

Structural Features of Boscan and Duri Asphaltenes

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The molecular structural units of Boscan and Duri asphaltenes have been investigated in ruthenium-ion-catalyzed oxidation (RICO) and pyrolysis. From the RICO reactions, homologous series of *n*-alkanoic acids (C_1 – C_{31}), representing aromatic-attached *n*-alkyl side chains, α,ω -di-*n*-alkanoic acids (C_4 – C_{26}), representing polymethylene bridges connecting two aromatic units, and benzenecarboxylic acids, indicating the major modes of aromatic condensations in the asphaltene molecules and the minor role of pericondensed aromatic structures in them, were detected and measured. The RICO reaction also yielded a nondistillable oxidized residue. Pyrolysis of this material after methylation yielded a homologous series of *n*-alkanes and *n*-alk-1-enes, *n*-alkanoic and *n*-alkenoic acid methyl esters, and free *n*-alkanoic acids with strong even-to-odd carbon preference. These products prove the presence of naphthenic-attached *n*-alkyl side chains and bridges, polymethylene bridges connecting aromatic to naphthenic systems, and *n*-alkanoic acid ester/*n*-alkanol ether side chains attached to naphthenic carbons in the asphaltene. Among the pyrolysis products of the whole asphaltene identified were homologous series of α - and α,α -*n*-alkyl-substituted thiolanes and thianes, a series of dicyclic terpenoid sulfides, along with a homologous series of 1-*n*-alkyldibenzothiophenes. In general, the nature of the products identified were the same as those found in the asphaltenes from Alberta tar sand, carbonate bitumens, heavy oils, and some immature oils from China, but their distributions showed some variance, reflecting differences in biotic source materials, source rocks, depositional environment, and diagenetic and thermal history.

Introduction

Asphaltene, the heteroatom-rich macromolecular component of petroleum capable of micellar-like aggregation even in low concentrations, may have an adverse effect on the processing of petroleum. In the recovery and movement of petroleum through pipes, precipitation of asphaltene itself or in association with waxes may cause the partial or complete blockage of flow and necessitate costly repair and cleaning operations. Also, in the refining of heavy crude oils and, in particular, in the upgrading of residues and bitumens, the presence of high concentrations of asphaltene, owing to its high heteroatom content and high molecular weight, requires more severe processing conditions and more complex technologies.

On the other hand, asphaltene precipitation may also be viewed as a beneficial natural self-upgrading process taking place in the reservoir under the influence of high-pressure reservoir gases and light paraffins, which act as precipitating agents for asphaltene and, to a lesser extent, resins. The precipitate settles to the bottom of the pooled oil, yielding a lighter supernatant crude oil.

Asphaltene, like other fractions of petroleum, contains chemically bound biomarkers which carry important information about the origin, biotic source material, and diagenetic history of the oil.

The molecular structure of asphaltene, which is the key to understanding the colloidal, solubility, thermal, and chemical properties of asphaltene, has been a contentious issue over the last 75 years. In the last two decades, however, many structural features of Athabasca (Alberta, Canada) asphaltene involving structural elements and building blocks have been recognized and isolated by thermolysis and chemolysis methods in the form of homologous series of compounds. These included *n*-alkanes, 2-*n*-alkylthiolanes and -thianes, 2,5-di-*n*-alkylthiolanes, 2,6-di-*n*-alkylthianes, 2- and 4-*n*-alkylbenzothiophenes, 2,4-di-*n*-alkylbenzothiophenes, 1-*n*-alkyldibenzothiophenes, 9-*n*-alkylfluorenes, etc.^{1,2} Thus, the structure of such random organic geomacromolecules is highly complex and represents a considerable challenge to its structural elucidation.

Both asphaltenes investigated in the present study, Boscan asphaltene derived from a marine source rock (Type II) from Venezuela and Duri asphaltene derived from a lacustrine source rock (Type I) from Indonesia, have been studied before by pyrolysis³ and transalky-

(1) Payzant, J. D.; Lown, E. M.; Strausz, O. P. *Energy Fuels* **1991**, *5*, 445–453.

(2) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M. *Fuel* **1992**, *71*, 1355–1363.

(3) (a) Behar, F.; Pelet, R. *J. Anal. Appl. Pyrolysis* **1984**, *7*, 121–135. (b) Behar, F.; Pelet, R.; Roucaché, J. *Org. Geochem.* **1984**, *6*, 587–595.

