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The occurrence and distribution of phenylnaphthalenes, terphenyls and quaterphenyls in selected lacustrine shales and related oils in China

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ABSTRACT

Phenylnaphthalenes (PhNs), terphenyls (TrPs), quaterphenyls (QtPs) and triphenylbenzenes were identified by the use of authentic standards in GC–MS analysis. Phenyl derivatives of fused ring polycyclic aromatic hydrocarbons (PhPAHs) and polyphenyls (PPhs) were observed in selected lacustrine shales and related oils from the Tarim, Liaohe and Bebuwan Basins in China. All isomers of phenylnaphthalene and terphenyl were observed in these oils. The more stable 2-PhN and *m*-Trp, *p*-TrP isomers are predominant among phenylnaphthalenes and terphenyls, respectively. The effect of maturity on the distribution patterns of phenylnaphthalenes and terphenyls in a set of lacustrine shales from the Liaohe Basin, East China was investigated. The depth trends of three currently used maturity indicators were investigated. Analysis was based on the relative abundance of phenylnaphthalene and terphenyl isomers, namely PhNR (2-PhN/1-PhN), TrP1 (*p*-TrP/*o*-TrP) and TrP2 ((*m*-TrP+*p*-TrP)/*o*-TrP) in lacustrine shales from well S202 in the Liaohe Basin, East China. The indicators increase slightly with relatively great deviations within low to intermediate maturation stages and then increase abruptly in high maturity stages. Therefore, they are not suitable maturity indicators for lacustrine source rocks in this study. An alternative thermal maturity indicator, defined as *p*-TrP/*m*-TrP was proposed. It exhibits a uniform increase with increasing maturity and is probably a more suitable indicator for use in maturity assessment in lacustrine source rocks and related oils. This study broadens the current understanding of the occurrence and distribution of PhPAHs and PPhs in sedimentary organic matter of various origins.

1. Introduction

Phenyl substituted (arylated) fused ring polycyclic aromatic hydrocarbons (PhPAHs), polyphenyls (PPhs) and their heterocyclic counterparts are important components in crude oils and sedimentary rock extracts (e.g. Püttmann et al., 1990; Marynowski et al., 2001, 2002; Rospondek et al., 2007, 2008). However, the occurrence and distribution of such phenyl derivatives and their application in organic geochemistry has received less attention than that of their alkylated analogues (e.g. Grafka et al., 2015).

1.1. The occurrence of phenyl polycyclic aromatic compounds

Biphenyl and alkylbiphenyls occur ubiquitously in comparable concentrations in ancient sedimentary rocks and oils (White and Lee, 1980; Alexander et al., 1986; Radke, 1987; Trolio et al., 1999). Phenylnaphthalenes, terphenyls and quaterphenyls have been detected in aromatic fractions of sedimentary rock extracts and oils (e.g. Püttmann et al., 1990; Marynowski et al., 2001). A series of m/z 254 compounds including phenylphenanthrenes, phenylanthracenes and binaphthyls have also been detected in aromatic fractions of sedimentary rock extracts (Rospondek et al., 2009; Li et al., 2012). Some of phenylphenanthrene isomers are products of fossil fuel combustion and were identified in deposited dust samples (Marynowski et al., 2004). In addition, some phenyl substituted heterocyclic aromatic compounds, such as phenyldibenzothiophene and phenyldibenzofuran positional isomers and phenylnaphtho[*b*]thiophenes have been identified in ancient sedimentary organic matter (Marynowski et al., 2002; Rospondek et al., 2007, 2008).

Phenylnaphthalenes (PhNs), i.e. 2-PhN and 1-PhN (Fig. 1, compounds **I** and **II**) have been found in Permian rock extracts (Püttmann et al., 1990) and in an organic-rich Permian marl (Sephton et al., 1999). PhNs are also widely present in bituminous coal extracts (White and Lee, 1980). The occurrence of terphenyls in high volatility bituminous coal has been reported by Bartle et al. (1975). Three terphenyl isomers, *o*-TrP, *m*-TrP and *p*-TrP

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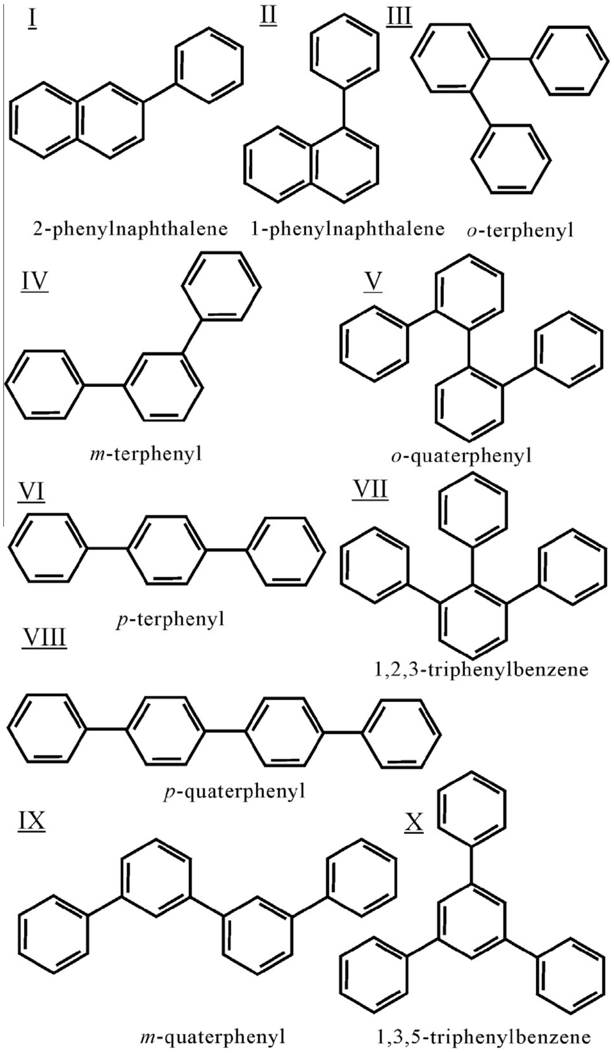

Fig. 1. Structures of phenylnaphthalene, terphenyl, quaterphenyl and their isomers discussed in the text.

