



## The origin of trimethyldibenzothiophenes and their application as maturity indicators in sediments from the Liaohe Basin, East China

Meijun Li <sup>a,\*</sup>, Ningning Zhong <sup>a</sup>, Shengbao Shi <sup>a</sup>, Lei Zhu <sup>a</sup>, Youjun Tang <sup>b</sup>

<sup>a</sup> State Key Laboratory of Petroleum Resources and Prospecting, College of Geosciences, China University of Petroleum, Beijing 102249, China

<sup>b</sup> Key Laboratory of Exploration Technologies for Oil and Gas Resources of the Ministry of Education, College of Geochemistry, Yangtze University, Jingzhou, Hubei 434023, China

### HIGHLIGHTS

- ▶ Trimethyldibenzothiophenes have product–precursor links with trimethylbiphenyls in sediments.
- ▶ A new maturity parameter  $2,4,6\text{-}/(2,4,7 + 2,4,8)\text{-}$ trimethyldibenzothiophene is proposed.
- ▶ This ratio shows a regular increase with the increasing maturity within oil generation window.
- ▶ It shows a reverse changing trend with increasing maturity in low maturity stages.

### ARTICLE INFO

#### Article history:

Received 3 March 2012

Received in revised form 17 September 2012

Accepted 17 September 2012

Available online 10 October 2012

#### Keywords:

Trimethyldibenzothiophene

Trimethylbiphenyl

Maturity indicator

Sedimentary organic matter

Thermodynamic stability

### ABSTRACT

The distributions of trimethyldibenzothiophenes (TMDBTs), the relationship between TMDBTs and trimethylbiphenyls (TMBPs) and the application of TMDBTs as maturity indicators have been investigated in a set of lacustrine shales from the Eocene Shahejie Formation in the Liaohe Basin, East China. The 3,5,3'-, 3,5,4'- and 3,4,4'-TMBP isomers can react to yield (2,4,6- + 2,4,8)-TMDBT, 2,4,7-TMDBT, and (3,4,7 + 2,3,7)-TMDBT by incorporating a sulfur atom into biphenyl, respectively. The absolute concentrations of (2,4,6 + 2,4,7 + 2,4,8)-TMDBT increase with those of (3,5,3' + 3,5,4')-TMBP. Similarly, the absolute concentrations of (3,4,7- + 2,3,7)-TMDBT show a similar increase with those of 3,4,4'-TMBP. The good straight line relationships ( $R^2 = 0.96$ ) indicate the product–precursor links between TMDBTs and TMBPs in the sediments. On the basis of the possible differences in the thermodynamic stability among TMDBT isomers, a new maturity indicator  $2,4,6\text{-}/(2,4,7 + 2,4,8)\text{-}$ TMDBT ratio is proposed in this study. This ratio has a good correlation with 4-/1-methyldibenzothiophen ratio (MDR) and  $T_{\max}$  (°C), respectively, indicating similar behavior with increasing maturity. Both of the  $2,4,6\text{-}/(2,4,7 + 2,4,8)\text{-}$ TMDBT ratio and MDR exhibit similar maturation trends. They gradually decrease with increasing maturity at the low maturity stages, and then are followed by a regular increase with the increasing maturity. Therefore, this ratio is an effective maturity indicator for source rocks and an oils maturity assessment ( $R_o > \approx 0.55\%$ ), and it must be applied with caution as a maturity indicator for extracts of immature sediments.

© 2012 Elsevier Ltd. All rights reserved.

### 1. Introduction

Polycyclic aromatic sulfur heterocyclics (PASHs), such as benzo-thiophene (BT), dibenzothiophene (DBT) and their alkylated homologues are important organosulfur aromatic compounds in oils and sedimentary organic matter. Their distribution patterns, relative

and absolute concentrations have been widely applied in maturation studies of sedimentary organic matter and oils [1–9], kerogen types in source rocks [10], depositional environments for sedimentation of organic matter [11,12], and oil migration pathways [13,14].

