Di-iso-propynaphthalenes: environmental contaminants of increasing importance for organic geochemists

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Abstract

Di-iso-propynaphthalenes (DIPNs) have distinctive mass spectra, including m/z 197 base peaks and m/z 212 molecular ions, and on the apolar columns typically used in organic geochemical applications resolve into 5 main peaks, although there are ten possible isomers. DIPNs have been recognised in rock matrix and solid bitumen samples from Oklo (Gabon), and in subsurface samples of Silurian – Devonian clastic sediments from southern Tunisia (borehole MG1, Ghadamis Basin). DIPNs have synthetic/anthropogenic origins and are used as plant growth regulators and in the manufacture of printed papers. The most likely source of the DIPNs in these organic geochemical samples is tissue paper used to wrap the samples. It is suggested that they are preferentially adsorbed by solid bitumens, and hence are not released during solvent extraction of surfaces. Although DIPNs have been reported in environmental and food samples, this appears to be their first report in organic geochemical samples.

Keywords: Di-iso-propynaphthalenes, diisopropynaphthalenes, contamination, paper, solvent extraction, Franceville Basin, Oklo, Ghadamis Basin, GC-MS
1. Introduction

Contamination of geological samples prior to or during organic geochemical analyses is an on-going problem for molecular compositional studies, particularly those involving trace amounts of biomarkers. It has long been known that phthalate esters, distinguished during gas chromatography-mass spectrometry (GC-MS) by \textit{m/z} 149 ions, are compounds typically found in plasticisers that can be leached from plastic bottles used to store samples or solvent extracts (e.g., Bowers et al., 1981). Unfortunately, contamination is often ignored or passed over in publications, as it has an essentially negative impact on geochemical interpretations (although see Brocks et al., 2008) and is often very difficult to identify and trace to its point of origin. However, a recent comprehensive study of organic contaminants encountered during a marine survey highlights the care that needs to be taken in handling samples destined for GC-MS analysis (Grosjean and Logan, 2007). In this study, sunscreen cream was shown to be the source of the UV adsorbers octabenzone and octyl methoxycinnamate, and plastic sampling bags the source of fatty acid amides and butylated hydroxytoluene. A series of branched alkanes with quaternary carbons (BACQs) are also derived from plastic bags, together with various methylalkanes, alkylcyclopentanes and alkylcyclohexanes (Grosjean and Logan, 2007). The latter three groups also occur naturally in geological samples, but it appears that BACQs are exclusively derived from plastic bags (Grosjean and Logan, 2007; Brocks et al., 2008).

Precautions such as wrapping organic geochemical samples in aluminium foil after sampling, non-use of plastic bags in contact with rock samples, the use of diamond saws free of oil-based fluids, and the removal of the outside surface of samples prior to crushing and solvent extraction can eliminate some of these issues. Comprehensive series of outside-rinse, procedural and system blanks can help understand contaminant distribution (e.g., George et al., 2008). Interior/exterior sub-sampling by sawing has also been advocated, in order to understand the past migration of contaminants deeper.
into core (Brocks et al., 2003, 2008; Sherman et al., 2007). On occasion, however, samples of rare material arrive at an organic geochemistry laboratory that may have been collected many years ago, have an uncertain storage history and may be too small for removal of outside surfaces prior to analysis. These are the circumstances in which samples from the FB Formation Proterozoic rocks from the Franceville Basin in Gabon (Dutkiewicz et al., 2007) arrived at the CSIRO Laboratories. In this note, the identification and distribution of di-iso-propynaphthalenes (DIPNs) discovered in these and other organic geochemical samples is shown, and their source and implications are discussed.

2. Methods

2.1. Samples

Two samples were obtained from the vicinity of the Oklo natural fission reactors within the Franceville Basin in Gabon. Sample #59 is from 147.7 m depth in borehole 212 and comprises the 2.1 Ga old FB black shale of the Franceville Series (Mossman et al., 2005). It contains a 3 mm wide veinlet of microscopically homogeneous solid bitumen, which obliquely cuts the black shale. The solid bitumen has a maximum reflectance in oil of 5.3% and a $\delta^{13}C$ value of -23.02‰ (Mossman et al., 2001). Sample SD90 is from near reactor #13, south of a major dolerite dyke, and is composed of “normal” (common) low-grade uranium ore (0.1 to 1.0%) (Gauthier-Lafaye and Weber, 1989). Solid bitumen in this sample has an H/C ratio of $<0.5$% and occupies secondary porosity in the sandstone caused by extensive microfracturing. For further information on the geological setting and geochemistry of the solid bitumens and associated fluid inclusions, see Mossman et al. (2001; 2005) and Dutkiewicz et al. (2007).

Eleven core samples come from borehole MG1, which was drilled by SEREPT from July 1958 to April 1959, and penetrates a Silurian-Devonian succession near the northern margin of the Ghadamis Basin in southern Tunisia (Romero-Sarmiento et al., 2009; Spina and Vecoli, 2009). These samples have been stored in plastic sampling bag
under uncertain conditions for a long time (tens of years). For further information on the
geological setting and geochemistry of the Tunisian clastic sediments, see Romero-
Sarmiento et al. (2009).

