## Note

---

# Identification and analysis of tetramethylnaphthalenes in petroleum

PETER G. FORSTER, ROBERT ALEXANDER* and ROBERT I. KAGI

*Centre for Petroleum and Environmental Organic Geochemistry, School of Applied Chemistry, Curtin University of Technology, Box U1987 GPO, Perth, Western Australia 6001 (Australia)*

(Received July 20th, 1989)

Aromatic compounds are major components of crude oils, representing 20–45% of the total hydrocarbons[1], and the alkylnaphthalenes often constitute a significant percentage of this material. It has been shown from analysis of dimethylnaphthalenes (DMNs), trimethylnaphthalenes (TMNs) and methylphenanthrenes (MPs) that the abundances of the less stable $\alpha$-methyl-substituted isomers decrease with increasing thermal maturity, relative to those of the more stable $\beta$-methyl-substituted isomers. Selected isomer ratios from the above classes of compounds have proven useful for the assessment of the geothermal histories of sediments and crude oils[2–8]. The extent of biodegradation of certain crude oils can also be assessed from examination of the DMN components[9,10].

With a view to expanding the geochemical utility of alkylnaphthalenes we have investigated the tetramethylnaphthalene (TeMN) components of crude oils. The occurrence of some TeMN isomers in petroleum has previously been noted in a number of reports. 1,2,5,6-TeMN has been identified in kerosene–gasoline fractions[11] and coal extracts[12]. Yew and Mair[13] have reported the occurrence of 1,3,5,7-TeMN, and Duswalt and Mayer[14] have identified 1,3,5,7-TeMN, 1,3,6,7-TeMN and 2,3,6,7-TeMN in high boiling dinuclear aromatic fractions of petroleum. Other publications report the occurrence of unidentified TeMN isomers from sources which include aromatic fractions from petroleum[15,16] and from coals[2,17].

Previous workers in this department have developed analytical procedures using gas chromatography (GC) for the analysis of DMNs and TMNs in crude oils and sediments[18,19]. In this paper we report the identification of nine TeMN isomers in crude oils using capillary GC–mass spectrometry (MS). Elution orders and retention indices relative to polycyclic aromatic hydrocarbon (PAH) standards are reported for the TeMN isomers used in this study.

EXPERIMENTAL

*Isolation of alkylnaphthalene fraction from crude oils*

In a typical separation, a crude oil sample (100 mg) containing the internal standard (1,2,3,4-TeMN) was subjected to preparative thin-layer chromatography on glass plates spread with alumina (Merck Alumina G; 0.6 mm, activated at 120–140°C for at least 12 h). The plates were developed with *n*-hexane, and the required bands,

comprising dinuclear and trinuclear aromatic compounds, were located relative to the reference compounds (naphthalene and phenanthrene) using UV light (254 nm). The organic material was recovered from the alumina by extraction with dichloromethane, the solvent removed in a Kuderna–Danish apparatus and the residue taken up in *n*-hexane (300 μl) to provide a sample ready for GC–MS analysis.

*Gas chromatography–mass spectrometry*

GC–MS was performed using a Hewlett-Packard (HP) 5970 mass-selective detector instrument (electron ionising voltage 70 eV), with a HP RTE/A data system and a HP 5890A gas chromatograph, fitted with a 60 m × 0.2 mm I.D. fused-silica column coated with 5% cross-linked phenylmethylsilicone (DB-5, J & W Scientific, U.S.A.). In a typical analysis, hydrogen was used as carrier gas at a linear velocity of 30 cm sec$^{-1}$. The transfer line temperature was 280°C, the sample was injected into a HP on-column injection system (accessory No. 19245A) using a HP 7673A automatic liquid sampler, and the oven temperature was programmed from 70 to 300°C at 2°C min$^{-1}$ and held isothermally at 300°C for 10 min.