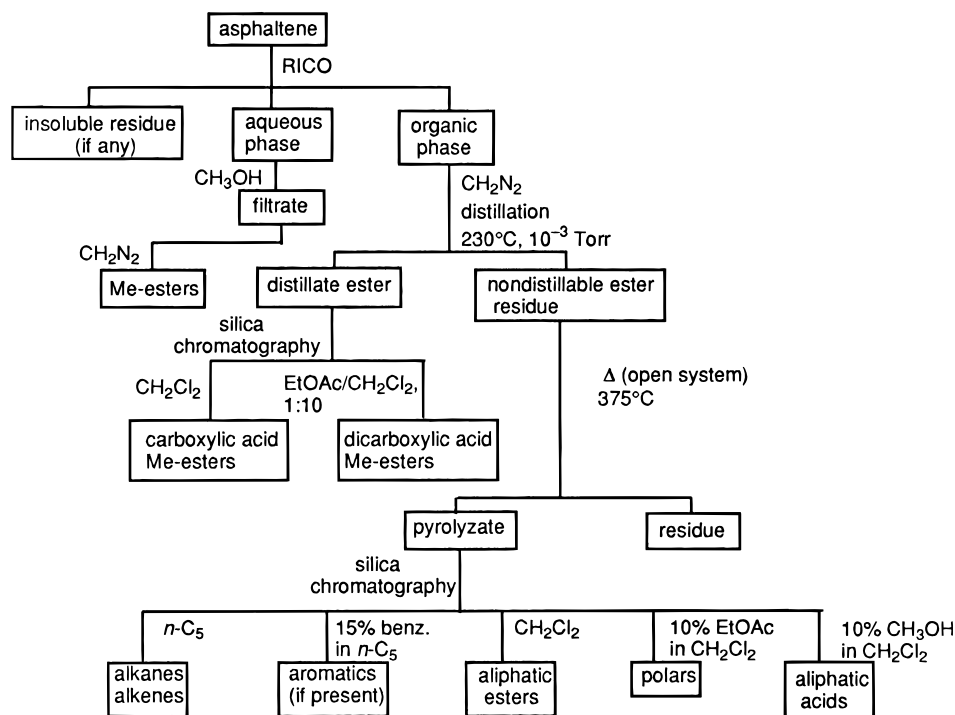


Figure 1. Flowchart showing the chromatographic/thermal/chemical procedures.

lation.⁴ The product recoveries in these types of operations, however, are generally low and do not provide an account of the functional types and amounts of alkyl moieties in the asphaltene structure. Therefore, we have undertaken a more detailed examination of the molecular structure of these two asphaltenes in order to obtain a more complete description of their alkyl moieties as well as other structural details, thereby extending our molecular structural knowledge of petroleum asphaltene.

Experimental Section

Sample Description. Asphaltene precipitation was done with *n*-heptane, followed by a 10-min reflux. The slurry was filtered, and the precipitated asphaltene was taken up from the filter with chloroform. After filtration and evaporation of the solvent, precipitation with *n*-heptane was repeated.

Analytical data characterizing the Boscan and Duri asphaltenes investigated in this study are as follows:

	elemental composition (wt %)					MMp/GPC (g mol ⁻¹)
	C	H	N	O	S	
Duri	87.35	8.22	1.47	2.07	0.39	8200
Boscan	81.10	7.79	1.11	1.43	6.10	10000
pyrolysis yields, wt % at 550 °C						
	total				saturates + unsaturates	
Duri	40				16	
Boscan	50				11	

Materials. Dichloromethane (CH₂Cl₂) and carbon tetrachloride (CCl₄) were distilled from calcium hydride. Methanol and ethyl acetate (EtOAc) were distilled prior to use. Other chemicals were used without further purification. Column chromatography was done on silica gel 60 (Terochem Laboratories, particle size 0.063–0.200 mm, activity according to Brockman 2–3).

GC-FID Analysis. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5730A gas chromatograph with a 18850A GC terminal in the flame ionization mode. A 30 m × 0.252 mm J&W fused silica capillary column coated with 0.25 μm DB-1 was used. In most experiments the gas chromatograph was programmed at a rate of 10 °C/min to 300 °C with the initial temperature set at 50 °C.

