10; 128.63; 129.01 (2C); 129.28; 131.15; 134.51; 136.85; 137.10; 144.10 Wiley MS database #200610	2-(2-naphthylthio)-1-phenylethanone cyclisation in hot polyphosphoric acid at 180 °C (Dann and Kokorudz, 1958)

2-phenylnaphtho[2,3-*b*]thiophene (VIII) 	Toluene (almost white leaflets) Purity >99%	^{1}H NMR (DMSO d_6, 300 MHz): 7.40–7.51 (m, 5H); 7.78–7.81 (m, 2H); 7.85 (s, 1H); 7.92–8.01 (m, 2H); 8.36 (s, 1H); 8.44 (s, 1H) ^{13}C NMR (DMSO d_6, 75 MHz): 119.95; 120.71; 122.24; 125.53; 125.80; 126.95 (2C); 127.59; 128.50; 129.25; 129.57 (2C); 131.52; 131.63; 134.26; 138.01; 140.41; 145.35	3-benzoyl-2-methyl-5-phenylthiophene 
	Mp 304–305 °C (mp 297 °C Demerseman et al., 1954)		thermal cyclisation (Elbs reaction) (Demerseman et al., 1954)
3-(2-naphthyl)benzo[*b*]thiophene (IX) 	Methanol Purity >99%	^{1}H NMR ($CDCl_3$, 500 MHz): 7.39–7.43 (m, 2H); 7.50 (s, 1H); 7.51–7.55 (m, 2H); 7.72 (dd, 1H, $J = 8.5$ Hz, $J = 1.6$ Hz); 7.89–7.91 (m, 2H); 7.93–7.96 (m, 2H); 7.97–8.00 (m, 1H); 8.05 (d, 1H, $J = 1.6$ Hz) ^{13}C NMR ($CDCl_3$, 125 MHz): 122.98 (2C); 123.78; 124.42; 124.49; 126.08; 126.39; 126.99; 127.39; 127.76; 128.04; 128.32; 132.77; 133.49; 133.61; 138.07 (2C); 140.77	1-(2-naphthyl)-2-(phenylthio)ethanone 
	Mp 62–64 °C (mp 59 °C, Murthy and Tilak, 1960)	Wiley MS database #200607	(A) cyclisation in polyphosphoric acid at 100 °C (Murthy and Tilak, 1960) (B) Suzuki cross-coupling of 3-thianaphtheneboronic acid with 2-bromo-naphthalene (Heynderickx et al., 2002)
2-(2-naphthyl)benzo[*b*]thiophene (X) 	Toluene (white flakes) Purity >97%	^{1}H NMR (DMSO d_6, 300 MHz): 7.36–7.43 (m, 2H); 7.50–7.59 (m, 2H); 7.86–8.01 (m, 7H); 8.25 (s, 1H) ^{13}C NMR (DMSO d_6, 75 MHz): 120.06; 121.77; 123.23; 123.63; 124.12; 124.20; 124.35; 125.95; 126.23; 127.06; 127.57; 128.16; 130.71; 132.36; 132.78; 138.48; 140.11; 142.90	(A) 1-(2-naphthyl)-2-(phenylthio)ethanone cyclisation in hot polyphosphoric acid at 180 °C (Lamberton and Paine, 1976) (B) Suzuki cross-coupling of 2-thianaphtheneboronic acid with 2-bromonaphthalene (Heynderickx et al., 2002)
	Mp 221–222 °C (mp 213–214 °C, Lamberton and McGrail, 1963)	Wiley MS database #200606	
3-(1-naphthyl)benzo[*b*]thiophene (XI) 	*n*-Hexane (white fine needles) Purity ca. 80%	^{1}H NMR ($CDCl_3$, 500 MHz): 7.23–7.28 (m, 1H); 7.33–7.41 (m, 3H); 7.46 (s, 1H); 7.48–7.58 (m, 3H); 7.69–7.75 (m, 1H); 7.90–7.96 (m, 3H) ^{13}C NMR ($CDCl_3$, 125 MHz): 122.69; 123.67; 124.18; 124.41; 124.98; 125.42; 125.94; 126.06; 126.16; 127.82; 128.26 (2C); 133.44; 133.65; 133.76; 136.36; 139.55; 139.97	1-(1-naphthyl)-2-(phenylthio)ethanone 

(*continued on next page*)

Table 2 (*continued*)

Thiophene (structure number)	Solvent, purity, melting point	Spectral data[a]	Reaction substrate
	Mp 89–91 °C (mp 90–92 °C, Schuetz and Ciporin, 1958; Buquet et al., 1981)	Wiley MS database #200605	(A) cyclisation in polyphosphoric acid at 100 °C (Schuetz and Ciporin, 1958) (B) Suzuki cross-coupling of 3-thianaphtheneboronic acid with 1-bromonaphthalene (Heynderickx et al., 2002)
2-(1-naphthyl)benzo[*b*]thiophene (XII) 	Toluene Purity >96% Mp 122–123 °C (mp 120–121 °C, Buquet et al., 1981)	^{1}H NMR ($CDCl_3$, 300 MHz): 7.36–7.43 (m, 2H); 7.45 (d, 1H, $J = 0.6$ Hz); 7.49–7.54 (m, 3H); 7.65 (dd, 1H, $J = 7.2$ Hz, $J = 1.2$ Hz); 7.82–7.92 (m, 4H); 8.27–8.30 (m, 1H) ^{13}C NMR ($CDCl_3$, 75 MHz): 122.24; 123.74; 124.19; 124.39; 124.62; 125.35; 125.89; 126.28; 126.76; 128.53; 128.60; 129.04; 131.94; 132.57; 133.97; 140.35; 140.45; 142.29	(A) 1-(1-naphthyl)-2-(phenylthio)ethanone cyclisation in hot polyphosphoric acid at 180 °C (B) Suzuki cross-coupling of 2-thianaphtheneboronic acid with 1-bromonaphthalene (Heynderickx et al., 2002)

[a] NMR spectra this work.

[b] 1-Phenylnaphtho[2,1-*b*]thiophene according to IUPAC.

thio)ethanones (Table 2; 0.36 mmol) in polyphosphoric acid (PPA; 5 g) was achieved in a 50 mL flask with magnetic stirring as described by Banfield et al. (1956) and Dann and Kokorudz (1958). As expected, the position of the aryl substituents depends strictly on reaction conditions (Fig. 1 and Table 2). A short time (~1 h) at 100 °C leads to 3-arylthiophenes, whereas prolonged time and higher temperature (~180 °C) favours formation of 2-arylthiophenes (Fig. 1 and Table 2). The reaction mixture was allowed to cool to room temperature, dissolved in 50 mL cold water and extracted with DCM (3 × 25 mL). Combined organic layers were dried over anhydrous $MgSO_4$. The following standards were synthesized: 3-phenylbenzo[*b*]thiophene (3-PhB[*b*]T) **I** (numbers refer to the structures in Table 2), 2-phenylbenzo[*b*]thiophene (2-PhB[*b*]T) **II**, 2,3-diphenylbenzo[*b*]thiophene (2,3-DPhB[*b*]T) **III**, and 3-phenylnaphtho[1,2-*b*]thiophene (3-PhN[1,2-*b*]T) **IV**. However, the PPA-catalysed cyclisation of 2-(1-naphthylthio)-1-phenylethanone (Table 2) led exclusively to 3-PhN[1,2-*b*]T **IV** and in situ rearrangement to 2-phenylnaphtho[1,2-*b*]thiophene (2-PhN[1,2-*b*]T) **V** was not achieved. The use of BF_3–CH_3COOH complex at 150 °C for a prolonged time (~6 h) led to formation of 2-PhN[1,2-*b*]T **V**, but in low yield (ca. 6%). In turn, the PPA-catalysed cyclisation easily led either to formation of 3-phenylnaphtho[2,1-*b*]thiophene (3-PhN[2,1-*b*]T) **VI** or 2-phenylnaphtho[2,1-*b*]thiophene (2-PhN[2,1-*b*]T) **VII**, depending on reaction conditions.

The compound 2-phenylnaphtho[2,3-*b*]thiophene (2-PhN[2,3-*b*]T) **VIII** was prepared in a three step synthesis, starting from 2-phenylthiophene. Reaction of 2-phenylthiophene with *n*-butyllithium and methyl iodide gave 2-methyl-5-phenylthiophene (Liu et al., 2002). Benzoylation of the latter and subsequent conversion of the resulting 3-benzoyl-2-methyl-5-phenylthiophene (Table 2) in the Elbs reaction (gentle reflux 3 h) led directly to 2-PhN[2,3-*b*]T **VIII** (Demerseman et al., 1954).

Additionally, syntheses of naphthylbenzo[*b*]thiophenes were performed using the PPA-catalysed cyclisation of appropriate 1-(naphthyl)-2-(phenylthio)ethanones. Cyclisation of 1-(2-naphthyl)-2-(phenylthio)ethanone (Table 2) led to a mixture of 3-(2-naphthyl)benzo[*b*]thiophene (3-(2-Naphthyl)B[*b*]T) **IX** (Table 2) and 2-(2-naphthyl)benzo[*b*]thiophene (2-(2-Naphthyl)B[*b*]T) **X** (Table 2). Similarly, starting from 1-(1-naphthyl)-2-(phenylthio)- ethanone (Table 2), a mixture of (1-naphthyl)-

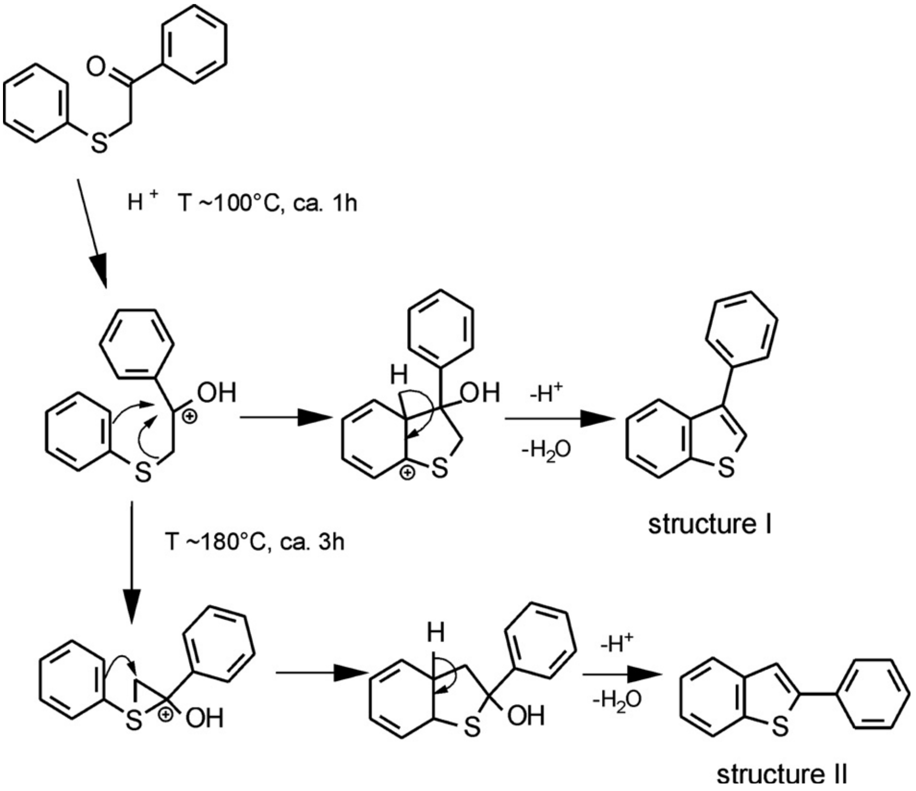


Fig. 1. Scheme for acid catalysed cyclisation of 1-aryl-2-(arylthio)ethanones as exemplified by cyclisation of 1-phenyl-2-(phenylthio)ethanone to 3-phenylbenzo[*b*]thiophene **I** or 2-phenylbenzo[*b*]thiophene **II** (adapted from Rao and Tilak, 1959).