The maturity indicators relative to polyaromatic aromatic hydrocarbons (PAHs) and PASHs change in a regular fashion with increasing maturity for source rocks and oils with moderate to high maturity. Therefore, they are effective maturity indicators, and particularly useful for high to over-mature oils and condensates [5]. Maturity indicators based on hopanes and steranes are restricted to relatively low maturation levels to early stage of the oil generation window [15]. Furthermore, the drastic decrease in the concentrations of those molecular biomarkers at elevated

\* Corresponding author. Present address: Energy and Resources Science Research Center, U.S. Geological Survey, Denver, CO 80225, USA. Tel.: +1 303 236 9367/+86 108 973 1709; fax: +86 108 973 1109.

E-mail address: [meijunli2008@hotmail.com](mailto:meijunli2008@hotmail.com) (M. Li).

thermal maturity levels, and the organic facies may influence the applications of these parameters in the maturation studies of organic matter and related oils [15,16]. Therefore, PAHs and PASHs-based maturity indicators are important supplements to those of hopanes and steranes.

Maturity indicators based on DBT, such as 4-/1-methyldibenzothiophene (MDR), 2,4-/1,4-dimethyldibenzothiophene (2,4-/1,4-DMDBT) and 4,6-/1,4-DMDBT ratios have been introduced and widely applied in organic geochemistry [1,5,17]. A maturity indicator relative to trimethyldibenzothiophene (TMDBT) – the TMDBT index, was also proposed [5]. However, the specific positions of these three methyl groups on dibenzothiophene have not yet been assigned [5].

The maturity parameters relative to PAHs and PASHs are mainly based on the differences in thermodynamic stability among positional isomers [17–19]. It was previously considered that methyl group (s) can shift in predominance from thermodynamically unstable towards more stable isomers with increasing maturity [17].

The MDR has been calibrated against  $R_m\%$  (mean vitrinite reflectance) with high correlation in the 0.56–1.32% range [5]. Thus, the MDR can also be rated as an equivalent maturity parameter and the influence of the organic facies appear to be negligible. However, MDR variations at early maturity stage (0.4–0.7%  $R_m$ ) exhibit significantly different maturation trends for Type II and III kerogens [5]. The influence of depositional environments and kerogen types of organic matter were also reported [2,20].

The compounds with the structure of thiophenic type ring in kerogen are probably the precursor of benzothiophene, dibenzothiophene and their alkylated homologues in ancient organic matter and crude oil [21]. The sulfur-bearing constituents of an organism from which the kerogen was formed are proteins. Due to the insufficient amount of sulfur in plants and animals to produce the large amounts of sulfur compounds in petroleum and sedimentary organic matter, extra sulfur must have been incorporated into the organic matter during the formation of source rocks, especially for high sulfur source rocks [22]. A thermal reaction between elemental sulfur and the organic matter of a sediment was proposed to be responsible for the genesis of the sulfur-containing organic compounds [23,24].

Laboratory simulation experiments showed that biphenyl (BP) and sulfur can react to yield DBT, and methylbiphenyls (MBPs) to corresponding methyldibenzothiophenes (MDBTs) [25,26]. The methyl group(s) position relationships between MBP and associated MDBT isomers, and dimethylbiphenyl (DMBP) and associated dimethyldibenzothiophene (DMDBT) isomers have also been reported [26]. The transformation reactions for MDBTs were also confirmed by the geochemical relationships between MBPs and MDBTs in crude oils and sediment extracts [26]. The product-precursor links between MDBTs and MBPs have been preliminarily established. However, the relationships between the isomer distributions of the trimethylbiphenyl (TMBP) and trimethyldibenzothiophene (TMDBT) and related geochemical observations have not yet been reported.

