Note

Analysis of methylbiphenyls, ethylbiphenyls and dimethylbiphenyls in crude oils

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In recent years considerable attention has been directed at analysis of alkyl aromatics in geological samples. In particular, selected dimethylnaphthalene, trimethylnaphthalene and methylphenanthrene isomer ratios have been shown to be useful indicators of thermal maturity in crude oils, coals and sediment extracts[1–4]. Such maturity indicators are usually based upon changes in abundances of less stable α-substituted isomers relative to those of more stable β-isomers, with increasing maturity.

Recently, alkylbiphenyls have been the subject of investigations because of their unusual behavior during analysis by gas chromatography (GC)[5,6]. Whereas alkyl-substituted aromatics usually have longer retention times than the parent aromatic compound, alkylbiphenyls with an *ortho*-methyl substituent may have shorter retention times than the related compound without the methyl substituent[5].

Methylbiphenyls and dimethylbiphenyls have previously been reported to occur in coal extracts and crude oils[7–11]. Using preparative GC, Mair and Mayer[7] and Yew and Mair[8] were able to identify the three isomeric methylbiphenyls, one ethylbiphenyl and five of the twelve dimethylbiphenyls in a crude oil; however, the remaining ethyl- and dimethylbiphenyls have not yet been identified. In this paper we report an analytical procedure for the isolation of aromatic fractions of crude oil by liquid chromatography, and subsequent quantitative analysis of these fractions by high resolution capillary GC for all methyl-, ethyl- and dimethylbiphenyls.

EXPERIMENTAL

Alkylbiphenyl standards

3- and 4-methylbiphenyl and 3,3'- and 4,4'-dimethylbiphenyl were purchased from Aldrich. 2-Methylbiphenyl, 2,2'-, 2,3'-, 2,4'-, 3,4'-, 2,3- 2,4- 2,5- 2.6- 3,4- and 3,5-dimethylbiphenyl and 2-, 3- and 4-ethylbiphenyl were prepared by the Gomberg reaction as described by Novrocík *et al.*[12] and purified by silica gel column chromatography and preparative GC. Individual isomers were isolated from mixtures by preparative GC (6 m, 15% SE-30 on Chromosorb W 60–80 mesh) using a Varian Aerograph 700 with helium carrier gas and oven temperatures of 180–220°C.

Crude oils

The sample described as Blina No. 1 DST No. 2 was recovered from an Upper Devonian reservoir in the Canning Basin, Western Australia. That described as Barrow No. 1 crude oil was recovered from the 6700-foot level in the Upper Jurassic formation in the Barrow Island oil field, Western Australia.

High-performance liquid chromatography (HPLC)

HPLC was performed using a system supplied by Waters Assoc. consisting of dual Model 510 pumps, a Rheodyne 7011 injector with a 50-μl injection loop, a gradient former, a Waters Assoc. radial compression module with a reversed-phase C_{18} cartridge and a Waters Assoc. Model 440 UV detector using an absorbance wavelength of 254 nm. Separations were obtained using acetonitrile–water mixtures at a flow-rate of 2 ml/min. Acetonitrile–water (2:3) was held for 10 min before increasing to 60% acetonitrile at 2%/min. This solvent composition was maintained for a further 5 min and then increased at 2%/min to 100% acetonitrile.

Capillary gas chromatography

All analyses were performed using a Hewlett-Packard 5880 gas chromatograph equipped with 50 m × 0.25 mm I.D. fused-silica columns coated with either BP-1, BP-5, BP-10 (SGE, Australia) or CP Wax 57CB (Chrompack). Hydrogen was used as the carrier gas at a linear flow velocity of 30 cm s^{-1}. The oven was programmed from 70°C at 1°C min^{-1} (BP-1, BP-5, BP-10) and 1.5°C min^{-1} (CP Wax 57CB) to 200°C. Peaks in capillary gas chromatograms were assigned on the basis of co-injection with authentic standard compounds.

Isolation of alkylbiphenyl fractions

A dinuclear aromatic fraction was isolated from each crude oil by preparative thin-layer chromatography (TLC)[13,14]. These fractions were then subjected to reversed-phase HPLC using a procedure similar to that described by Radke and co-workers[15]. Two fractions were collected. The first-eluting fraction contained C_2-naphthalenes and C_1-biphenyls, and the second-eluting fraction contained C_3-naphthalenes and C_2-biphenyls. Each fraction (5 ml) was diluted with water (500 ml) and extracted with pentane (2 × 50 ml). The pentane solution was treated with *m*-chloroperoxybenzoic acid to remove sulphur compounds and set aside for analysis by GC.