benzo[*b*]thiophenes **XI** and **XII** (Table 2) was produced. The subordinate compound was 3-(1-naphthyl)benzo[*b*]thiophene (3-(1-Naphthyl)B[*b*]T) **XI**, while the prevailing one was 2-(1-naphthyl)benzo[*b*]thiophene (2-(1-Naphthyl)B[*b*]T) **XII**. This was found after the independent synthesis of the pure standards via Suzuki cross-coupling with $Pd(PPh_3)_4$ catalyst according to the protocol recently described by Heynderickx et al. (2002). In brief, a solution of 2-thianaphtheneboronic acid (0.45 g; 2.5 mmol), Na_2CO_3 (0.53 g; 5.0 mmol) and 2-bromonaphthalene (0.47 g; 2.25 mmol) in dimethoxyethane/water (1:1, v/v; 9 mL) was refluxed under stirring for 3 h (or 24 h for coupling of 3-thianaphtheneboronic acid with 1-bromonaphthalene). After the usual work-up, pure 2-(2-Naphthyl)B[*b*]T **X** (Table 2; yield ~92%) was isolated. In addition, the procedure gave 2-(1-Naphthyl)B[*b*]T **XII** (Table 2; ~81%) and 3-(1-Naphthyl)B[*b*]T **XI** (Table 2; ~84%).

Separation and purification of the synthesized thiophene derivatives were performed using column chromatography (600 mm × 12 mm) on silica gel (Fluka, Silica gel 60, 70–230 mesh) with *n*-hexane or preparative TLC (Merck, silica gel) with *n*-hexane and crystallisation from solvents as indicated in Table 2. After re-crystallisation, the procedure yielded mostly compounds with purity > 95% (Table 2), although that of 2,3-DPh[*b*]T **III** was 92% (impurity 1-bromonaphthalene) and that of 3-PhB[*b*]T **I** ca. 90% (impurities ca. 3% 2-PhB[*b*]T, 90% biphenyldisulfide). Biphenyldisulfide was the most common impurity, in addition to traces of other *m*/*z* 260 isomers, whose abundances can be traced in Fig. 5. Identification of the synthesized thiophenes was carried out by comparison of melting points with those in the literature (Table 2). In the literature, NMR data are scarce. Heynderickx et al. (2002) reported the spectrum of 2,3-DPh[*b*]T **III**, which is identical to that of our synthetic standard (Table 2). Due to the lack of literature NMR data, our data on the synthesized thiophenes are reported in Table 2. As for compounds possessing three or more aromatic rings, the signals corresponding to the "aromatic" moieties in the NMR spectra are difficult to interpret. For most of the synthesized benzannulated aryl-substituted thiophenes reported here, structure confirmation on the basis of NMR is difficult. A set of multiplets in the spectra is not sufficiently informative to provide precise information on the aryl substitution pattern. Chemical shifts of H-2 and H-3 (singlets) for the thiophene ring are usually not different enough to allow the position of the aryl substituent to be determined with certainty, even if they are not superimposed on multiplet signals from other protons.

The synthesized arylated thiophenes were also characterised from their mass spectra (Fig. 2), which are discussed with respect to those available in databases (cf. references in Table 2). The spectra of 3-PhB[*b*]T **I** and 2-PhB[*b*]T **II** have been published (Porter, 1967). Both are characterised by an intense $M^{+\cdot}$ at *m*/*z* 210, accompanied by signals ions at $[M-1]^{+}$ and $[M-2]^{+\cdot}$ arising from dehydrogenation. Both eliminate $^{\cdot}$CHS [M−45] to give *m*/*z* 165, so phenyl migration is important. A fundamental difference between both isomers is the intensity of $[M-1]^{+}$ and $[M-2]^{+\cdot}$, which are more intense for 3-PhB[*b*]T **I**. The spectra of our synthesised compounds are identical to those of Porter (1967). The 2,3-DPhB[*b*]T **III** (Table 2) spectrum (Fig. 2a) has $M^{+\cdot}$ (base peak) at *m*/*z* 286, accompanied by weaker ions at $[M-1]^{+}$, $[M-2]^{+\cdot}$, $[M-3]^{+}$ and $[M-4]^{+\cdot}$. A relatively abundant $[M-2]^{+\cdot}$ arises from the molecular geometry, allowing cyclisation via dehydrogenation to a structure of the phenanthrobenzothiophene type (cf. Buquet et al., 1981). An abundant $[M-15]^{+}$ is at *m*/*z* 271. Loss of H_2S leads to a fragment $[M-34]^{+\cdot}$ at *m*/*z* 252, possibly cyclic in nature (Porter, 1985). The spectrum has quite a number of low intensity ions, notably at *m*/*z* 247, 239, 226, 213, 200, 189, 176, 163, 134 and 126. Doubly charged ions at 142/143 are relatively strong (Fig. 2).

In contrast to the spectrum of 3-PhN[1,2-*b*]T **IV** (Fig. 2b), that of 3-PhN[2,1-*b*]T **VI** has been described (Porter, 1985) and is the same as ours (Fig. 2c). Spectra of both our 3-phenyl isomers (Fig. 2b and c) show $M^{+\cdot}$ at *m*/*z* 260 (base peak) and $[M-1]^{+}$ and $[M-2]^{+\cdot}$ ions. The spectrum of 3-PhN[2,1-*b*]T **VI** (Fig. 2c) shows very intense $[M-1]^{+}$ and $[M-2]^{+\cdot}$ ions, presumably from a cyclic phenanthrobenzothiophene-type structure (Porter, 1985). $[M-15]^{+}$ at *m*/*z* 245 is abundant. $[M-32]^{+\cdot}$ at *m*/*z* 228 and $[M-34]^{+\cdot}$ at *m*/*z* 226 are from sulfur and H_2S expulsion, respectively. Elimination of $^{\cdot}$CHS [M−45] and $^{\cdot}CH_3S$ [M−47] gives ions at *m*/*z* 215 and 213, respectively and $[M-127]^{+}$ at *m*/*z* 139 reveals that phenyl migration is also important here. Doubly charged ions at *m*/*z* 129 and 130 are relatively strong (Fig. 2b and c).

The spectra of the 2-phenylnaphtho[*b*]thiophenes: 2-PhN[1,2-*b*]T **V** (Fig. 2d), 2-PhN[2,1-*b*]T **VII** (Fig. 2e) and 2-PhN[2,3-*b*]T **VIII** (Fig. 2f) are very similar. Fragmentation is like that of the 3-phenylnaphtho[*b*]thiophenes, though there are important differences in ion abundances. $M^{+\cdot}$ at *m*/*z* 260 strongly dominates (base peak). The lower abundance of $[M-1]^{+}$ relative to $[M-2]^{+\cdot}$ is a characteristic of the 2-phenylnaphtho[*b*]thiophene isomers (Fig. 2d–f). Ions at *m*/*z* 215/213 are also of lower abundance relative to the 3-isomers. Peaks from doubly charged ions are dominated by a relatively strong *m*/*z* 130 and weaker *m*/*z* 129 (Fig. 2d–f), the opposite of the 3-isomers. Comparison of the reference spectrum of 2-phenylnaphtho[2,1-*b*]thiophene (Table 2, Wiley ref. #200610) confirms the identity of our compound as **VII**. Unfortunately, the spectra of 2-PhN[1,2-*b*]T and 2-PhN[2,3-*b*]T are not available.

The spectra of 3-(2-Naphthyl)B[*b*]T **IX** (Fig. 2g) and 2-(2-Naphthyl)B[*b*]T **X** (Fig. 2h), 3-(1-Naph-

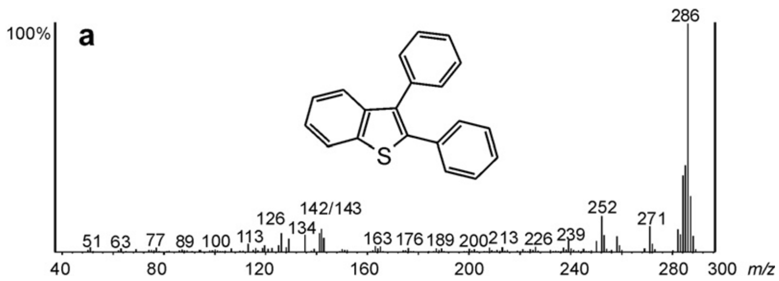


Fig. 2a. Mass spectra of synthesized arylated thiophene standards: (a) 2,3-diphenylbenzo[*b*]thiophene.