*Tetramethylnaphthalene standards*

1,3,5,7-TeMN and 1,3,6,8-TeMN were synthesized using the method of Cannone *et al*[20]. 1,3,6,7-TeMN was obtained by acid-catalysed isomerisation of 1,3,6,8-TeMN[21]. A sample of 1,2,5,7-TeMN, previously synthesized by Cyrot[22] from 3,3,6,8-tetramethyltetralone, was more conveniently obtained from 2,3-dimethylbenzyl chloride using the general method of Boudjouk *et al.*[23]. 2,3,6,7-TeMN and 1,2,3,7-TeMN were synthesized using the methods of Rieke *et al.*[24] and Chen *et al.*[25], respectively. 1,2,5,6-TeMN was prepared in moderate yield by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) of the readily available[26] 1,1,5,6-tetramethyltetralin. Similarly, DDQ oxidation of 1,1,6,7-tetramethyltetralin gave 1,2,6,7-TeMN. Although the synthesis of 1,1,6,7-tetramethyltetralin has been reported[27], an alternative route, involving the addition of CH$_3$MgI to γ-(3,4-dimethylphenyl)butanoic acid and cyclodehydration of the resultant tertiary alcohol, was utilised. Gattermann formylation of 2,3,6-TMN and Huang–Minlon reduction of the resultant mixture of aldehydes using the method of Aslam *et al.*[28] gave 1,2,3,6-TeMN, together with the 1,2,3,7-, 1,2,6,7- and 1,2,4,7-isomers which were identified by co-chromatography with authentic samples.

New synthetic compounds were characterised by $^1$H and $^{13}$C NMR spectroscopy and MS. Pure samples of known TeMN isomers were identified by comparison of physical and spectral data with published data.

A sample of 1,2,4,7-TeMN was obtained from Professor L. H. Klemm (University of Oregon, U.S.A.). Professor D. Wege (University of Western Australia) generously donated a sample of 1,2,3,4-TeMN.

*Retention indices*

Retention indices relative to PAH standards were calculated using the method of Lee *et al.*[29] from GC–MS retention times obtained under programmed-temperature conditions (70 to 300°C at 2°C min$^{-1}$) on a capillary column coated with DB-5 stationary phase. For compounds eluting between naphthalene and phenanthrene, the index (*I*) is calculated from the linear relationship:

$$I_{(\text{substance})} = I_{(\text{naphthalene})} + \left( \frac{t_{R(\text{substance})} - t_{R(\text{naphthalene})}}{t_{R(\text{phenanthrene})} - t_{R(\text{naphthalene})}} \right) \times 100$$

where $I_{(\text{naphthalene})} = 200$ and $I_{(\text{phenanthrene})} = 300$, and $t_R$ is the retention time of the substance or PAH standard.

TABLE I

GEOLOGICAL DATA FOR CRUDE OIL SAMPLES

| Crude oil | Location | Age of reservoir |
|---|---|---|
| Barrow | Carnarvon Basin, Australia | Jurassic |
| Volador | Gippsland Basin, Australia | Cretaceous |
| Safaniya | Saudi Arabia | Cretaceous |
| Petapahan | Sumatra, Indonesia | Miocene |
| Buena Vista hills | Califoria, U.S.A. | Miocene |
| Great Sandy | Canning Basin, Australia | Ordovician |

RESULTS AND DISCUSSION

Table I shows geological data for the crude oil samples we have examined in this study. A variety of samples were chosen to illustrate the occurrence of the various TeMN isomers in oils that represent vastly different geographical locations and geological age.

Due to co-elution with unidentified components and the relatively low abundances of some of the TeMN isomers, it was found more convenient to routinely analyse crude oil nuclear and trinuclear aromatic fractions for TeMNs by capillary GC–MS, rather than capillary GC–flame ionization detection. Fig. 1 shows $m/z$ 184 mass chromatograms of a mixture of authentic TeMN standards, and a dinuclear and trinuclear aromatic fraction from the Barrow crude oil sample. Peaks in the mass chromatograms of the crude oil samples were assigned to the indicated TeMN isomers by comparison of mass spectra and co-chromatography with authentic isomers on a DB-5 capillary column. Attempts to obtain further confirmation of these assignments by co-chromatography on columns coated with different phases (methylsilicone, 7% phenylmethylsilicone) were of limited value due to the poor resolution obtained. A DB-5 column has previously been found to give the best results for analysis of the TMNs[19], and appears to be the column of choice for analysis of the TeMNs.