RESULTS AND DISCUSSION

Because C_1- and C_2-biphenyls are eluted from polar and non-polar capillary columns with retention times similar to C_2-, C_3- and C_4-naphthalenes and C_3-biphenyls, the resulting complex pattern from these compounds makes identification and quantification of these alkylbiphenyls extremely difficult. To overcome these co-elution problems, a fractionation procedure was adopted which involved a preliminary isolation using preparative TLC, previously described by Alexander and co-workers[13,14], followed by reversed-phase HPLC, similar to that used by Radke *et al.*[15].

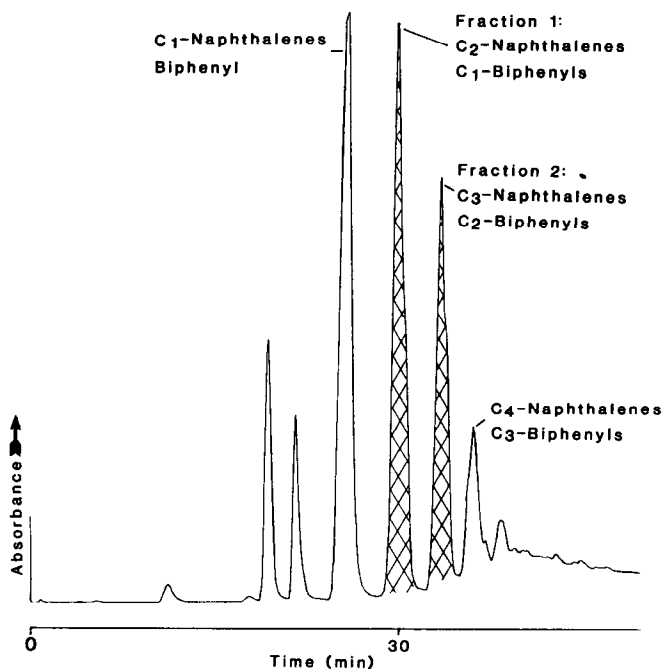Reversed-phase HPLC was selected as an isolation procedure because it en-

Fig. 1. Liquid chromatogram (reversed-phase HPLC) of the dinuclear aromatic fraction of Barrow Upper Jurassic crude oil.

ables separation of aromatic compounds according to their degree of substitution. Combined with preparative TLC on alumina, which separates aromatic compounds into groups containing the same number of aromatic rings, reversed-phase HPLC enables the isolation of alkylbiphenyl-rich fractions from crude oils. Fig. 1 shows a typical liquid chromatogram obtained from the dinuclear fraction of a crude oil. Two fractions were collected during the HPLC procedure: fraction 1 contained the C_2-naphthalenes and the C_1-biphenyls and fraction 2 contained the C_3-naphthalenes and the C_2-biphenyls. These fractions were then extracted with pentane to obtain samples suitable for analysis of the aromatic compounds by gas chromatography. To assess the efficiency of the HPLC isolation procedure, replicate experiments were performed using a mixture of C_1- and C_2-biphenyls of known concentrations. Results obtained from these experiments showed that recoveries of all isomers were greater than 95%.