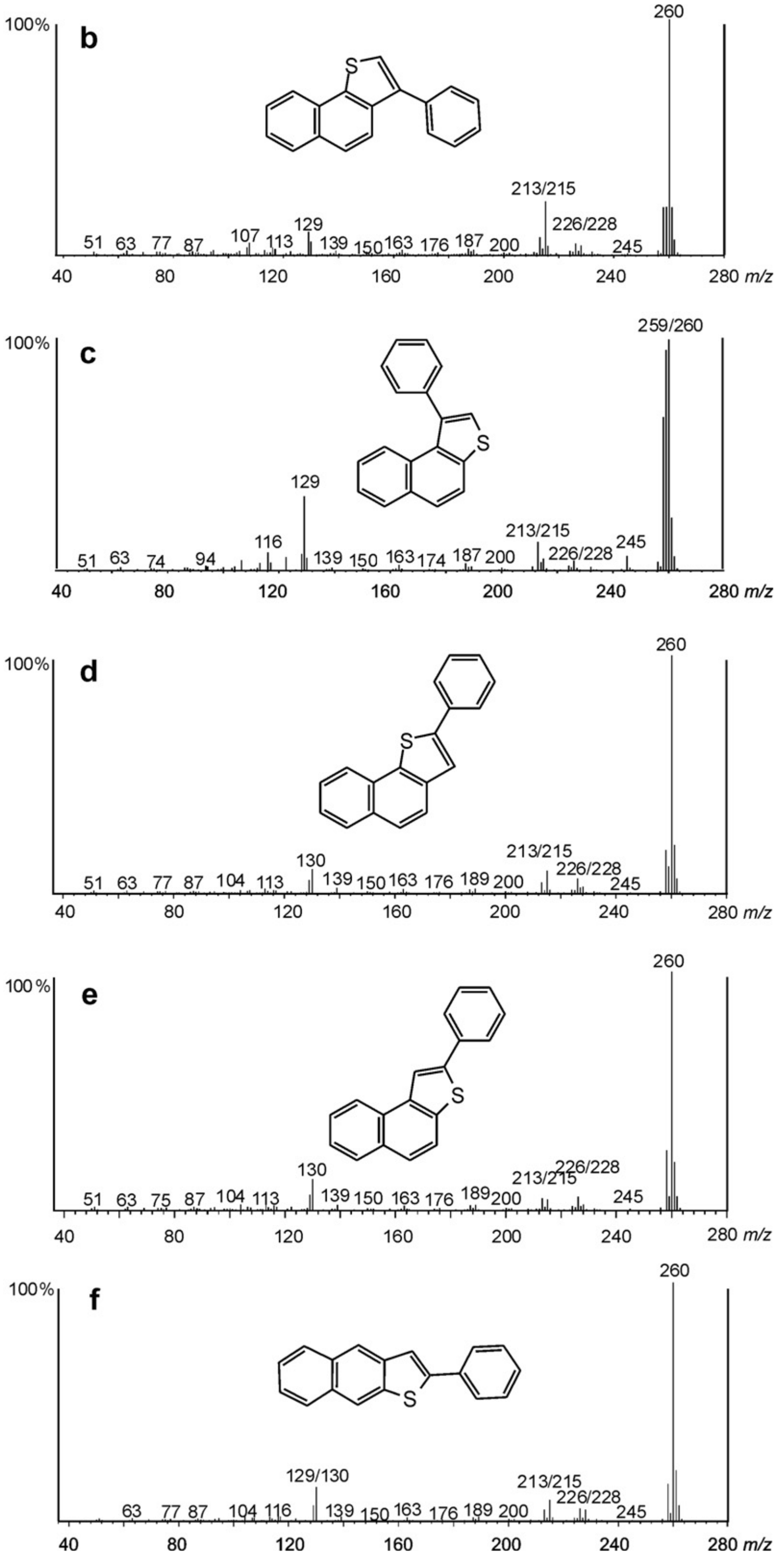


Fig. 2b–f. Mass spectra of synthesized arylated thiophene standards: (b) 3-phenylnaphtho[1,2-*b*]thiophene; (c) 3-phenylnaphtho[2,1-*b*]thiophene; (d) 2-phenylnaphtho[1,2-*b*]thiophene; (e) 2-phenylnaphtho[2,1-*b*]thiophene; (f) 2-phenylnaphtho[2,3-*b*]thiophene.

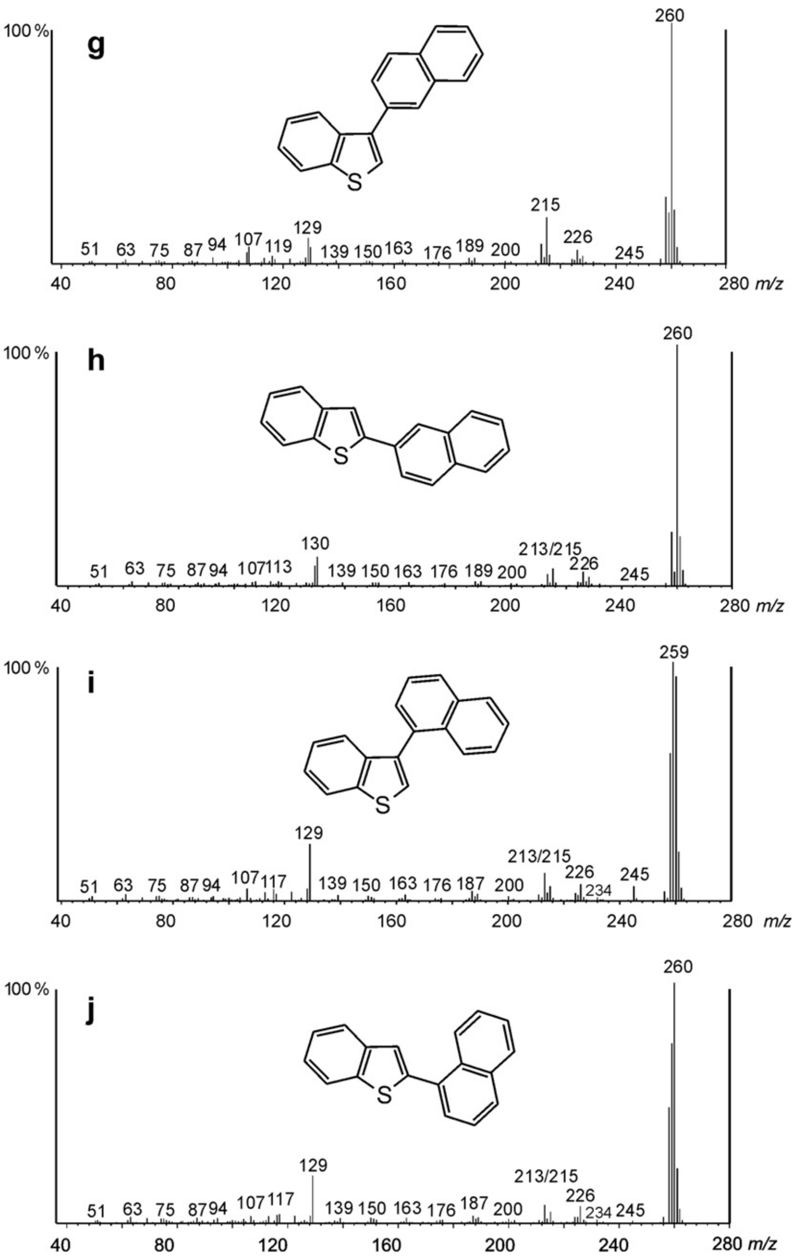


Fig. 2g–j. Mass spectra of synthesized arylated thiophene standards: (g) 3-(2-naphthyl)benzo[*b*]thiophene; (h) 2-(2-naphthyl)benzo[*b*]thiophene; (i) 3-(1-naphthyl)benzo[*b*]thiophene; (j) 2-(1-naphthyl)benzo[*b*]thiophene.

thyl)B[*b*]T **XI** (Fig. 2i) and 2-(1-Naphthyl)B[*b*]T **XII** (Fig. 2j) are generally similar to those of the phenylnaphtho[*b*]thiophenes (Fig. 2b–f), although that of 3-(1-Naphthyl)B[*b*]T **XI** (Fig. 2h) has base peak at *m*/*z* 259 (Fig. 2i). Significant differences lie in the intensities of the [M−1] and $[M-2]^{+\cdot}$ between (1-naphthyl)benzo[*b*]thiophene and (2-naphthyl)-benzo[*b*]thiophene isomers. These are intense for the former (Fig. 2i and j), but not the latter (Fig. 2g and h). In this respect, the spectra of (2-naphthyl)benzo[*b*]thiophenes are similar to the 2-phenylnaphtho[*b*]thiophenes (Fig. 2d–f). For both (2-naphthyl)benzo[*b*]thiophene spectra a characteristic gap in the molecular ion cluster is due to a lower abundance of $[M-1]^{+}$. Interestingly, 2-(2-Naphthyl)B[*b*]T **X** (Fig. 2h) shows the doubly charged ion of highest intensity at m/z 130, as opposed to m/z 129 for the other three isomers (Fig. 2g, i and j). In the case of 3-(2-Naphthyl)B[*b*]T **IX** (Fig. 2g) and to lesser extent of 3-(1-naphthyl)B[*b*]T **XI** (Fig. 2i) a slightly higher abundance of ions at m/z 215 and at m/z 213 (elimination of $^{\cdot}$CHS ($[M-45]^+$) and $^{\cdot}CH_3S$ ($[M-47]^+$)) is observed in relation to 2-benzo[*b*]thiophene isomers (Fig. 2g and i), which is explicable on structural grounds. In addition, all the naphthylbenzo[*b*]thiophenes have quite a number of non-characteristic fragment ions of low intensity at m/z 245, 234, 228/226, 215/213, 200, 189, 176, 163, 150, 139, etc. (Fig. 2g–j), as for the phenylnaphthylo[*b*]thiophenes (Fig. 2d–f). In summary, the spectra of all the synthesized naphthylbenzo[*b*]thiophenes show small but significant differences, enabling their differentiation.

2.6. Phenylation experiments

2.6.1. Free radical phenylation

Phenyl radicals were generated by reaction of aniline with pentyl nitrite (Spagnolo et al., 1972) in the presence of dibenzothiophene. Freshly distilled aniline (0.01 mol DBT equiv., 0.09 mL) and pentyl nitrite (0.1875 mL; Merck) were added to dibenzothiophene (0.001 mol, 184 mg; Fluka, $> 98\%$). Dibenzothiophene was first checked for any m/z 260 compounds. The reaction mixture was homogenised by dissolving it in a minimal volume of DCM in a glass ampoule. After solvent evaporation at room temperature, the ampoule was sealed and kept at 40 °C (48 h). The reaction products were extracted with benzene and dried. The residue was fractionated as described in Section 2.3 to give an aromatic fraction.

2.6.2. Ionic phenylation

The reaction procedure, related to the Scholl reaction, was adopted from Clark and McKinnon (1981). To dibenzothiophene (0.001 mol, ca. 184 mg; Fluka, 98%) in benzene (80 mL) or benzene/chlorobenzene (80 mL, 1:1, v/v) was added a 0.002 mol DBT equivalent of (ca. 268 mg) anhydrous $AlCl_3$ (Merck). The mixture was stirred and heated under reflux (4 h). An intense brown colour developed after addition of $AlCl_3$, which disappeared after addition of 20% ice cold HCl (100 mL), terminating the reaction. The organic fraction was isolated from the reaction mixture by repeated (3×) extraction with ethyl acetate and the extracts combined. The extract was washed with aqueous saturated NaCl, dried ($MgSO_4$) and fractionated (TLC) to give an aromatic fraction. The yield of coupling products, which, apart from phenyldibenzothiophenes, also contained the partly hydrogenated counterparts (m/z 262 and 264), was $< 3\%$ of the phenyldibenzothiophene isomers. An attempt to oxidise the reduced compounds to phenyldibenzothiophenes with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) according to Clark and McKinnon (1981) failed. The reaction products obtained using a mixture of chlorobenzene and benzene contained lower amounts of reduced phenyldibenzothiophenes and are discussed further in the text.

2.7. Maturation experiments

The phenyldibenzothiophene isomer mixture (25 mg) from the phenylation experiment at 40 °C (Section 2.6.1), was dissolved in DCM and absorbed on aluminium montmorillonite mixed with Cu powder (10:2; v/v). The mixture was sealed at atmospheric pressure in a glass ampoule, which was heated isothermally at 330 °C for one week. After cooling to room temperature, the crude mixture was extracted with DCM. The solvent was allowed to evaporate at room temperature to give a residue fractionated as described in Section 2.3. Analogous experiments were conducted with 3-PhN[2,1-*b*]T **VI** and 2-PhN[2,1-*b*]T **VII** at 200 °C (48 h).

2.8. Determination of relative abundance of arylated thiophenes

Due to the significant variation in MS fragmentation patterns within the series, especially between positional isomers with an aryl substituant at the second and third thiophenic carbon position of naphtho[*b*]thiophenes, correction factors were calculated by relating peak area of the standards in the TIC chromatograms to those from the m/z 260 chromatograms. For phenyldibenzothiophenes the factors are: 1-PhDBT 4.96; 4-PhDBT 3.00; 2-PhDBT 3.35; 3-PhDBT 2.95; for phenylnaphthothiophenes: 3-PhN[2,1-*b*]T 5.94; 3-PhN[1,2-*b*]T 3.40; 2-PhN[1,2-*b*]T 2.87; 2-PhN[2,1-*b*]T 2.80; 2-PhN[2,3-*b*]T 2.62 and for naphthylbenzo[*b*]thiophenes: 3-(1-Naphthyl)B[*b*]T 5.42; 2-(1-Naphthyl)B[*b*]T 4.28; 3-(2-Naphthyl)B[*b*]T 3.60; 2-(2-Naphthyl)B[*b*]T 2.89. Relative abundances of arylated thiophenes were calculated by multiplying the peak area in the m/z 260 chromatograms by the appropriate factor.