Concentration data for the TeMN isomers found in the six crude oil samples are shown in Table II. The absolute concentrations of individual isomers were determined by the addition of the internal standard (1,2,3,4-TeMN) to the crude oil prior to thin-layer chromatography. This isomer was utilised as an internal standard as it is not present in any of the crude oils examined and could be directly measured in the $m/z$ 184 mass chromatogram. As the analysis involves measurement of the TeMN isomers using the $m/z$ 184 ion, response factors were applied to obtain weight ratios for the isomers. It is interesting to note that the absolute concentrations of individual TeMNs range from 15 to 665 $\mu g/g$ of crude oil for the sample site examined in this study.
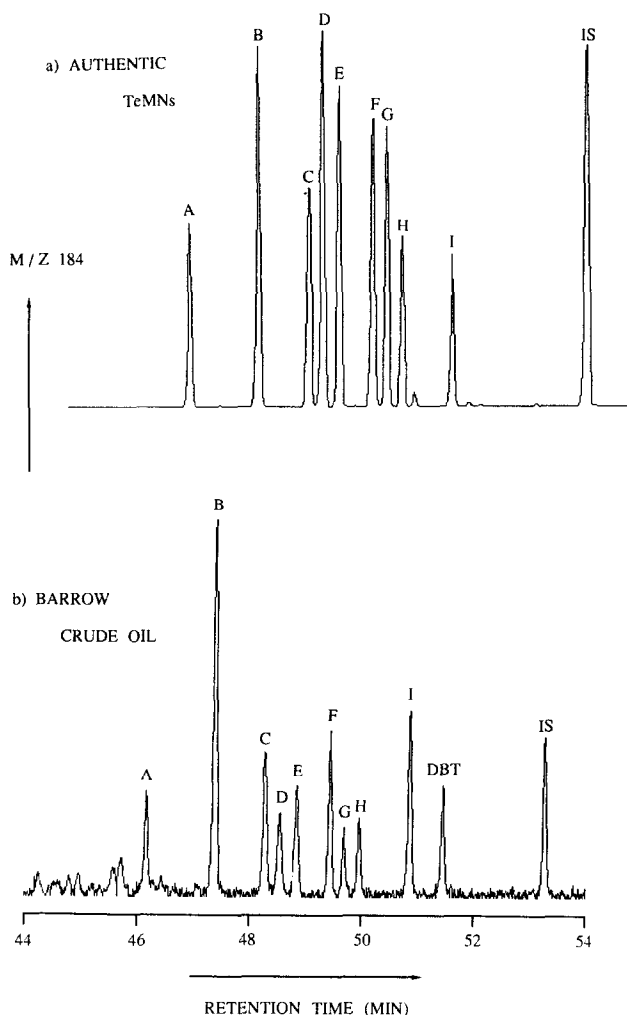
Fig. 1. Partial $m/z$ 184 mass chromatograms of (a) a mixture of authentic TeMN standards and (b) Barrow crude oil dinuclear and trinuclear aromatic fraction. Peaks: A = 1,3,5,7-TeMN; B = 1,3,6,7-TeMN; C = 1,2,4,7-TeMN; D = 1,2,5,7-TeMN; E = 2,3,6,7-TeMN; F = 1,2,6,7-TeMN; G = 1,2,3,7-TeMN; H = 1,2,3,6-TeMN; I = 1,2,5,6-TeMN; DBT = Dibenzothiophene; IS = internal standard (1,2,3,4-TeMN). See Experimental section for GC–MS conditions.

It is evident from examination of the values in Table II that the relative concentrations of the isomers varies from sample to sample. It should also be noted that TeMN isomers which possess *peri*-disubstituted methyl groups (*e.g.* 1,3,6,8-TeMN) were not found in the crude oils examined in this study. These observations are consistent with those reported for the analysis of TMNs and DMNs in some crude oils, in that analogous TMN isomers with *peri*-disubstituted methyl groups (*e.g.* 1,3,8-TMN) are not found in significant abundances[19], and 1,8-DMN was only found in

TABLE II

CONCENTRATIONS ($\mu$g/g OIL) OF TeMN ISOMERS IN CRUDE OILS

Values in parentheses are relative concentrations (%).