Fig. 2 shows some typical gas chromatograms obtained from fractions isolation at various stages of the procedure. It is evident from a comparison of the gas chromatograms of the dinuclear aromatic fraction obtained by TLC with that of fraction 1 from the HPLC procedure that removal of biphenyl and C_3-naphthalenes is necessary for identification and quantification of the C_1-biphenyls. Further, the separation of the C_2-biphenyl components from C_2- and C_4-naphthalenes and C_3-biphenyls is required if reliable identification and quantification of the C_2-biphenyls is to be made. A close comparison of the gas chromatograms of fraction 2 and fraction 3 reveals just how effectively the HPLC procedure enables separation of the
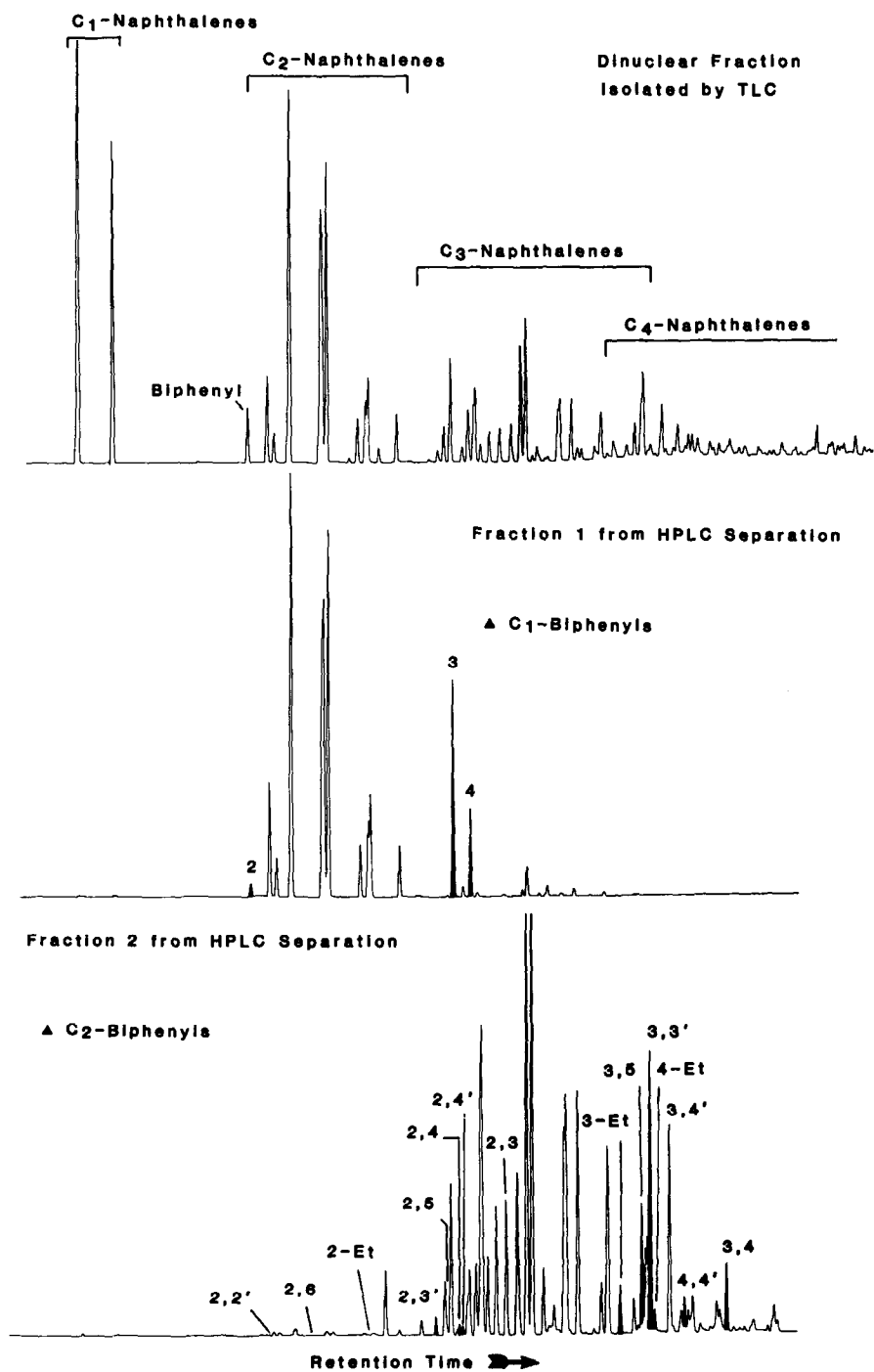
Fig. 2. Capillary gas chromatograms (BP-10) of fractions obtained from Barrow Upper Jurassic crude oil. Peaks have been assigned to methylbiphenyls, ethylbiphenyls and dimethylbiphenyls. Numbers refer to position of ring substitution.