3. Results

3.1. Identification of novel arylated polycyclic aromatic thiophenes

3.1.1. Phenylbenzo[b]thiophenes and diphenylbenzo[b]thiophenes

The tentative identification of a single isomer of phenylbenzo[*b*]thiophene in Kupferschiefer samples (Püttmann et al., 1990) was of help in choosing a synthesis strategy for the standards. The mass spectrum of the phenylbenzo[*b*]thiophene isomer in our samples suggests it corresponds to 2-PhB[*b*]T **II**. $M^{+\cdot}$ (base peak) at *m*/*z* 210 is accompanied by relatively weak *m*/*z* 209 and 208 ions, in contrast to 3-PhB[*b*]T **I,** which shows more intense *m*/*z* 209 and 208 peaks (Porter, 1967). On this basis, 2-PhB[*b*]T **II** was synthesized first. Comparison of the synthetic standard with the naturally occurring phenylbenzo[*b*]thiophenes (Fig. 3) using three different capillary columns proved that 2-PhB[*b*]T **II** is the main isomer, with the others present in only trace amounts; 3-PhB[*b*]T **I** was also identified. It elutes before the main isomer and is accompanied by traces of two other isomers (Fig. 3). The phenylbenzo[*b*]thiophenes were separated only using more polar stationary phases (e.g., DB-17 ms). On apolar phases (e.g., HP-1 and HP-5 ms) co-elution occurs, though the 2- and 3-isomers are still well separated. Diphenylbenzo[*b*]thiophenes were detected in the *m*/*z* 286 chromatograms (Fig. 3b; DB-17 ms); 2,3-DPhB[*b*]T **III** was identified from GC co-elution with the synthetic standard on three different phases. It elutes first and has identical mass spectrum to that of the standard (Fig. 2a). At least

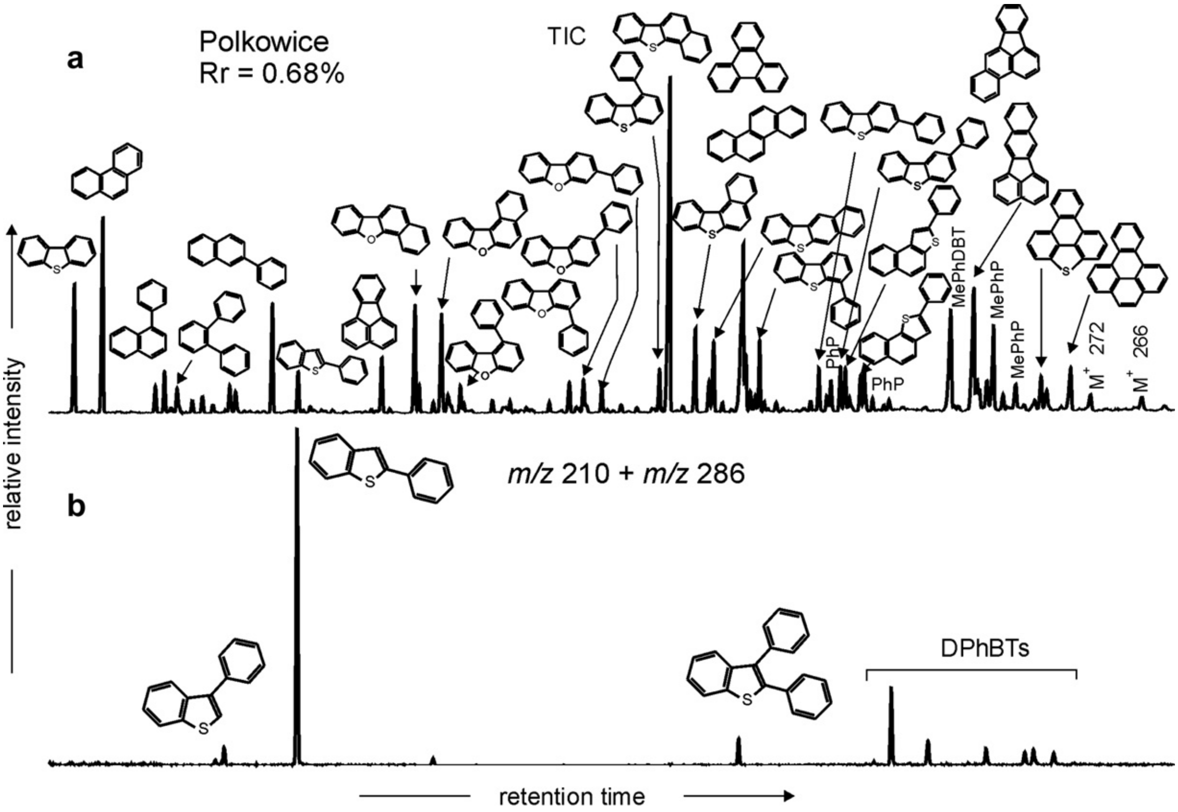


Fig. 3. Distribution of PACs in Polkowice samples, showing phenyl PACs derivatives as major constituents: (a) partial TIC (for structures see: Appendix), (b) the phenylbenzo[*b*]thiophene isomers are dominated by 2-phenylbenzo[*b*]thiophene (partial *m*/*z* 210 chromatogram) and 2,3-diphenylbenzo[*b*]thiophene is the first eluting diphenylbenzo[*b*]thiophene (DPhBT) isomer (partial *m*/*z* 286 chromatogram from DB-17 ms column). NB: the abundance of 3-phenylbenzo[*b*]thiophene is higher than displayed in the *m*/*z* 210 mass chromatogram due to different fragmentation patterns (Porter, 1967). PhP – phenylphenanthrenes; MePhDBT – methylphenyldibenzothiophene; MePhP – methylphenylphenanthrene.

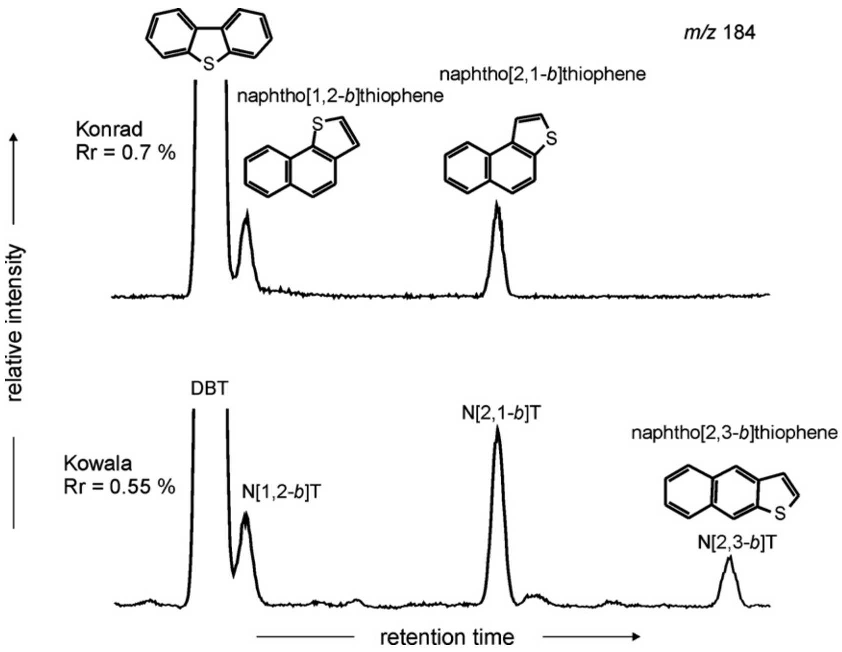


Fig. 4. Distribution of asymmetric structural isomers of dibenzothiophene: naphtho[1,2-*b*]thiophene, naphtho[2,1-*b*]thiophene and naphtho[2,3-*b*]thiophene in aromatic fractions of rock extracts as revealed by the partial *m*/*z* 184 chromatogram (DB-35 ms column).

six other isomers of diphenylbenzo[*b*]thiophenes were present (Fig. 3b).

3.1.2. Naphtho[b]thiophenes

DBT has three asymmetric structural isomers, which are naphtho[*b*]thiophenes (Appendix). Naphtho[*b*]thiophenes have only been reported in thermally treated petrochemicals like shale oil distillate (Andersson and Schmid, 1995) and pyrolysates of coal tar pitch (Meyer zu Reckendorf, 1997). This is perhaps due to co-elution problems on apolar stationary phases (Andersson and Schmid, 1995; Mössner et al., 1999), the most common columns for routine geochemical analysis. One isomer, naphtho[1,2-*b*]thiophene, co-elutes with DBT and the other, naphtho [2,1-*b*]thiophene, with phenanthrene. However, on more polar phases (e.g., the DB-35 ms or DB-17 ms used here), the problem can be overcome (Mössner et al., 1999). Use of a column with such a phase for our aromatic fractions resulted in detection of two additional DBT isomers and sporadically of a third in the *m*/*z* 184 chromatograms (Fig. 4), albeit in trace amounts. The spectra of naphtho[*b*]thiophenes and dibenzothiophene are very similar and so of little use for their differentiation (e.g., Meyerson and Fields, 1968). However, comparison of the retention times with those published by Mössner et al. (1999) reveals that the isomers are naphtho[1,2-*b*]thiophene, naphtho[2,1-*b*]thiophene and sometimes also naphtho[2,3-*b*]thiophene, respectively (Fig. 4). The naphtho[2,3-*b*]thiophene spectrum differs from the other two isomers in having a somewhat greater *m*/*z* 126 ($[M-58]^{+\cdot}$) intensity (Porter, 1985).

3.1.3. Phenylnaphtho[b]thiophenes

Interestingly, when these naphtho[*b*]thiophenes are present, the same samples often contain a series of unidentified compounds characterised by $M^{+\cdot}$ at *m*/*z* 260 (base peak; cf. Figs. 5 and 6). This unknown series co-occurs with the abundant PhDBTs with $M^{+\cdot}$ at *m*/*z* 260 identified recently (Marynowski et al., 2002). In some samples, the unidentified compounds are the major constituents in the *m*/*z* 260 chromatograms (Fig. 5, Kowala sample). Their spectra are very similar to each other and to those of PhDBTs, suggesting they may be derivatives of the $C_{18}H_{12}S$ PhDBT structural isomers. It has been suggested that they could be phenylnaphtho[*b*]thiophenes or naphthylbenzo[*b*]thiophenes (Marynowski et al., 2002), though their exact identification by synthesis of reference compounds was not possible due to the fact that each of three naphtho[*b*]thiophenes (Fig. 4) has eight possible positional phenylated isomers (24 in total) and benzo[*b*]thiophene has 12 naphthyl derivatives.