(Fig. 1, compounds **III**, **IV** and **VI**), were detected in coals (Radke et al., 1982; Chaffee et al., 1986; Willsch and Radke, 1995) and marine sedimentary rocks (Marynowski et al., 2001). The chromatographic behavior of two phenylnaphthalene isomers and three terphenyl isomers has been determined by co-elution of authentic standards (Marynowski et al., 2001).

However, the occurrence and distribution of phenylnaphthalenes and terphenyls in rock extracts from lacustrine depositional environments has not yet been reported.

1.2. The origin of phenyl polycyclic aromatic compounds

Diagenetic/catagenetic oxidation of sedimentary organic matter at the redox interface in buried sedimentary rocks is a major source of phenyl PACs (policyclic aromatic compounds) in the geosphere (e.g., Marynowski et al., 2002; Rospondek et al., 2007, 2009). It has been proposed that free radical phenylation of phenanthrene and anthracene moieties would account for the distribution of phenylphenanthrenes and phenylanthracenes in oxidized rock samples (Rospondek et al., 2009). It has also been proposed that the formation of *o*-TrP involves reductive elimination of oxygen and sulfur in furan and thiophene products (Marynowski et al., 2001).

Incomplete combustion can produce phenyl polycyclic aromatic compounds in industrial processes (e.g. Meyer zu Reckendorf, 1997, 2000; Ricking et al., 2003; Wang et al., 2007). For example, 9-phenylphenanthrene has been found in volatiles formed during pyrolytic carbonization of coal tar pitches (Meyer zu Reckendorf, 1997). The consecutive reaction of free radical phenyl with unsubstituted PACs in the gaseous phase during combustion may generate phenyl substituted PACs (Meyer zu Reckendorf, 1997, 2000). Shock wave synthesis of PAHs from benzene, which resembles a pyrolytic reaction of benzene at high temperatures, produced higher-molecular weight PAHs, including PhPAHs and some PPhs (Mimura, 1995). Peri-condensed aromatic compounds can be formed by dehydrocyclization processes from phenyl- and naphthyl-PAC precursors (Grafka et al., 2015).

Quaterphenyls (QtPs) have been detected in waste products and polymers following combustion (Hawley-Fedder et al., 1984). Some quaterphenyls (e.g. 1,3,5-triphenylbenzene) have been detected in $PM_{2.5}$ particles from an e-waste dismantling area in Taizhou China (Gu et al., 2010) and in heavy products from coal and petroleum (Zhang et al., 2007). The occurrence of quaterphenyls in Paleozoic marine-derived sedimentary rocks has been described (Marynowski et al., 2001). The formation of triphenylbenzenes from burning of plastic was reported by Simoneit et al. (2005). Gorka et al. (2014) detected triphenylbenzenes in the atmosphere. However, the occurrence of quaterphenyls and triphenylbenzenes in lacustrine sedimentary rocks has not been reported.

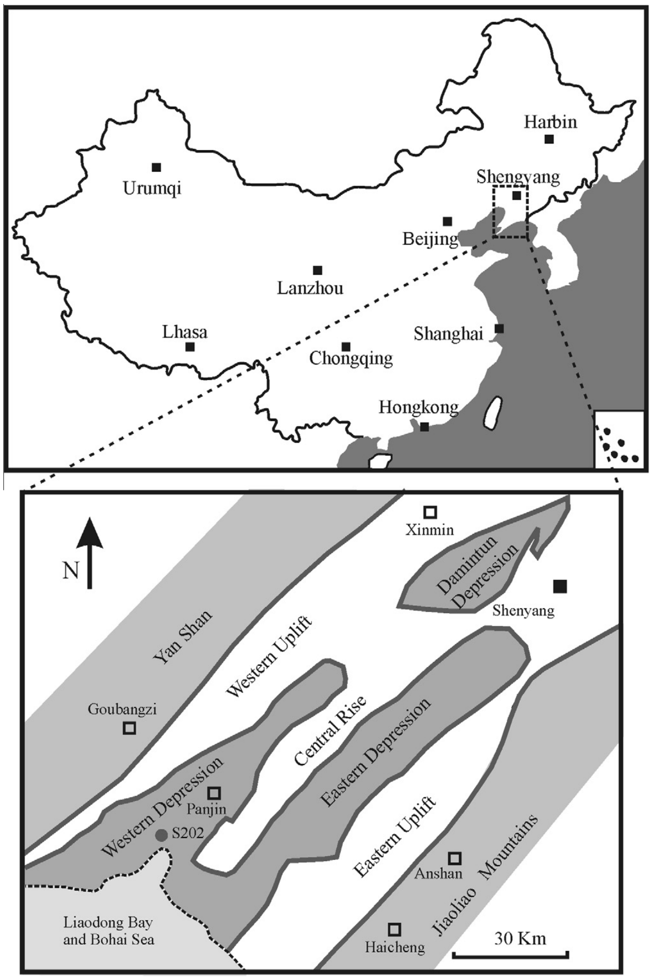

Fig. 2. Location and structural sketch maps of the Liaohe Basin (modified after Li et al., 2013). Well S202 is situated in the Western Depression.