GC-MS Analysis. For gas chromatographic-mass spectrometric (GC-MS) analysis, a Varian Vista gas chromatograph with a splitless injector and helium carrier gas was used along with a J&W fused silica column (30 m × 0.32 mm coated with 0.25 μm DB-1). Samples were injected in the form of a toluene solution. The GC was temperature programmed from 50 to 300 °C at a rate of 10 °C/min. The end of the column was introduced into the ion source of a VG 7070E mass spectrometer. Typical mass spectrometer operating conditions were as follows: transfer line 290 °C, ion source 250 °C, electron energy 45 eV. Data acquisition was done with a PDP 11/24 computer using VG11-250 software. The mass range, *m/z* 50–600 Daltons, was scanned every 0.5 s.

FTIR Analysis. The Fourier transform infrared spectra were recorded on a Nicolet 7199 instrument in the transmittance mode. The spectra were obtained as a CH₂Cl₂ cast.

Ruthenium-Ion-Catalyzed Oxidation (RICO) and Recovery of Products.⁵ A flowchart representation of the procedure is depicted in Figure 1. In a typical oxidation experiment, 300 mg of the asphaltene, 3.4 g of NaIO₄, 10–15 mg of RuCl₃·3H₂O, 30 mL of CCl₄, 20 mL of CH₃CN, and 30 mL of H₂O were added to a 125-mL Erlenmeyer flask equipped with a magnetic stirrer. The heterogeneous solution was stirred vigorously for 18 h at room temperature. The initial black solution slowly converted to a light tan color. The solution was poured into a separatory funnel, and the two phases were separated. The lower organic phase was washed with ~20 mL of H₂O and the aqueous phase with ~20 mL of

(4) Desbène, P.-L.; Abderrezag, A.; Desmazières, B.; Basselier, J.-J.; Behar, F.; Vandenbroucke, M. *Adv. Org. Geochem.* **1989**, *16*, 969–980.

(5) Mojelsky, T. W.; Ignasiak, T. M.; Frakman, Z.; McIntyre, D. D.; Lown, E. M.; Montgomery, D. S.; Strausz, O. P. *Energy Fuels* **1992**, *6*, 83–96.

CH_2Cl_2 . The CH_2Cl_2 washings were combined with the original CCl_4 extract and termed the organic layer. The two aqueous solutions were combined and called the aqueous layer.

The organic layer was directly reacted with 50 mL of ethereal diazomethane solution. After standing with periodic gentle swirling, the solution was concentrated by passing a stream of nitrogen gas onto the surface. When the volume was reduced by about one-fourth, the solution was dried over Na_2SO_4 , filtered, and subjected to further concentration under nitrogen to a final volume of 1.0 mL.

Next, the concentrate was transferred to the well of the thick-walled sublimation apparatus (7 cm in diameter and 20 cm deep). The coldfinger, when inserted, was 3 cm from the inner well surface. The inside of the well was lined with a layer of glass beads. Dry ice/acetone was added to the coldfinger. The entire apparatus was immersed in an oil bath which was heated to 230 °C while being evacuated ($\sim 10^{-3}$ Torr). The distillable esters were collected on the outer surface of the coldfinger. They were washed off with CH_2Cl_2 then dried (anhydrous Na_2SO_4) and concentrated. The undistillable esters were removed from the glass beads by dissolution in CH_2Cl_2 .

(i) *n*- C_{5+} Alkanoic and C_{7+} α,ω -Dialkanoic Acids. The organic concentrate of distillable methyl esters was chromatographed on 20 g of silica gel 60 prepared as a slurry in CH_2Cl_2 . The concentrate was eluted initially with 100 mL of CH_2Cl_2 and then with 100 mL of 10% EtOAc in CH_2Cl_2 . Care was taken to concentrate the two eluant fractions. A gentle stream of nitrogen gas was blown onto the surface of the solvent until the final volume was 1.0 mL. To an aliquot of each was added a volume of *n*- C_{24} alkane in such a quantity that its GC peak would be comparable in area to the most intense ester peak. The peak areas were taken directly from the gas chromatograph integrator.

For the *n*-alkanoic acid esters, methyl decanoate was used as the standard and its response factor was applied for the quantitative estimation of the esters from methyl pentanoate to methyl tetradecanoate. The response factor for methyl octadecanoate was used to estimate the quantities of the remaining *n*-alkanoic acid esters.