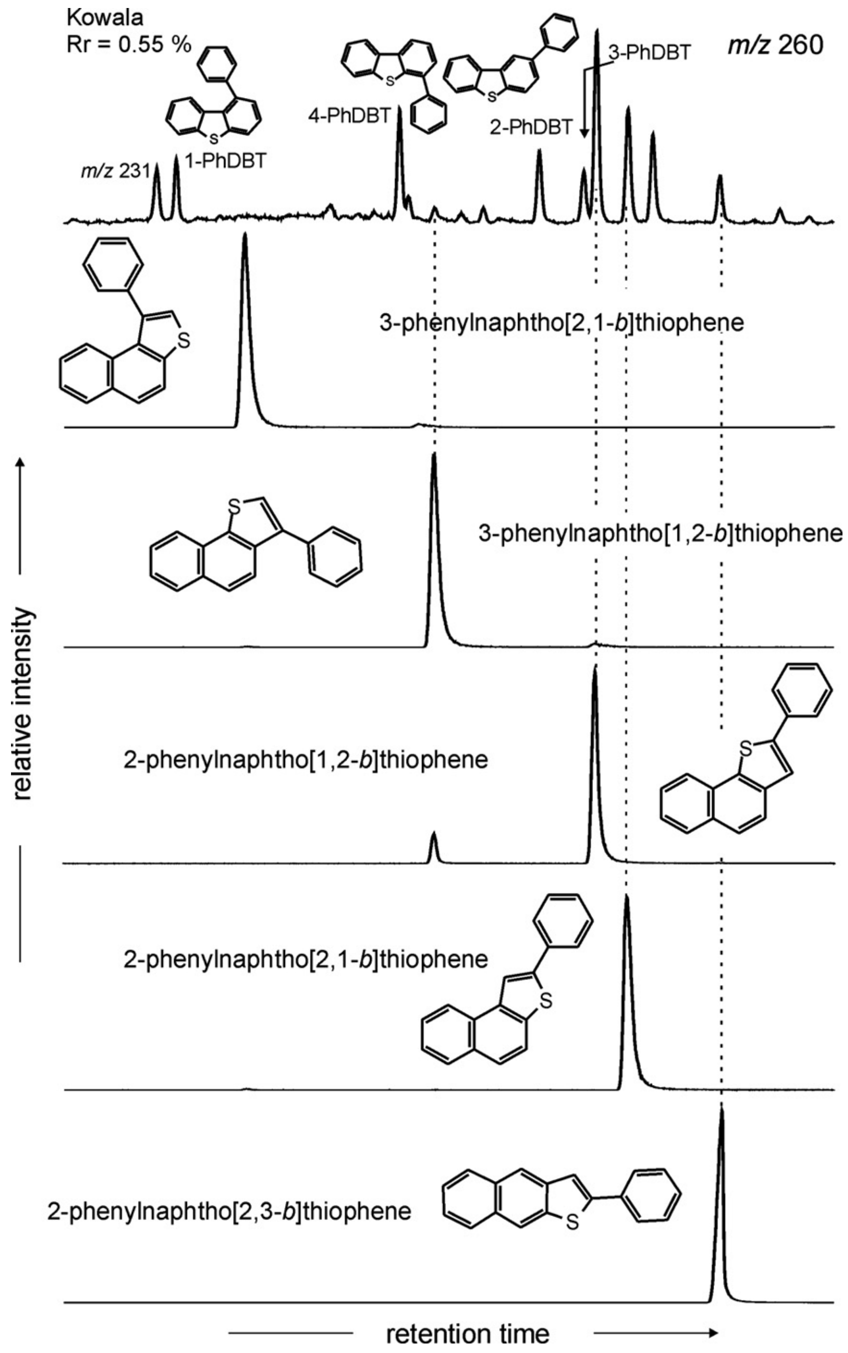


Fig. 5a. Partial *m*/*z* 260 chromatogram of the aromatic fraction from the Kowala sample and corresponding mass chromatograms of synthesized reference compounds: phenylnaphtho[*b*]thiophenes (DB-35 ms column).

2-Phenylnaphtho[b]thiophenes. Considering the presence in our samples of 2-PhB[*b*]T **II** as the dominant compound, with lower abundances of the other phenylbenzo[*b*]thiophenes (Fig. 3) and the suspected parent thiophenes i.e., naphtho[1,2-*b*]thiophene and naphtho[2,1-*b*]thiophene (Fig. 4) of the unidentified series, the most probable isomers, 2-PhN[1,2-*b*]T **V** and 2-PhN[2,1-*b*]T **VII**, were synthesized first. Comparison of the mass spectra and retention times of the standards via co-elution on

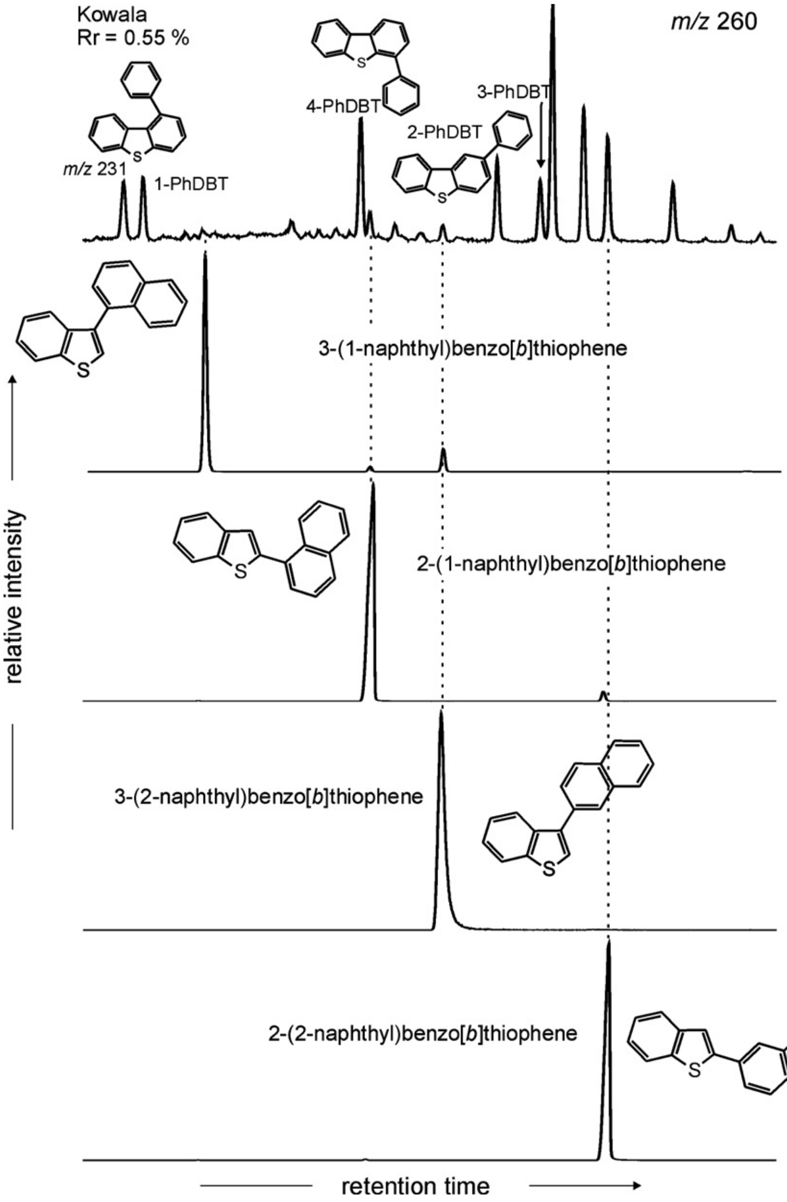


Fig. 5b. Partial *m*/*z* 260 chromatogram of the aromatic fraction from the Kowala sample and corresponding mass chromatograms of synthesized reference compounds: naphthylbenzo[*b*]thiophenes (DB-35 ms column).

three different phases with those of the components in the aromatic fractions revealed that 2-PhN[1,2-*b*]T **V** is the first eluting member of the unknown series (Fig. 5a). Usually, it is the major constituent of the unreported series (Fig. 5a, Kowala). In some aromatic fractions, the second eluting compound, identified as 2-PhN[2,1-*b*]T **VII**, is the most abundant compound (Fig. 6, Piskrzyn). Interestingly, the third compound of the series is 2-(2-Naphthyl)B[*b*]T **X** (see: Section 3.1.4). Finally, the presence of 2-PhN[2,3-*b*]T **VIII** as the fourth minor compound (Fig. 5, Kowala) is consistent with the fact that its parent thiophene is the least abundant among the naphtho[*b*]thiophenes (Fig. 4). This shows that, in natural samples, the quantitatively dominant compounds are arylated polyaromatic thiophenes substituted at the second carbon of the thiophenic ring.

3-Phenylnaphtho[b]thiophenes. In a limited number of samples, 3-phenylnaphtho[*b*]thiophenes were

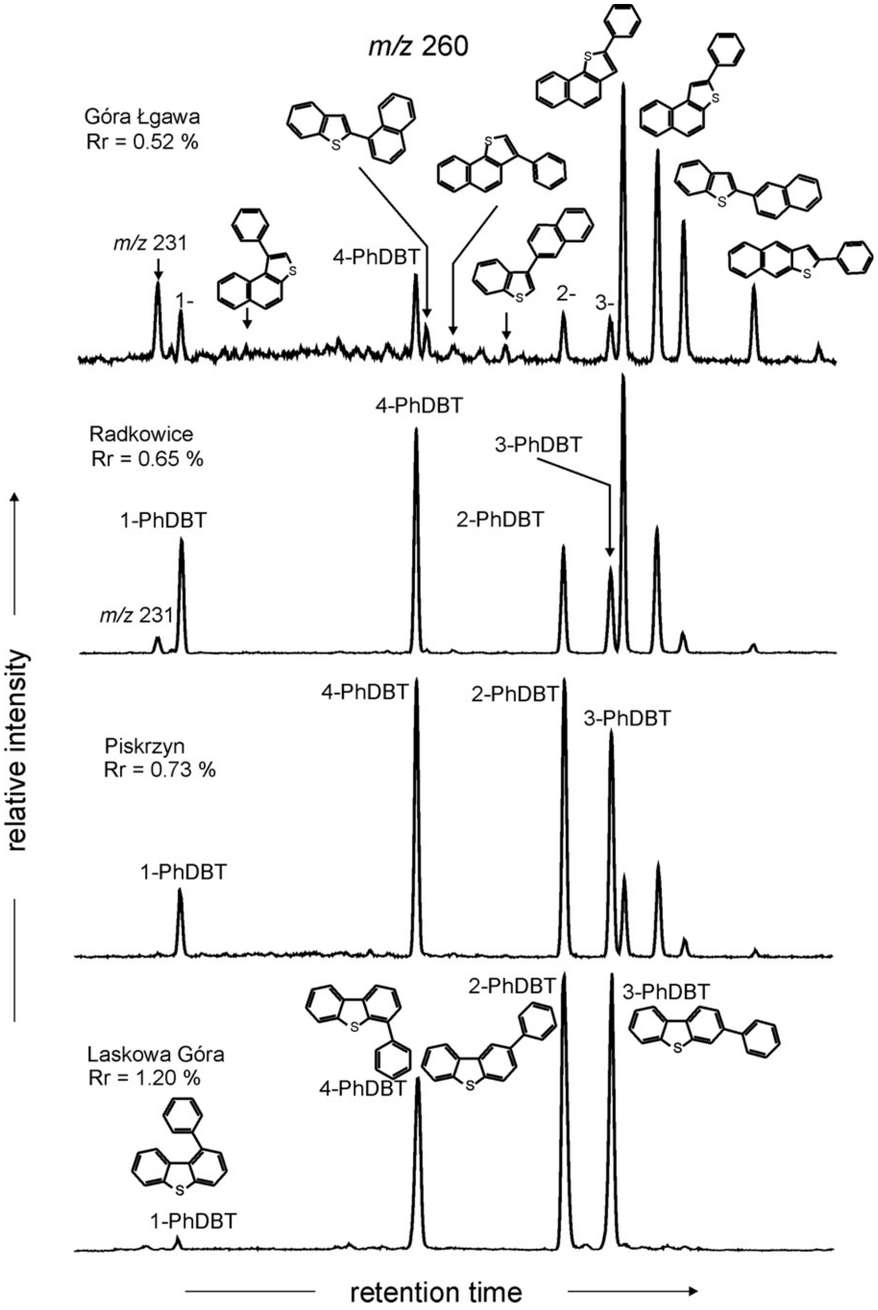


Fig. 6. Effect of increasing maturity on distribution of phenyldibenzothiophenes (PhDBTs) and novel series of phenylnaphtho[*b*]thiophenes and naphthylbenzo[*b*]thiophenes as revealed by the partial *m*/*z* 260 mass chromatograms (DB-35 ms column); *m*/*z* 231 denotes presence of triaromatic steroids.