| TeMN | Response factor[a] | Crude oils | | | | | |
|---|---|---|---|---|---|---|---|
| | | Barrow | Volador | Safaniya | Petapahan | Buena Vista hills | Great Sandy |
| 1,3,5,7- | 0.89 | 51 (6.1) | 40 (5.2) | 29 (7.5) | 67 (8.3) | 15 (3.4) | 170 (6.7) |
| 1,3,6,7- | 0.89 | 223 (26.7) | 140 (17.9) | 64 (16.5) | 138 (16.9) | 67 (14.8) | 665 (25.6) |
| 1,2,4,7- | 1.06 | 118 (14.1) | 98 (12.6) | 65 (16.7) | 157 (19.3) | 61 (13.6) | 201 (7.7) |
| 1,2,5,7- | 0.82 | 54 (6.4) | 70 (9.0) | 42 (10.6) | 86 (10.5) | 29 (6.3) | 203 (7.8) |
| 2,3,6,7- | 0.91 | 79 (9.4) | 36 (4.6) | 19 (4.9) | 28 (3.5) | 33 (7.4) | 310 (11.9) |
| 1,2,6,7- | 0.97 | 108 (12.9) | 89 (11.5) | 40 (10.2) | 75 (9.2) | 85 (18.9) | 430 (16.6) |
| 1,2,3,7- | 0.85 | 36 (4.3) | 21 (2.7) | 16 (4.2) | 20 (2.5) | 26 (5.8) | 86 (3.3) |
| 1,2,3,6- | 0.88 | 43 (5.2) | 35 (4.5) | 37 (9.4) | 47 (5.8) | 65 (14.4) | 143 (5.5) |
| 1,2,5,6- | 0.94 | 125 (14.9) | 249 (32.0) | 78 (20.1) | 196 (24.0) | 69 (15.4) | 387 (14.9) |
| Total TeMNs | | 732 | 778 | 390 | 814 | 449 | 2529 |

[a] Response factors used to relate peak areas measured from $m/z$ 184 mass chromatograms to weight ratios.

trace amounts (0.003% of total DMNs) in a crude oil[18]. A discussion of the geochemical significance of the distribution of TeMN in sediments and crude oils is beyond the scope of this report and will be presented elsewhere.

Retention indices relative to PAH standards for the TeMNs which are found in the crude oils anaysed in, this study, are listed in Table III. The indices were readily calculated using the method of Lee et al.[29] because the reference compounds (naphthalene, phenanthrene and chrysene) were present in the crude oils we examined. Indices for the DMNs are not listed in this report as they have been reported elsewhere[29,30].

TABLE III

RETENTION INDICES FOR TMNs AND TeMNs

See Experimental section for a description of the method used to calculate retention indices.

| Compound | Retention index (I)[a] | Compound | Retention index (I)[a] |
|---|---|---|---|
| 1,3,7-TMN | 259.22 | 1,3,6,7-TeMN | 283.57 |
| 1,3,6-TMN | 260.03 | 1,2,4,7-TeMN | 286.26 |
| 1,4,6-TMN | 262.72 | 1,2,5,7-TeMN | 286.80 |
| 1,3,5-TMN | 262.72 | 1,3,6,8-TeMN[b] | 286.98 |
| 2,3,6-TMN | 263.20 | 2,3,6,7-TeMN | 287.67 |
| 1,2,7-TMN | 265.29 | 1,2,6,7-TeMN | 289.39 |
| 1,6,7-TMN | 265.58 | 1,2,3,7-TeMN | 289.92 |
| 1,2,6-TMN | 265.86 | 1,2,3,6-TeMN | 290.91 |
| 1,2,4-TMN | 268.29 | 1,2,5,6-TeMN | 293.51 |
| 1,2,5-TMN | 269.47 | 1,2,3,4-TeMN[b] | 300.05 |
| 1,3,5,7-TeMN | 280.06 | | |

[a] Values are an average of four measurements.
[b] 1,3,6,8-TeMN and 1,2,3,4-TeMN were not observed in crude oils.