2.2. Experimental procedure

The outside surfaces of the two Oklo samples (#59: 50.7 g; SD90: 21 g) were ultrasonicated in dichloromethane (DCM): methanol (MeOH) (93:7) for 10 minutes. Small portions of solid bitumen (2.1 and 1.4 g, respectively) were manually scraped and cut from the parent samples, crushed with a pestle and mortar and analysed separately. The remaining matrix of each sample (which contained some solid bitumen) was crushed in a Tema mill (39.2 and 29.0 g, respectively). Sub-samples of the solid bitumen were ultrasonically extracted for 40 minutes (5 minute bursts) using 3 mL DCM:MeOH (93:7) in a 4 mL vial. The extracts were filtered on a short silica column. The matrix samples were Soxhlet extracted for 72 hours using DCM:MeOH (93:7). Any elemental sulfur present was removed from the four extracts using activated copper, and the extracts analysed by gas chromatography-mass spectrometry (GC-MS) on a Hewlett Packard 5890 gas chromatograph (DB5MS, 60 m x 0.25 mm i.d, 0.25 µm film thickness) interfaced to a VG AutospecQ Ultima mass spectrometer. The oven temperature started at 40°C (held for 2 mins), increased at a rate of 4°C/min to 310°C, and was held for 40 mins (for further instrument method details, see George et al., 2007).

Biomarker analyses were performed on the samples from borehole MG1 (Romero-Sarmiento et al., 2009). The Tunisian samples were crushed in coarse fragments and soaked in DCM for contaminant removal (extract 0). The samples were then pulverised, extracted using DCM:MeOH (1/2, v/v), dried and separated into aliphatic and aromatic fractions that were analysed by GC-MS using a Trace GC 2000 gas chromatograph (DB5ht, 30 m x 0.25 mm i.d, 0.1 µm film thickness). For further analytical details, see Romero-Sarmiento et al. (2009).
3. Results

The Oklo matrix sample #59 total ion chromatogram (TIC) is dominated by a cluster of five major peaks eluting between \(n\)-C\(_{16}\) and \(n\)-C\(_{18}\), as well as peaks due to \(n\)-alkanes (C\(_{10}\) to C\(_{30}\)), alkylbenzenes, phthalates, benzothiazole and diethyltoluamide (Fig. 1a). The separated solid bitumen from sample #59 is even more strongly dominated by the five major peaks (Fig. 1b). Expansion of this area using the \(m/z\) 197 chromatogram (Fig. 1c) shows that the first two peaks are a doublet, the three later peaks are a triplet, and that \(n\)-C\(_{17}\) elutes shortly after the doublet on the DB5MS column phase used. These five peaks have identical mass spectra (Fig. 1d) consistent with C\(_{16}\)H\(_{26}\) hydrocarbons, including \(m/z\) 197 base peaks, \(m/z\) 212 molecular ions and significant ions at \(m/z\) 155. NIST Library searching (NISTREP; VG OPUS, 1994) and comparison with published spectra (Franke et al., 2007) indicates these are very likely to be di-\(iso\)-propylnapththalenes. The SD90 matrix sample also contains major phthalates and DIPNs, with subordinate \(n\)-alkanes (C\(_{12}\) to C\(_{30}\)) and some elemental sulphur that was not fully removed from the sample by the initial treatment with activated copper (Fig. 1e). The separated solid bitumen from sample SD90 has a similar compound distribution, except that toluene and the early eluting non-identified peaks are more abundant (Fig. 1f). Seven of the Tunisian sample aromatic fractions contain DIPNs in the \(m/z\) 197 mass chromatogram, generally in low amounts, except for sample MG1-2519.3 in which DIPNs are the major peaks (Fig. 2). This sample comes from the Ouan Kasa Formation, and consists of a shallow-marine sandstone of Early Devonian age (Romero-Sarmiento et al., 2009). At least 8 possible DIPN isomers were detected in this sample (Fig. 2), eluting between the retention time positions of \(n\)-C\(_{16}\) and \(n\)-C\(_{18}\).

The retention time characteristics of DIPNs have recently been unambiguously determined (Franke et al., 2007; Bouvier et al., 2009), confirming and extending earlier reports (Sturaro et al., 1994; Brzozowski et al., 2002). There are ten possible DIPN isomers, but one (1,8-) is extremely sterically hindered and very rare (Franke et al.,...
The other nine DIPN isomers are fully resolvable on polar columns such as INNOWAX and CP-SIL-88, but are only partially resolvable on apolar columns. A GC×GC method to fully separate DIPNs has recently been published, allowing quantitative analysis of the DIPN isomers even in complex reaction mixtures (Bouvier et al., 2009). The DIPN retention time pattern reported by Franke et al. (2007) on apolar columns is very similar to that found on DB5MS here (Fig. 1b): 1,3- and 1,7-DIPN form the early eluting doublet, the next minor peak is due to co-eluting 1,2- and 2,3-DIPN (sterically hindered and hence typically in low abundance), and the triplet eluting after n-C_{17} is composed of 1,4-DIPN, then co-eluting 2,7- and 1,6-DIPN, then 2,6-DIPN (1,5-DIPN would elute slightly later, and it appears not to be present). However, on DB5ht the resolution over the triplet region appears to be superior (Fig. 2). The DIPN isomer distribution is similar in all samples analysed, and the mass spectra only vary slightly as previously noted (Franke et al., 2007).