also present. They were unambiguously identified as standards were synthesised due to detection of 3-PhB[*b*]T **I** as a minor component in the phenylbenzo[*b*]thiophenes mixture; 3-phenylnaphtho[2,3-*b*]thiophene was not synthesized. The two identified 3-phenylnaphtho[*b*]thiophenes elute before the series of 2-phenylnaphtho[*b*]thiophenes. The first eluting is 3-PhN[2,1-*b*]T **VI**, which elutes after 1-PhDBT (Fig. 5a), the isomer of which seems to be practically absent; 3-PhN[1,2-*b*]T **IV** elutes later and is present in noticeable amounts (Figs. 5a and 4). This shows that the elution sequence is reversed vs. the analogous 2-phenyl isomers. Isomers with the phenyl substituent located on the naphthalene rings are practically absent, as revealed by the presence of only very minor peaks in the m/z 260 chromatograms.

3.1.4. Naphthylbenzo[b]thiophenes

Four isomers with naphthyl substitution at the thiophenic ring are discussed in this section. The first eluting, 3-(1-Naphthyl)B[*b*]T **XI**, co-elutes with 3-PhN[2,1-*b*]T **VI** on DB-35 ms (Fig. 5b). However, the two are well separated on HP-5 ms with 3-(1-Naphthyl)B[*b*]T **XI** eluting first. The second isomer is 2-(1-Naphthyl)B[*b*]T **XII** eluting just after 4-PhDBT (Fig. 5b). The third is 3-(2-Naphthyl)B[*b*]T **IX** (Fig. 5b). The last-eluting two isomers are present in low abundance. It is worth noting, however, that the 3-substituted isomers have a fragmentation pattern producing $[M-1]^{+}$ and $[M-2]^{+\cdot}$ in higher relative abundance than $[M]^{+\cdot}$, lowering their apparent abundance in the m/z 260 chromatograms. The only major naphthylbenzo[*b*]thiophene, 2-(2-Naphthyl)B[*b*]T **X**, elutes as the third compound in the main cluster after PhDBTs, together with the 2-phenylnaphtho[*b*]thiophenes (Fig. 5b). It is common in the pyrolysates of coals (Lamberton and Paine, 1976), though is surprisingly missing from the pyrolysates of coal tar pitch, where all isomers of phenyldibenzothiophenes only are present (Meyer zu Reckendorf, 1997).

4. Discussion

4.1. Maturity control on arylated polycyclic aromatic thiophenes

The 3-phenylnaphtho[*b*]thiophenes were only detected in samples with low maturity ($R_r < 0.6$), i.e., at very beginning of the oil generation peak (0.5–1.3% R_r; e.g., Radke et al., 2000). They are present in low abundance, in addition to the prevailing 2-phenylnaphtho[*b*]thiophenes like 2-PhN[1,2-*b*]T **V**, 2-PhN[2,1-*b*]T **VII** and 2-PhN[2,3-*b*]T **VIII**, 2-(2-Naphthyl)B[*b*]T **X** and phenyldibenzothiophenes in the Kowala (R_r 0.55%; Fig. 5) and Góra Łgawa (R_r 0.52%; Fig. 6) samples. Exclusively, in these samples, naphthylbenzo[*b*]thiophenes, other than the common 2-(2-Naphthyl)B[*b*]T **X** were detected, albeit in small amounts (Fig. 6). These rare isomers are 3-(2-Naphthyl)B[*b*]T **IX** and 2-(1-Naphthyl)B[*b*]T **XII**.

At the oil generation threshold, concentrations of 2-phenylnaphtho[*b*]thiophenes – **V**, **VII** and **VIII**, together with 2-(2-Naphthyl)B[*b*]T **X** – reach similar concentration levels to phenyldibenzothiophenes, as exemplified by the Radkowice sample (R_r 0.65%; Fig. 6). With further maturity, as for the Piskrzyn sample (R_r 0.73%), the abundance of 2-phenylnaphtho[*b*]thiophenes, i.e., 2-PhN[1,2-*b*]T **V**, 2-PhN[2,1-*b*]T **VII** and 2-PhN[2,3-*b*]T **VIII**, together with 2-(2-Naphthyl)B[*b*]T **X** decreases significantly, while phenyldibenzothiophenes become dominant (Fig. 6). A similar distribution, with a predominance of 4-, 2-, and 3-phenyldibenzothiophenes and traces of 2-phenylnaphthyl[*b*]thiophenes, is observed for the Winterberg bitumen, revealing generation at the main onset of oil generation. Finally, all phenylnaphtho[*b*]thiophenes, together with 2-(2-Naphthyl)B[*b*]T **X**, disappear at 1.2% R_r (Laskowa Góra sample; Fig. 6), indicating rather low thermal stability for these compounds. At this maturity stage, 3- and 2-phenyldibenzothiophenes, with a substantial abundance of 4-PhDBT and very minor 1-PhDBT, comprise the whole m/z 260 chromatogram. High temperature hydrothermal oil from the rift zone of the Guaymas Basin, apparently generated at > 300 °C (Kawka and Simoneit, 1990), also contains the dominant 3-isomer, followed by 2- and 4-(ane traces of 1-)PhDBT (Marynowski et al., 2002).

The maturity dependent distribution of phenylnaphtho[*b*]thiophenes agrees well with the maturation experiments consisting of heating some of the synthesized phenylnaphtho[*b*]thiophenes at 200 °C for 48 h. Heating 3-PhN[2,1-*b*]T **VI** leads to formation of 2-PhN[2,1-*b*]T **VII**. This is in agreement with the known thermodynamic properties of 3-phenyl isomers, which tend to isomerise to 2-phenyl counterparts (e.g., Dann and Kokorudz, 1958). This can be interpreted as a result of a phenyl shift along the terminal thiophene double bond. In turn, prolonged heating of 2-PhN[2,1-*b*]T **VII** leads to complete disappearance and formation of dibenzothiophene and four phenyldibenzothiophenes. The phenyl group cannot be transferred to the naphthalene ring system, as concluded from the absence of other phenylnaphtho[*b*]thiophene isomers from the reaction mixture. Among the products, biphenyl, 2-PhB[*b*]T **II**, benzo[*b*]naphtho[*d*]thiophenes (for structure see Appendix) and benzo[*b*]naphtho[*d*]-furans were identified.

In contrast, PhDBTs reacted differently on prolonged heating. At temperatures when 2-PhN[2,1-*b*]T **VII** decomposes, a drastic change in the PhDBT isomer ratio is observed. After heating at 330 °C a mixture of all four PhDBT isomers was present (as obtained from free radical phenylation, Fig. 9b and Section 4.2.), 2- and 3-PhDBTs became dominant, 4-PhDBT was still present, but 1-PhDBT was hardly noticeable. Thus, the distribution obtained in the laboratory heating experiment is like that encountered in mature samples (e.g., Laskowa Góra and the hydrothermal oil from Guaymas Basin; Fig. 6; Marynowski et al., 2002). This can be interpreted as a result of preferential decomposition of the less stable isomers or of a 1,2-phenyl shift-type reaction leading to the thermodynamically more stable DBTs substituted at positions 2 and 3. This is in agreement with the 1,2-methyl shift widely used to rationalise changes in the distribution of alkyl polycyclic aromatic compounds with increasing maturity e.g., for methyldibenzothiophenes (Radke and Willsch, 1991, 1994; Radke et al., 2000 and references therein). Furthermore, cyclisation reactions of 1-phenyldibenzothiophene must be involved in lowering the abundance of this isomer, as revealed by the finding of triphenyleno[1,12-*bcd*]thiophene in both the artificial maturation products and the hydrothermal oil from the Guaymas Basin (Marynowski et al., 2002).

The maturity dependent behaviour of the *m*/*z* 260 arylated polycyclic aromatic thiophenes is shown best when plotting PhDBTs/($\sum$2-PhN[*b*]T + 2-(2-Naphthyl)B[*b*]T + PhDBTs) ratio vs. mean vitrinite reflectance R_r (Fig. 7). The best correlation is obtained via a logarithmic regression, due to the disappearance of phenylnaphtho[*b*]thiophenes and napththylbenzo[*b*]thiophenes with maturity, with a regression index $R^2 = 0.85$.

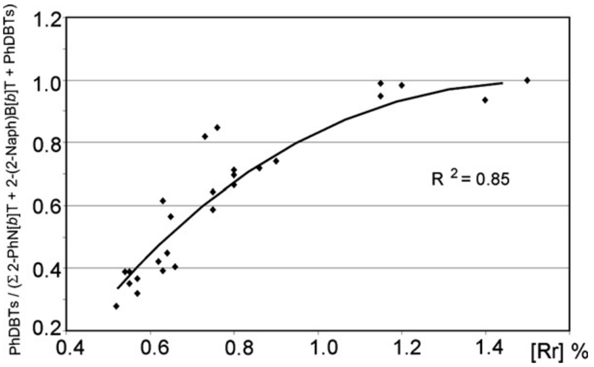


Fig. 7. Correlation between PhDBTs/($\sum$2-PhN[*b*]T + 2-(2-Naphthyl)B[*b*]T + PhDBTs) ratio and random vitrinite reflectance (R_r). Abundances of arylated *m*/*z* 260 polyaromatic thiophenes are corrected for differences between isomers in MS fragmentation patterns.