REFERENCES

1  B. P. Tissot and D. H. Welte, *Petroleum Formation and Occurrence*, Springer, Berlin, 1984.
2  M. Radke, H. Willsch, D. Leythaeuser and M. Teichmüller, *Geochim. Cosmochim. Acta*, 46 (1982) 1831.
3  R. Alexander, R. Kagi and P. Sheppard, *Nature (London)*, 308 (1984) 442.
4  R. Alexander, R. I. Kagi, S. I. Rowland, P. N. Sheppard and T. V. Chirila, *Geochim. Cosmochim. Acta*, 49 (1985) 385.
5  M. Radke, D. H. Welte and H. Willsch, in D. Leythaeuser and J. Rullkötter (Editors), *Advances in Organic Geochemistry 1985*, Pergamon, Oxford, 1986, p. 51.
6  M. Radke, D. H. Welte and H. Willsch, *Geochim. Cosmochim. Acta*, 46 (1982) 1.
7  M. Radke and D. H. Welte, in M. Bjorøy, P. Albrecht, C. Cornford, K. de Groot, G. Eglinton, E. Galimor, D. Leythaeuser, R. Pelet, J. Rullkötter and G. Speers (Editors), *Advances in Organic Geochemistry 1981*, Pergamon, Oxford, 1983, p. 504.
8  P. Garriques, R. De Vazelhes-De Sury, M. Ewald, J. L. Oudin and J. Connan, *Org. Geochim.*, 6 (1984) 829.
9  J. K. Volkman, R. Alexander, R. I. Kagi, S. J. Rowland and P. N. Sheppard, in P. A. Schenck, J. W. de Leeuw and G. W. M. Lijmbach (Editors), *Advances in Organic Geochemistry 1983*, Pergamon, Oxford, 1984, p. 619.
10  S. J. Rowland, R. Alexander, R. I. Kagi, D. M. Jones and A. G. Douglas, *Org. Geochem.*, 9 (1986) 153.
11  P. S. Makovetskii, Z. S. Smutkina and D. F. Serdyuk, *Chem. Technol. Fuel Oils*, 1 (1965) 263.
12  W. Püttmann and H. Villar, *Geochim. Cosmochim. Acta*, 51 (1987) 3023.
13  F. F-H. Yew and B. J. Mair, *Anal. Chem.*, 38 (1966) 231.
14  J. M. Duswalt and T. J. Mayer, *Preprints, Div. Petrol. Chem., ACS*, 16 (1971) A17.
15  V. N. Garg, B. D. Bhatt, V. K. Kaushik and K. R. Murthy, *J. Chromatogr. Sci.*, 25 (1987) 237.
16  M. Radke, H. Willsch and D. Welte, *Anal. Chem.*, 56 (1984) 2538.
17  W. Püttmann, M. Wolf and E. Wolff-Fischer, in D. Leythaeuser and J. Rullkötter (Editors), *Advances in Organic Geochemistry 1985*, Pergamon, Oxford, 1986, p. 625.
18  R. Alexander, R. I. Kagi and P. N. Sheppard, *J. Chromatogr.*, 267 (1983) 367.
19  S. J. Rowland, R. Alexander and R. I. Kagi, *J. Chromatogr.*, 294 (1984) 407.
20  P. Cannone, P. Holm and L. C. Leitch, *Can. J. Chem.*, 45 (1967) 2151.
21  A. Oku and Y. Yuzen, *J. Org. Chem.*, 40 (1975) 3850.
22  E. Cyrot, *Ann. Chim.*, 6 (1971) 413.
23  P. Boudjouk, W. H. Ohrbom and J. B. Woell, *Synthetic Comm.*, 16 (1986) 401.
24  R. D. Rieke, K. White and E. McBride, *J. Org. Chem.*, 38 (1973) 1430.
25  T. S. Chen, P. Cannone and L. C. Leitch, *Synthesis*, (1973) 620.
26  D. Murali and G. S. Krishna Rao, *Ind. J. Chem.*, 21B (1982) 1033.
27  G. Mehta, *Ind. J. Chem.*, 7 (1969) 835.
28  F. M. Aslam, P. H. Gore and M. Jehangir, *J. Chem. Soc., Perkin Trans. I*, (1972) 892.
29  M. L. Lee, D. L. Vassilaros, C. M. White and M. Novotny, *Anal. Chem.*, 51 (1979) 768.
30  D. L. Vassilaros, R. C. Kong, D. W. Later and M. L. Lee, *J. Chromatogr.*, 252 (1982) 1.