The objectives of this research are to investigate the distributions of TMDBT and TMBP isomers in a series of source rock samples from the Tertiary lacustrine shales in the Liaohe Basin, East China. The product-precursor relationships between some isomers of TMDBT and TMBP are studied. A new maturity parameter 2,4,6-/(2,4,7 + 2,4,8)-TMDBT ratio on the basis of the relative concentrations of TMDBT isomers is proposed. The relationships between this maturity indicator and MDR and  $T_{max}$  (°C) are preliminarily discussed. The variations of the absolute concentrations of TMDBT isomers with depth are discussed to interpret the maturation trend of this new maturity indicator with increasing maturity.

## 2. Samples and experimental methods

### 2.1. Sampling site

A total of 5 cores and 16 cuttings were collected from Well SG1 in the Western Depression of the Liaohe Basin, East China. The geological setting for the petroleum reservoirs in the Western Depression has been summarized in previous publications [20,30,31]. Located in Liaoning Province of northeast China, adjacent to the northeast end of the Bohai Sea, the Liaohe Basin is one of the main hydrocarbon-bearing basins in East China (Fig. 1). It is a wedge-shaped rift basin with a Cenozoic sedimentary thickness of more than 3000–4000 m [31]. The Paleogene sequence is composed of Fangshenpiao, Shahejie and Dongying formations. The Eocene Shahejie Formation (Es) is widely distributed in the entire basin and contains the most important source rock and reservoir units. It can be further subdivided into four members (Es<sub>4</sub>, Es<sub>3</sub>, Es<sub>2</sub>, and Es<sub>1</sub>, oldest to youngest). During the early Es<sub>3</sub>, drastic subsidence resulted in the development of an extensive deep lacustrine environment and this member consists of dark mudstones, shales and oil shales of deep lacustrine origin. The Es<sub>3</sub> member is the main source rock in the entire Liaohe Basin. The Es<sub>2</sub> member was deposited during a contraction of the lake in the basin because of tectonic uplift [31]. All rocks samples in this study were collected from the second (Es<sub>2</sub>) and the third members (Es<sub>3</sub>) of the Shahejie Formation.

### 2.2. Sample description

All of the samples are good source rocks with an average total organic carbon (TOC) content of 1.88%. All samples display relatively high HI values of up to 409 mg HC/g TOC and are mainly in the immature to the main phase of the oil generation stages (Li et al., unpublished data). The organic matters are mainly comprised of kerogen of type II with some type III. All source rocks of the Es<sub>3</sub> and Es<sub>2</sub> members have relatively low Pr/Ph ratios (0.40–1.43) with an average of 0.92, and high gammacerane contents with an average gammacerane/C<sub>30</sub> hopane ratio of 0.19 (0.09–0.40), which indicate the suboxic to anoxic and brackish water depositional environments.

### 2.3. Sample extraction

All the rocks were ground in a crusher to <80 mesh. The powdered samples were extracted for 24 h using a Soxhlet apparatus with 400 ml of dichloromethane and methanol (93:7, v:v) to obtain soluble bitumen. The extracts were deasphalted using n-hexane and then fractionated by liquid chromatography using silica gel/alumina columns into saturated and aromatic hydrocarbon fractions using n-hexane with dichloromethane (50:50, v:v) and dichloromethane as respective eluents.

### 2.4. Sample analysis

The GC–MS analyses of the aromatic hydrocarbon fractions were performed on an Agilent 5975i mass spectrometer system coupled with an HP-5MS fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm coating). The GC operating conditions are as follows: the GC oven temperature was set to an initial 80 °C for 1 min, programmed to increase to 310 °C at 3 °C/min, and then kept isothermal for 16 min. Helium was used as the carrier gas. The injector temperature was set to 300 °C. The MS was set to electron ionization (EI) mode with electron energy of 70 eV, and full-scan mode with a scanning range of 50–600 Da.

The identification and elution order of trimethylbiphenyl isomers and trimethyldibenzothiophene isomers were determined

Download English Version:

<https://daneshyari.com/en/article/6643192>

Download Persian Version:

<https://daneshyari.com/article/6643192>

[Daneshyari.com](https://daneshyari.com)