4.2. Formation of arylated polycyclic aromatic thiophenes

Polycyclic aromatic compounds (PACs) represent a group of compounds with wide structural diversity. Given this, they and their alkyl derivatives are applied as biomarkers (e.g., Blumer, 1962; Radke et al., 2000; Otto and Simoneit, 1999), molecular maturity indicators (Radke and Willsch, 1991, 1994; Radke et al., 2000 and references therein) and markers of ancient wildfires (Jiang et al., 1998; Venkatesan and Dahl, 1989; Killops and Massoud, 1992). While oils and source rocks contain predominantly alkylated PACs like alkyl naphthalenes and alkyl phenanthrenes, combustion products typically contain specific unsubstituted PACs (Jiang et al., 1998; Venkatesan and Dahl, 1989; Killops and Massoud, 1992), often comprising pericondensed or five membered fused rings like, e.g., coronene, benzo[*ghi*]perylene, fluoranthene, benzofluoranthenes, benzo[*e*]pyrene, benzo[*a*]pyrene and benzo[*a*]anthracene (for structures see Appendix). Some of these are present in the aromatic fractions (Fig. 3). However, the fractions contain a number of specific arylated PACs, which are pyrolysis products of coal tar pitch PACs, the pyrolysis process itself also forming a benzene and naphthalene enriched atmosphere (Meyer zu Reckendorf, 1997, 2000). Among the arylated PACs encountered, derivatives of benzo[*b*]thiophene, naphthalene, dibenzofuran, dibenzothiophene, phenanthrene and benzo[*b*]naphtho[*d*]thiophenes are quantitatively the most important compounds (Fig. 3). Furthermore, compounds like biphenyls, terphenyls and quarterphenyls, which can be considered as arylated benzenes, are abundant. This group can be further extended to arylated benzo[*b*]thiophenes, including 3-PhB[*b*]T **I** and 2-PhB[*b*]T **II** (Fig. 3a), eight diphenylbenzo[*b*]thiophenes with the firmly identified 2,3-DPh[*b*]T **III** (Fig. 3) and at least three naphthylbenzo[*b*]thiophenes with prevailing 2-(2-Naphthyl)B[*b*]T **X** (Fig. 5b). The family of arylated naphthalenes identified comprises both isomers of phenylnaphthalene and three binaphthyls (Marynowski et al., 2001). Recently identified arylated dibenzofurans and dibenzothiophenes are represented by all four possible phenylated positional isomers (Marynowski et al., 2002; Rospondek and Marynowski, 2004). Furthermore, diphenyldibenzothiophenes are present, though in lower concentration.

An early diagenetic, low temperature mechanism for the formation of many thiophenes, involving intramolecular incorporation of reduced sulfur species into biogenic lipids and subsequent cyclisation (e.g., Sinninghe Damsté et al., 1987) is commonly invoked. The reaction is formally an oxidation. In our samples, such a process of incorporation into the most common linear precursors (Rospondek et al., 1994) was initially considered for producing the distributions of arylated PACs encountered, such a hypothesis having been briefly discussed with regard to the formation of polyphenyls from polysaccharides (Marynowski et al., 2001) and phenyldibenzothiophenes from any linear precursors (Marynowski et al., 2002). In the case of the studied arylated thiophenes, such a process would lead exclusively to the formation of 1-phenyldibenzothiophene and 2-phenylnaphtho[*b*]thiophene isomers, though most likely with an extra and unique dialkyl substitution pattern. However, such compounds were not observed. For example, taking into consideration the distribution of phenyldibenzothiophenes, the following scenario can be predicted: Incorporation of reduced sulfur species into linear precursor molecules and subsequent cyclisation/aromatisation is capable of yielding exclusively 1,9-dialkylphenyldibenzothiophenes (Fig. 8), as proposed by Sinninghe Damsté et al. (1987), further cyclisation/aromatisation leading to 1-(2-alkylphenyl)-9-alkyldibenzothiophene (Fig. 8). Such possible intermediates, i.e., 1-alkyldibenzothiophenes, have been described by van Aarssen et al. (2001), but are not present in any of our or similar samples (Rospondek et al., 1994). Subsequent oxidation or β-cleavage (relatively to the aromatic moiety) of the alkyl side chains of 1-(2-alkylphenyl)-9-alkyldibenzothiophene could lead to 1-(2-methylphenyl)-9-methyldibenzothiophene (Fig. 8), whose oxidation could give 9-(2-carboxyphenyl)dibenzothiophene-1-carboxylic acid, which with subsequent oxidative decarboxylation could lead to 1-phenyldibenzothiophene. With increasing maturity, the

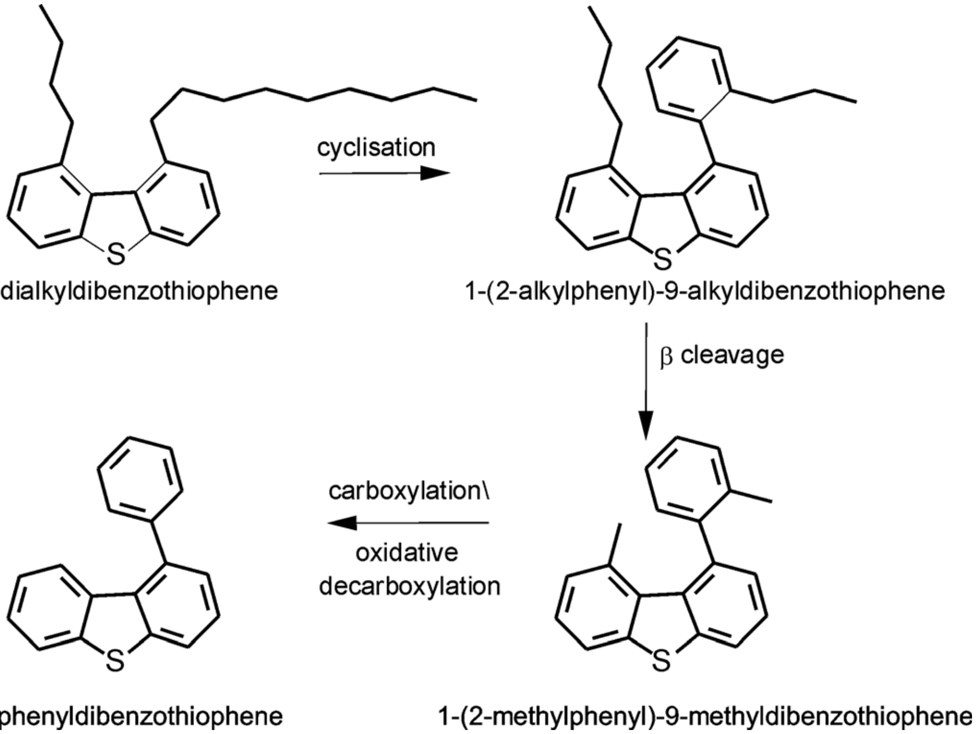


Fig. 8. Hypothetical scheme of diagenetic reactions leading from 1,9-dialkylphenyldibenzothiophene to 1-phenyldibenzothiophene, the dibenzothiophene derivative possessing a linear carbon skeleton.

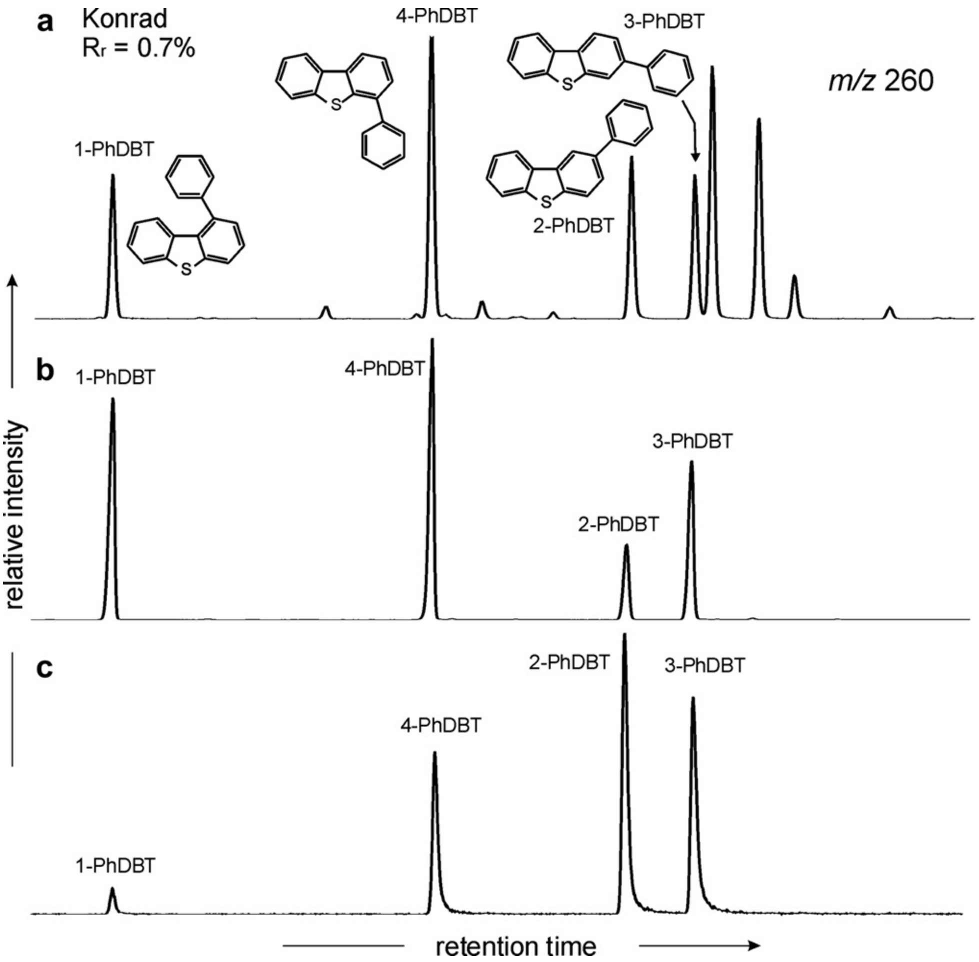


Fig. 9. Comparison of phenyldibenzothiophene distribution resulting from natural and laboratory experimental processes. (a) Konrad sample (R_r 0.7%); (b) free radical phenylation of dibenzothiophene; (c) ionic phenylation of dibenzothiophene.

formation of 2- and 3-phenyldibenzothiophene from the 1-substituted isomer by a 1,2-phenyl shift is, assuming low activation energy, thermodynamically favoured due to lowering of the free enthalpy, whereas formation of the 4-substituted isomer is not. The 4-phenyldibenzothiophene is as abundant as the 1-substituted isomer in our samples, even in those of low maturity (Figs. 5 and 6).

The presence of all possible phenylbenzo[*b*]thiophene positional isomers in relatively early mature samples (Figs. 5 and 6) decreases the credibility of the reduced sulfur incorporation/cyclisation/aromatisation hypothesis in the case of our hydrothermally oxidised samples. Similarly, cyclisation/aromatisation reactions are not able to explain the presence of all possible positional isomers of other PACs like those shown in Fig. 3. A great diversity of phenyl thiophenes and other PAC isomers is possibly more consistent with a low regioselective mechanism involved in their formation, i.e., reaction of parent aromatic compounds with very reactive species like phenyl radicals or benzene cation. It has been noted that the concentration of the alkylated PACs decreases towards oxidised zones, while that of unsubstituted PACs increases (Püttmann et al., 1988), independent of the location of the oxidised zone. Oxidative dealkylation of alkylated PACs could be a mechanism for producing unsubstituted PACs (Püttmann et al., 1988; Bechtel et al., 2001). The latter could then be available for reaction with benzene and naphthalene species, whose origin is likely related to oxidising hydrothermal solutions often containing abundant benzene, which is relatively soluble in water (McCollom et al., 2001). The phenylated PAC derivatives dominate the naphthylated ones due to the ubiquitous occurrence of benzene in such hydrothermal systems.