For the α,ω -diacid esters, the same technique was employed except that the dimethyl octanedioate response factor was used to evaluate the diacid esters up to C_{12} . The remaining esters were estimated using the response factor obtained from the standard dimethyl tridecanedioate.

(ii) *Benzenepolycarboxylic Acids and C₄–C₇ α,ω -Dicarboxylic Acids*. The aqueous layer was diluted with 100 mL of CH_3OH . After standing for 3 h, the solid was filtered and washed with 10 mL of CH_3OH . The cooled and stirred combined filtrates were treated with ethereal diazomethane 3 times, separating the two layers after each addition. The extracts were dried (Na_2SO_4), filtered, and concentrated to 1.0 mL under a gentle stream of nitrogen gas. An aliquot was combined with a known aliquot of *n*- C_{24} alkane as an internal standard. The response factor of dimethyl adipate was used to estimate the quantities of dimethyl succinate to dimethyl octanedioate.

(iii) *C₂–C₄ n-Alkanoic Acids*. The two asphaltene samples (300 mg portions) were subjected to RICO as previously described. The reaction product mixture was separated into the organic and aqueous layers. The organic portion was extracted in a separatory funnel with 20 mL of water in which four pellets of KOH were dissolved. The layers were separated, and the organic portion was washed with 20 mL of water. The combined aqueous extracts were concentrated on the rotary evaporator. The original aqueous layer from the oxidation reaction was mixed with 100 mL of CH_3OH and permitted to stand 2–3 h. The precipitated inorganic salts were filtered and washed with a fresh 20-mL aliquot of CH_3OH . The combined filtrates were reacted with four pellets of KOH and concentrated on the rotary evaporator. Since the methyl esters of these acids are very volatile, the acids were converted to higher molecular weight esters, namely phenacyl esters (see below).

In the quantitation of acetic acid, the cosolvent $\text{CH}_3\text{CH}_2\text{CN}$ was substituted for CH_3CN , which under RICO conditions undergoes partial hydrolysis and/or oxidation to acetic acid.

The basic concentrates of the organic and aqueous layers were carefully neutralized with 5% aqueous HCl. When neutral, an extra drop of HCl solution was added to each. The volume was adjusted to 5 mL. The aqueous solution was transferred to a 100-mL round-bottom flask equipped with a magnetic stirrer. A 15-mL ethanol solution of 80 mg of phenacyl bromide⁶ recrystallized from ethanol was added, and the solution was heated to reflux for 3 h. Upon cooling, the solution was concentrated and the concentrate was extracted with ether (2×20 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated.

The concentrates of the aqueous and organic layers of each asphaltene sample were made up to 1.0 mL with toluene. An aliquot from each was combined with a volume of *n*- C_{18} alkane of known concentration, so that the area of the peak of the largest phenacyl ester was similar to that of the hydrocarbon standard. The solutions were analyzed under isothermal conditions at a 170 °C column temperature. For calibration, standards of each ester (acetic, propanoic, and butanoic) were synthesized.

Pyrolysis of Undistillable Ester Residues. The asphaltene samples were oxidized as previously described,⁵ except that 500-mg sample sizes were used and the quantities of other reagents were increased proportionately.

The reactor for the pyrolysis consisted of a 125-mL Erlenmeyer flask to which was fused a 20-cm tube of 2.5 cm diameter. A 24/40 ground-glass joint was located at the opposite end of the tube. Near the top of the flask was fused a second tube of 1-cm diameter. This tube extended vertically 15 cm prior to bending and then ran a further 20 cm perpendicular to the fused tube. A ground-glass joint fitting directly into the receiver was located at the tip of the tube.

The entire reactor was immersed into a sandbath kept at 375 ± 3 °C. To the 2.5-cm wide tube bearing the 24/40 joint was attached a dropping funnel. The receiver was cooled in a dry ice–acetone bath. From one outlet of the three-necked receiver was attached a condenser. The other end of the condenser directed the gas stream through a bubbler containing aqueous KOH. Finally, the gas stream was passed through a tower of solid KOH to absorb any residual H_2S . Nitrogen gas flow was introduced at the top of the dropping funnel.