TABLE I

CONCENTRATIONS OF METHYLBIPHENYLS, ETHYLBIPHENYLS AND DIMETHYLBI-
PHENYLS IN TWO AUSTRALIAN CRUDE OILS

Compound	Crude oil			
	Blina No. 1 DST No. 2 ($\mu g/g$)		Barrow No. 1 6700 ft. ($\mu g/g$)	
2-Methylbiphenyl	5.6	(2.7)*	37.0	(1.0)
3-Methylbiphenyl	33.0	(15.8)	720.0	(19.9)
4-Methylbiphenyl	11.0	(5.3)	300.0	(8.2)
2-Ethylbiphenyl	1.7	(0.8)	1.0	(0.03)
3-Ethylbiphenyl	19.0	(9.2)	130.0	(3.5)
4-Ethylbiphenyl	9.2	(4.4)	59.0	(1.6)
2,3-Dimethylbiphenyl	2.4	(1.1)	10.0	(0.3)
2,4-Dimethylbiphenyl	4.0	(1.9)	28.0	(0.8)
2,5-Dimethylbiphenyl	2.5	(1.2)	15.0	(0.4)
2,6-Dimethylbiphenyl	1.1	(0.5)	0.8	(0.02)
3,4-Dimethylbiphenyl	21.0	(10.1)	190.0	(5.1)
3,5-Dimethylbiphenyl	23.0	(11.0)	350.0	(9.6)
2,2'-Dimethylbiphenyl	1.9	(0.9)	2.5	(0.07)
2,3'-Dimethylbiphenyl	5.6	(2.7)	44.0	(1.2)
2,4'-Dimethylbiphenyl	2.5	(1.2)	23.0	(0.6)
3,3'-Dimethylbiphenyl	36.0	(17.3)	1000.0	(28.6)
3,4'-Dimethylbiphenyl	24.0	(11.4)	560.0	(15.5)
4,4'-Dimethylbiphenyl	4.9	(2.4)	130.0	(3.6)

* Values in brackets are expressed as percentage of the total C_1- and C_2-biphenyls.

two sets of components. No peaks due to components which belong in fraction 2 are
evident in fraction 1. In fraction 2 there are very small amounts (1%) of major
dimethylnaphthalenes carried over from fraction 1.

From the chromatogram of fraction 2 it is evident that 2,3-dimethylbiphenyl
and 2,5-dimethylbiphenyl cannot be resolved from C_3-naphthalenes using a BP-10
column. These co-elution problems can be overcome, however, by the use of BP-1
and CP Wax 57CB phases. Although the non-polar BP-1 phase enabled quantifica-
tion of 2,5-dimethylbiphenyl, unfortunately on this column 2,3'-, 2,4'-, 2,3- and
2,4-dimethylbiphenyl and 3-ethylbiphenyl were found to co-elute with C_3-naphthal-
enes. 2,3-Dimethylbiphenyl could be measured using the CP Wax 57CB phase; how-
ever, co-elution problems with C_3-naphthalenes and C_2-biphenyls occurred again,
and only 3,4-, 3,4'- and 4,4'-dimethylbiphenyl and 3-ethylbiphenyl could be mea-
sured. Therefore analyses using three phases (BP-1, BP-10 and CP Wax 57CB) are
required for analysis of all methylbiphenyls, ethylbiphenyls and dimethylbiphenyls.

The concentrations of C_1- and C_2-biphenyls in two Australian crude oils are
shown in Table I. Absolute concentrations of individual alkylbiphenyls were deter-
mined by the use of an external standard (biphenyl). The error associated with this
method of quantitation was assessed by replicate analyses and found to be $< \pm 5\%$.
From Table I, it is evident that concentrations of alkylbiphenyls in the Barrow crude
are much higher than those in the Blina crude oil. Such differences between the two

crude oils probably result from combinations of factors such as the type of organic matter from which the oils were derived, the depositional environment, the thermal history of the samples and the maturity of the source beds at the time of oil migration[1–4].

Differences in the relative concentrations of particular C_1- and C_2-biphenyl isomers are also apparent from the values for the two oils shown in Table I. In particular, *ortho* and di-*ortho* substituted isomers are present in very low concentrations, whereas the *meta*-isomers are found to be the most abundant. This variation in isomer abundance may be explained in terms of relative thermodynamic stabilities. Studies of dimethylbenzenes have shown that substitution in the *meta*-position is thermodynamically most favoured whereas the *ortho*-position is the least favoured[16]. Insofar as biphenyl can be considered as a substituted benzene, the relative thermodynamic stabilities of substituted biphenyls is predicted to be *meta* > *para* > *ortho*. Such an order is consistent with the observed distribution in the two crude oils. This correlation of relative abundance with thermodynamic stability is also observed for methyl-substituted naphthalenes, where the more stable β-substituted compounds are present in higher concentration than the less stable α-substituted compounds[1,2].

Comparison of the distributions of biphenyls for the two crude oils shows that the concentrations of *ortho*-substituted biphenyls with respect to the *meta*-substituted isomers are higher in the Blina crude than in the Barrow crude oil. Previous geochemical studies of these crude oils indicate that the sediments from which they are derived have had very different thermal histories[17,18]. This variation in levels of *ortho*-substituted compounds may therefore be a result of differences in thermal histories. If so, alkylbiphenyls may serve as useful thermal maturity indicators for crude oils and sediments.

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