In order to further test the relevance of a mechanism promoting introduction of aryl groups into unsubstituted PACs in natural systems, experimental low temperature free radical phenylation and electrophilic substitution of dibenzothiophene were undertaken. The phenyldibenzothiophenes resulting from the free radical phenylation experiment have a very similar distribution to those in the geochemical samples (Fig. 9). The 1- and 4-substituted isomers dominate, while the 2- and 3-substituted isomers are less abundant. This distribution differs from that obtained from the ionic phenyldibenzothiophene reaction (Fig. 9), for which the 2-substituted isomer dominates over almost equally abundant 3- and 4-substituted isomers and very minor 1-phenyldibenzothiophene (Fig. 9c). In this experiment, other important products formed are biphenyl and terphenyls. Ionic phenylation, carried out under reducing conditions, also yields partly hydrogenated products of phenylated dibenzothiophenes. Additionally, methyldibenzothiophenes were also formed, which are practically absent from the oxidised samples investigated. At this point, it is tempting to suggest that the described aryl thiophene derivatives are generated by a free radical reaction under geochemical conditions, although the mechanism producing phenyl radicals remains unclear. The co-occurrence of hematite/goethite formed by oxidation of sedimentary framboidal pyrite (Oszczepalski, 1989; Sawłowicz et al., 2000) and an extraordinary enrichment in phenylated polycyclic aromatics, including diverse phenylthiophenes (Fig. 3), is of particular importance in the samples from so-called Rote Fäule facies. These samples, in addition to the arylated compounds, are also characterised by very low amounts of aliphatic fractions consisting only of short chain alkanes indicative of hydrolytic hydrocarbon disproportionation reactions (Püttmann et al., 1988, 1990).

Interestingly, the hypothetical involvement of free radical reactions is capable of explaining the presence in the samples of some polycyclic aromatic thiophenes having the thiophene ring at the terminal position, like naphtho[1,2-*b*]thiophene, naphtho[2, 1-*b*]thiophene and naphtho[2,3-*b*]thiophene (Fig. 4), which are rare in other geological samples. In contrast, they are frequently present among pyrolysis products of coal-related products and petrochemicals (Andersson and Schmid, 1995; Meyer zu Reckendorf, 1997). These thiophenes may originate from an *ipso*-hydrogen radical addition to the polycyclic aromatic thiophenes having the thiophene ring at an inner position of the molecule, followed by the elimination–decomposition reaction tentatively proposed by Dartiguelongue et al. (2006) for benzo[*b*]thiophene generation from dibenzothiophene. Their low abundance in the samples may be due to the oxidative reaction conditions, which must have drastically limited the amount of hydrogen radicals. If present, *ipso*-hydrogen radical addition to benzo[*b*]naphtho[2,1-*d*]thiophene (the first eluting isomer in Fig. 3) and subsequent elimination–decomposition of the benzene ring would lead to the formation of naphtho[1,2-*b*]thiophene (the first eluting compound in Fig. 4). Interestingly, all three naphtho[*b*]thiophene abundances (Fig. 4) are usually proportional to the abundances of the corresponding presumed substrates, which are three benzo[*b*]naphtho[*c*]thiophenes (Fig. 3). Thus, naphtho[2,3-*b*]thiophene (Fig. 4), originating from the least abundant benzo[*b*]naphtho[2,3-*d*]thiophene, is always present in subordinate amount. An interesting extension of the *ipso*-radical addition hypothesis is *ipso*-phenyl radical addition to the benzo[*b*]naphtho[*d*]thiophenes. This may lead directly to the 2-phenyl derivatives of the parent molecules by decomposition–elimination of remnants of the benzene ring. For example, *ipso*-phenyl radical addition to benzo[*b*]naphtho[2,1-*d*]thiophene would lead directly to the formation of the newly identified 2-PhN[1,2-*b*]T **V** in the samples.

5. Conclusions

Three isomeric naphtho[*b*]thiophenes, the asymmetrical isomers of dibenzothiophene, occur in specific sedimentary rock samples. If traces of naphtho[*b*]thiophenes are present, the same samples often contain their phenylated derivatives, phenylnaphtho[*b*]thiophenes, not reported previously for geological samples. Phenylnaphtho[*b*]thiophenes are accompanied by their structural isomers, phenyldibenzothiophenes. Both groups are accompanied by yet other structural isomers i.e., naphthylbenzo[*b*]thiophenes. All these isomeric $C_{18}H_{12}S$ arylated polycyclic thiophenes have been identified using synthesized standards.

The presence of all these arylated thiophenes can be traced only in samples of relatively low maturity, i.e., at the onset of the oil generation window. Three 2-phenylnaphtho[*b*]thiophenes, together with 2-(2-naphthyl)benzo[*b*]thiophene, dominate the whole series, followed by four phenyldibenzothiophenes and minor amounts of 3-phenylnaphtho[*b*]thiophenes, 2-(1-naphthyl)benzo[*b*]thiophene and 3-(2-naphthyl)benzo[*b*]thiophene. The mass spectra of the predominant compounds show little fragmentation, consisting predominantly of the molecular ion as base peak. This differs from the 3-isomers, which show a greater tendency to fragment. Indirectly, this fits with the lower stability of 3-phenylbenzo[*b*]thiophenes and 3-phenylnaphtho[*b*]thiophenes in nature, resulting in an easy phenyl shift along the thiophenic double bond, isomerisation presumably proceeding by acid clay mineral catalysis. Within the oil generation window, 3-phenylnaphtho[*b*]thiophenes are transformed to 2-phenylnaphtho[*b*]thiophenes and the whole isomeric series becomes dominated by phenyldibenzothiophenes, as evidenced by our study of rocks varying in maturity and laboratory maturation experiments. Of all the isomeric compounds, only 4-, 2- and 3-phenyldibenzothiophenes persist at high temperature, as in the case of hydrothermal systems above 300 °C. Such a thermodynamically controlled distribution of phenyldibenzothiophenes is reached at about 1.2% R_r. Consequently, the distributions of the novel arylated thiophenes are maturity controlled, so the variation in the ratio between the sum of all phenyldibenzothiophenes and 2-phenylnaphtho[*b*]thiophene plus 2-(2-naphthyl)benzo[*b*]thiophene is potentially applicable as a molecular maturity indicator.

Some of the novel arylated polycyclic thiophenes can be considered as intermediate compounds, which can be further transformed into pericyclic aromatic thiophenes, as exemplified by cyclisation of 1-phenyldibenzothiophene, leading to the triphenyleno[1,12-*bcd*]thiophene found in the most mature samples.

These arylated polycyclic thiophenes occur exclusively in oxidised marine sedimentary rocks having in common a hydrothermal oxidation event. Such an oxidative diagenetic process could favour dehydrogenation/cyclisation reactions. A process involving free radical phenylation of parent PAC molecules is considered likely for explaining the formation of these novel arylated thiophenes, based on laboratory simulation experiments. Naphtho[*b*]thiophenes could arise from *ipso*-hydrogen radical addition to the common benzo[*b*]naphtho[*d*]thiophenes and subsequent benzene ring decomposition–elimination. Alternatively, 2-phenylnaphtho[*b*]thiophenes could arise directly from *ipso*-phenyl radical addition to benzo[*b*]naphtho[*d*]thiophenes. The composition of the polyaromatic thiophenes and their arylated derivatives in the hydrothermally oxidised samples resembles that of pyrolysis products obtained from benzo[*b*]thiophene and dibenzothiophene at high temperature, involving free radical reactions, as described by Dartiguelongue et al. (2006) and Winkler et al. (2002), though there are differences in the isomer distributions of the arylated compounds.

Further analytical studies of geological samples and laboratory experiments are necessary for determining the mechanisms involved in the genesis of these novel arylated thiophenes in hydrothermally oxidised sedimentary rocks.

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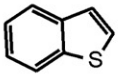
Appendix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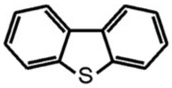
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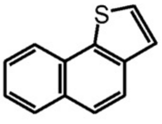
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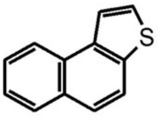
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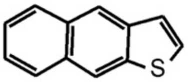
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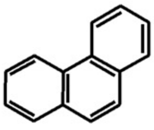
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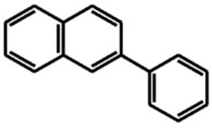
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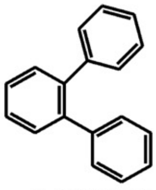
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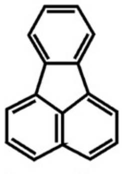
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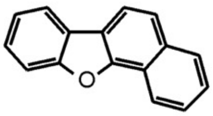
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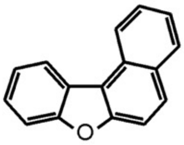
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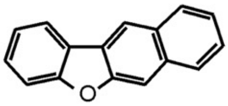
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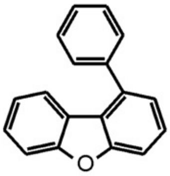
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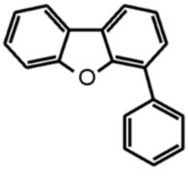
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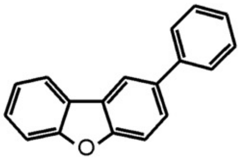
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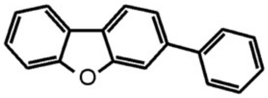
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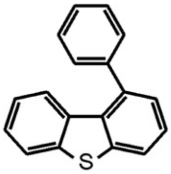
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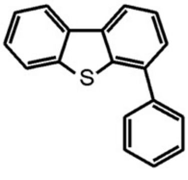
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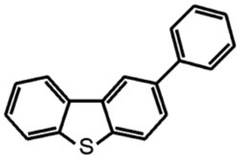
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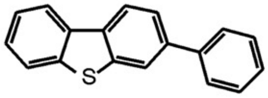
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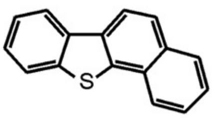
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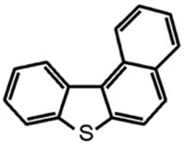
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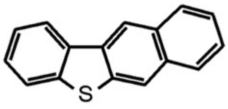
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Appendix (*continued*)

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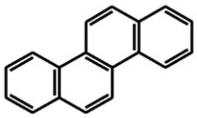

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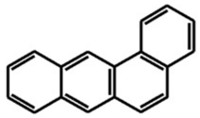

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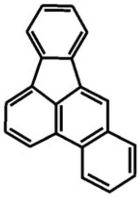

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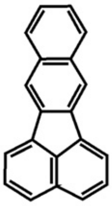

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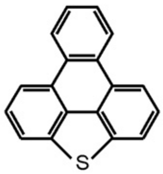

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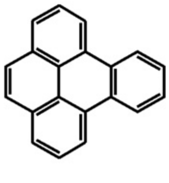

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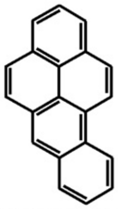

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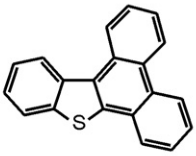

phenanthro[9,10-*d*]benzo[*b*]thiophene

benzo[*ghi*]perylene

coronene

Associate Editor—**P. Schaeffer**

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