The undistillable ester residue to be pyrolyzed was dissolved in 25 mL of toluene, and the solution was added to the dropping funnel. A flow of nitrogen at 30 mL/min was maintained. The toluene solution was introduced down the column into the Erlenmeyer flask at a rate of about 20 drops/min (~ 15 s residence time). The pyrolysates were yellowish in color. A CH_2Cl_2 solution of the pyrolysates was dried (Na_2SO_4), filtered, and concentrated.

The concentrate was chromatographed on 20 g of silica gel 60. Aliquots of 100-mL *n*-pentane, 20% toluene in pentane, CH_2Cl_2 , 10% EtOAc in CH_2Cl_2 , and 10% CH_3OH in CH_2Cl_2 were used for elution, giving *n*-alkanes + *n*-alk-1-enes (*n*-pentane), alkyl + alkenyl esters (CH_2Cl_2), and carboxylic acids (10% EtOAc in CH_2Cl_2).

Pyrolysis of Boscan Asphaltene. A 690-mg sample of Boscan asphaltene was dissolved in 40-mL toluene. This solution was subjected to open-system pyrolysis using the apparatus described above for the pyrolysis of undistillable esters. As in previous studies,¹ the sand bath was kept at 430 °C. Nitrogen flow at 30 mL/min was maintained through the apparatus. The asphaltene solution was introduced from the dropping funnel at a rate of 20 drops/min. The pyrolysate from the dry ice–acetone cooled receiver was dried over anhydrous Na_2SO_4 , filtered, and concentrated to yield a reddish-brown material, 204 mg ($\sim 30\%$ of the asphaltene).