4. Discussion and conclusions

The DIPNs are not known to be naturally occurring hydrocarbons in the environment, but certainly have synthetic/anthropogenic origins. Single DIPN isomers, especially 2,6-DIPN, are used in agriculture as plant growth regulators (Everest-Todd, 1988; Lewis et al., 1997). This is based on the structural and functional similarity of 2,6-DIPN to naturally occurring plant growth regulators found in plant tissues, such as 1-isopropyl-4,6-dimethylnaphthalene (USEPA, accessed 2009). Therefore, one possible source of this compound is customs spraying of geochemical samples. However, it is unlikely that this is the source of the contaminants in these samples, because at least six isomers can be detected (Figs. 1c and 2).

“Technical” DIPN consists mainly of a mixture of seven isomers (1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-) and is used in a variety of applications as a replacement for polychlorinated biphenyls, especially in the manufacture of printed papers (Terasaki et al., 2008) and food packaging materials (e.g., Nerín and Asensio, 2007). This is the
most likely source of the DIPNs in the Proterozoic rocks from Gabon, which prior to receipt in the organic geochemistry lab had been wrapped in tissue paper and stored in a cardboard box. This could not be confirmed as these materials were previously discarded, but is supported by the higher abundance of DIPNs relative to other hydrocarbons in the solid bitumen compared to the matrix extract in sample #59. Regarding the Tunisian samples, since extract 0 and the polar fraction were not analysed, the contaminant origin of the detected DIPNs cannot be proven. However, the absence of phthalates or BACQ in the aliphatic and aromatic fractions indicates that these were not contaminated since fractionation. Interestingly, core sample MG1-2519.3 where DIPNs are the most abundant (Fig. 2) has a very different Rock-Eval pyrogram to that of the other samples (Romero-Sarmiento et al., 2009), with two $S_2$ peaks: the first and smaller one has a $T_{\text{max}}$ similar to that of the other samples from core MG1 (around 435°C), and the second larger peak has a $T_{\text{max}}$ at 543°C, revealing the presence of another non-identified organic phase, possibly solid bitumen.

The higher amounts of DIPNs in samples associated with solid bitumen, and their presence despite solvent extraction of external surfaces, suggests that DIPNs migrated into the samples from the storage media, and penetrated more deeply than just the surface of the samples, tending to be preferentially adsorbed by solid bitumens. Once strongly adsorbed on solid bitumens, solvent extraction of sample surfaces would not yield them; they would only be released during later crushing followed by solvent extraction. The samples from Gabon were not sufficiently large to sequentially analyse layers towards the centre of the sample, as can be done to trace surficial contamination (Brocks et al., 2003; Sherman et al., 2007).

DIPN mixtures are becoming more commonly detected in rivers and aquatic sediments as environmental contaminants (Terasaki et al., 2008; Mansuy-Huault et al., 2009). The lack of published reports to 2010 of DIPNs in organic geochemical samples...
is probably due to a combination of (1) their non-identification because of low abundance or analysis by single ion monitoring (SIM), (2) their mis-identification or non-identification because it was not know what the mysterious peaks with large $m/z$ 197 ions were, and (3) their recognition and identification, but an unwillingness to disclose contamination issues or just that they were ignored. Feedback at an IMOG09 poster (George et al., 2009) suggested that DIPNs have been noticed in organic geochemical samples, but not published. For example, DIPNs have been noted in Australian oils and source rock extracts (Ben van Aarssen, pers. comm.) As more organic geochemists acquire $m/z$ 197 mass chromatograms during SIM so as to identify 6-isopropyl-1-isohexyl-2-methylnaphthalene (ip-iHMN) (Ellis et al., 1996; van Aarssen et al., 2000), the presence of DIPNs may become more apparent. It is likely that in the future other organic geochemistry groups will detect these compounds in modern and ancient samples.

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References


Figure captions
Fig. 1. Total ion chromatograms (TICs) of (a) sample #59 matrix, (b) sample #59 solid bitumen, (e) sample SD90 matrix and (f) sample SD90 solid bitumen. (c) Partial m/z 197 mass chromatogram of the sample #59 solid bitumen, showing the elution order of the di-iso-propynaphthalenes relative to n-C_{17}. (d) Mass spectra of 1,3-di-iso-propynaphthalene in sample #59 solid bitumen. Peak identifications in TICs: numbers = n-alkanes, T = toluene, N = naphthalene, MN = methylnaphthalene, P = phthalate, S = elemental sulphur, and DIPNs = di-iso-propynaphthalenes.

Fig. 2. Total ion chromatogram (a) and partial m/z 197 mass chromatogram (b) of the aromatic fraction of sample MG1-2519.3 (Early Devonian Ouan Kasa Formation), showing the identification of DIPNs.