(6) Rather, J. B.; Reid, E. E. *J. Am. Chem. Soc.* **1919**, *41*, 75–83

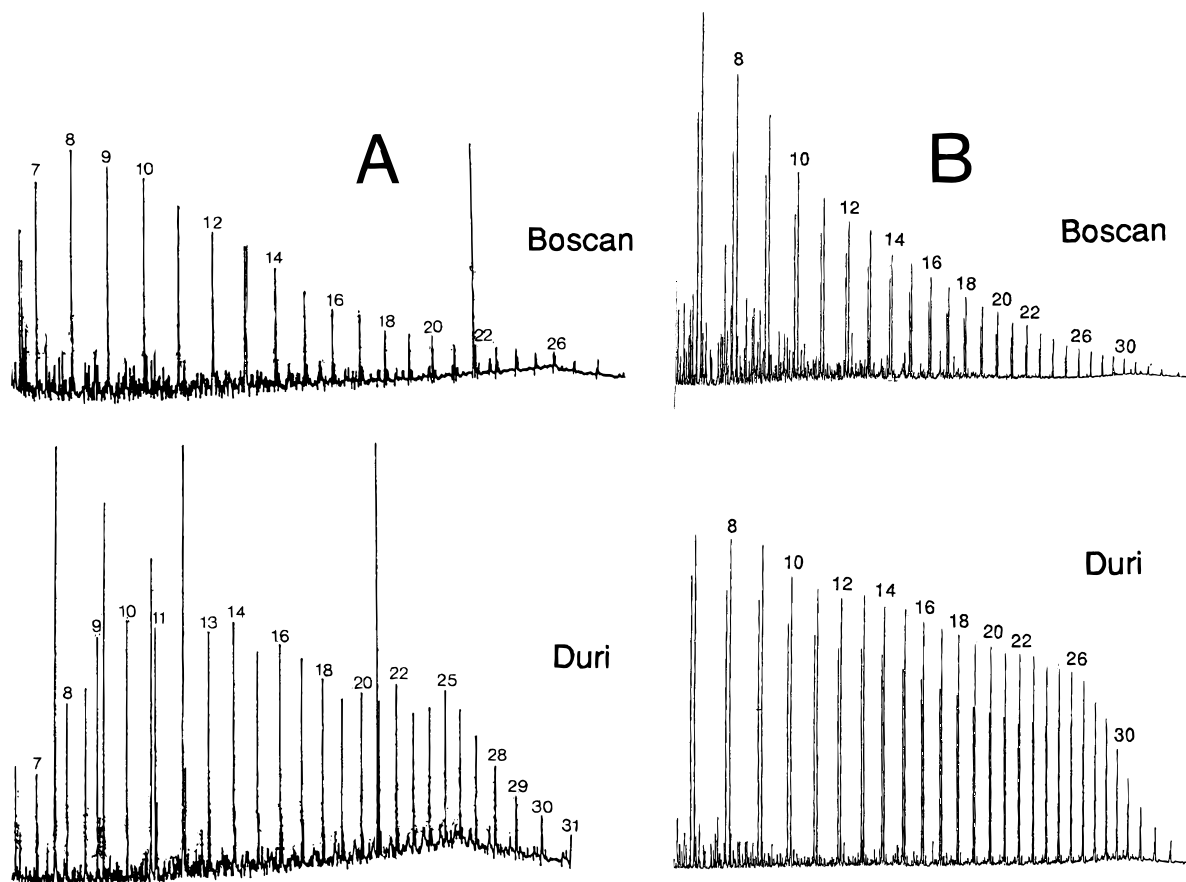


Figure 2. (A) Total ion current mass chromatograms of *n*-alkanoic acid methyl esters by RICO from the organic phase. The numbers refer to the carbon numbers of the acids. (B) Gas chromatograms of the alkanes and alkenes generated from the pyrolysis (600 °C) of the asphaltenes.

(i) *Removal of Alkenes.* The alkenes that result from the pyrolysis were converted to alcohols by hydroboration–oxidation with $\text{BH}_3\cdot\text{THF}$, H_2O_2 , and KOH . The polar alcohols were separated from the nonpolar residual alkanes, aromatics, and sulfur compounds using column chromatography on silica gel.

(ii) *Isolation of Sulfides.* The nonpolar eluants from section i were oxidized selectively with *tert*-butylammonium periodate to convert the sulfides to sulfoxides.⁷ The polar sulfoxides were separated from the saturates, aromatics, and thiophenes of the pyrolysate using column chromatography. After separation, the sulfoxides were reduced with lithium aluminum hydride (LiAlH_4) in dioxane. The sulfides were separated by column chromatography, being eluted with 20% toluene/pentane, yielding 2 mg (1% of pyrolysate) of sulfides.

(iii) *Isolation of Thiophenes.* The nonpolar eluant from the isolation of sulfides was oxidized with *m*-chloroperbenzoic acid as described previously.⁷ The thiophenes were converted to sulfones, which are polar and easily separable from the remainder of the pyrolysate by column chromatography. Next, the isolated sulfones were reduced by refluxing with LiAlH_4 in dioxane for 1 h. The thiophenes (3 mg, 1.5% of pyrolysate) were eluted with 50% toluene/pentane on 20 g of silica gel 60.

Results and Discussion

Ru(VIII)-Ion-Catalyzed Oxidation (RICO). Both the Duri and Boscan samples were subjected to RICO. The oxidation proceeded smoothly; however, in the case of the Duri sample, some complication was encountered in that a water- and CH_2Cl_2 -insoluble interfacial mate-

rial was formed. An ash determination revealed that this material contained 18.6% ash! Up to 16% of the Duri asphaltene, containing 14% organic material (C, 58.9%; H, 5.3%; S, 1.4%; O, 29.3%; $(\text{H/C})_a$, 1.08) based on the asphaltene, was not converted into organic or water-soluble material. Neither the Boscan nor any of the previously studied Alberta oil sand asphaltenes produced insoluble matter, and this behavior appears to be unique for the Duri asphaltene. The IR spectrum of this insoluble material revealed carboxylic, alcoholic, and perhaps phenolic hydroxyl and naphthenic hydrocarbon structural elements, along with smaller amounts of aromatics.

Ruthenium ions in the +8 oxidation state are effective oxidants of aromatic carbon. The alkyl chains attached to aromatic groups are liberated as alkanolic acids,⁵ which separate into the solvents of the reaction product mixture in which they are soluble. Accordingly, the *n*-alkanoic acids and the higher homologues of α,ω -dialkanoic acids formed from alkyl bridges connecting two aromatic carbons appear in the organic phase and the lower homologues of the α,ω -dicarboxylic acids and the benzenepolycarboxylic acids from the oxidation of condensed aromatic rings, in the water phase. Acetic, propanoic, and butanoic acids partition between the solutions. For identification purposes, the acids are converted to methyl esters cleanly and quantitatively by reaction with ethereal diazomethane and chromatographed on silica gel. The *n*-alkanoic methyl esters are readily eluted with dichloromethane, and the α,ω -

(7) Payzant, J. D.; Mojelsky, T. W.; Strausz, O. P. *Energy Fuels* **1989**, 3, 449–454.

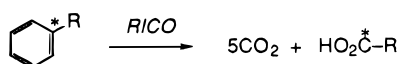
Table 1. Determination of *n*-Alkyl Groups Attached to Aromatic Moieties of Boscan and Duri Asphaltene

<i>n</i> -alkyl group	no. of alkyl groups per 100 C atoms in asphaltene		no. of C atoms per 100 C atoms in asphaltene	
	Boscan	Duri	Boscan	Duri
C ₁	0.558 ^a	0.412 ^a	0.558	0.412
C ₂	0.204 ^a	0.171 ^a	0.408	0.342
C ₃	0.154 ^a	0.087 ^a	0.462	0.262
C ₄	0.150 ^b	0.142 ^b	0.540	0.540
C ₅	0.123 ^b	0.111 ^b	0.600	0.600
C ₆	0.107	0.107	0.642	0.642
C ₇	0.084	0.099	0.588	0.693
C ₈	0.063	0.064	0.504	0.672
C ₉	0.050	0.046	0.450	0.414
C ₁₀	0.037	0.045	0.370	0.450
C ₁₁	0.027	0.038	0.292	0.418
C ₁₂	0.021	0.035	0.252	0.420
C ₁₃	0.016	0.033	0.208	0.429
C ₁₄	0.019	0.050	0.266	0.700
C ₁₅	0.014	0.037	0.210	0.555
C ₁₆	0.011	0.031	0.176	0.496
C ₁₇	0.007	0.025	0.119	0.425
C ₁₈	0.006	0.020	0.108	0.360
C ₁₉	0.005	0.019	0.095	0.361
C ₂₀	0.003	0.015	0.060	0.300
C ₂₁	0.003	0.014	0.063	0.294
C ₂₂	0.002	0.013	0.044	0.286
C ₂₃	0.002	0.009	0.046	0.207
C ₂₄	0.001	0.009	0.024	0.216
C ₂₅	0.001	0.006	0.025	0.150
C ₂₆	0.001	0.003	0.026	0.078
total	1.67	1.64	7.14	10.7

^a Determined as phenacyl esters. ^b Interpolated values.

dicarboxylic acid esters are eluted with 10% ethyl acetate in dichloromethane, Figure 1.

(i) *Determination of Alkyl Side Chains Attached to Aromatic Carbons.* Alkyl side chains attached to aromatic carbons in the asphaltene molecule can be converted to alkanic acids by RICO as shown before.⁵ Unsubstituted aromatic carbons are selectively oxidized to carbon dioxide and alkyl-substituted aromatic carbons to alkanic acids, the site of attachment becoming the carboxylic carbon:



If the R groups are *normal* alkyl groups, then the resultant acids form a series of *n*-alkanoic acids. This is indeed the case with both samples. Some methyl-branched and cycloalkyl acids are also formed, but their quantities are significantly lower than those of the *n*-acids. The monocarboxylic acids were separated from the other products, as described in the Experimental Section and illustrated in Figure 1, and quantified by gas chromatography in the form of methyl esters, except for the C₂–C₄ members which were measured as their phenacyl esters, RCO₂CH₂C(O)Ph. Illustrative gas chromatograms of the methyl esters from the organic phase are presented in Figure 2 (the light ends, i.e., <C₁₄, of the esters are seriously depleted because of volatility losses and partial solubility in the aqueous phase), and the combined quantitative data derived from the organic and aqueous phases are tabulated in Table 1. The total number of *n*-alkyl groups in the Duri sample is 1.64, and the number of carbon atoms in them is 10.7 per 100 C in the asphaltene. The corresponding numbers for the Boscan asphaltene are 1.67 and 7.14 per 100 C in the asphaltene. This is in line with the combined

Table 2. Aromatic-Attached *n*-Alkyls in Petroleum Asphaltenes: Side Chains and Methylene Bridges

sample	no. of <i>n</i> -alkyls per 100 C	no. of C atoms per 100 C	average chain length
Duri	1.64	10.7	6.5
Boscan	1.67	7.14	4.3
Athabasca	1.84	9.2	5.0

	no. of bridges per 100 C	no. of C atoms per 100 C	average chain length
Duri	1.0	7.8	7.3
Boscan	0.58	3.8	6.4
Athabasca	0.61	3.8	6.3

yields of saturates and unsaturates at 550 °C, which are 16% and 11% for the Duri and Boscan samples, respectively. Thus, the number of aromatic-attached *n*-alkyl groups in the two samples is about the same, but the number of carbon atoms in the Duri sample substituents is larger; in other words, the average length of the *n*-alkyl side chains is greater in the Duri asphaltene by about a factor of 1.5. Another difference between the two samples is that the distribution of the *n*-alkanoic acids from the Boscan asphaltene is fairly smooth, as in the case of Alberta oil sand asphaltenes, but the distribution from the Duri asphaltene appears to show a slight preference for the even carbon number acids between C₁₁ and C₂₃. Beyond C₂₃, however, the distribution becomes smooth, maximizing at C₂₆. In the case of the Alberta asphaltenes, a slight preference was found for the C₁₆ and C₁₈ acids; this was due to either the presence of free *n*-C₁₆ and *n*-C₁₈ acids and salts in the asphaltene, which are liberated in the RICO, or slight hydrolysis of saturated attached *n*-alkanoic acid esters in the asphaltene. No such interferences were observed in the samples studied here. A point of particular interest with regard to chain-length distributions is the similarity between the RICO results for *n*-alkanoic acid methyl esters and the pyrolysis results for *n*-alkanes/*n*-1-alkenes shown in Figure 2.

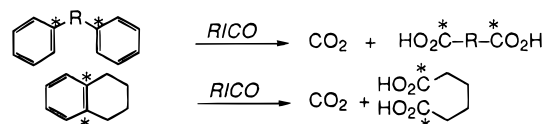
In both samples studied, the methyl group is the most abundant alkyl substituent on the aromatic carbon and the concentrations of the higher *n*-alkyl groups monotonically decline with increasing length of the alkyl chain, first rapidly, then more gradually up to C₃₀–C₃₁ and probably beyond. This trend parallels that established before for Athabasca asphaltene and points to the generality of the aromatic-attached *n*-alkyl side chain as a structural element in native petroleum asphaltene. The three asphaltenes studied quantitatively and the Peace River, Lloydminster, and Carbonate Triangle asphaltenes studied qualitatively⁵ in RICO all contain aromatic-attached *n*-alkyls in similar but somewhat differing amounts and distributions, Table 2. The two Type II kerogen-derived oils, Athabasca and Boscan, appear to have somewhat shorter average chain lengths than the Type I kerogen-derived Duri oil. Undoubtedly, a fraction of the *n*-alkanes + *n*-alk-1-enes, which are major hydrocarbon products in the open-system pyrolysis of all native asphaltenes studied thus far, Table 3, come from the decomposition of the *n*-alkyl aromatic structural elements of the asphaltene molecules. Pyrolysis is a complex random process upon which some selectivity is conferred by thermodynamic and kinetic effects, whereas the chemolysis of RICO is a highly

Table 3. Asphaltene Pyrolyses Reported in the Literature

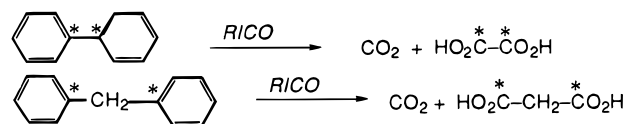
source and type	ref
Prudhoe Bay, Alaska, USA; conventional oil	Rubinstein, I.; Spyckerelle, C.; Strausz, O. P. <i>Geochim. Cosmochim. Acta</i> 1979 , 43, 1–6.
Pembina, Judy Creek, Lomell, Alberta, Canada; conventional oils	Ekwenchi, M. M.; Lown, E. M.; Montgomery, D. S.; Strausz, O. P. <i>AOSTRA J. Res.</i> 1984 , 1, 127–137.
Athabasca, Wabasca, Peace River, Cold Lake, Lloydminster, Alberta, Canada; oil sand bitumens. Sunnyside, Utah, USA; oil sand bitumen	Strausz, O. P.; Jha, K. N.; Montgomery, D. S. <i>Fuel</i> 1977 , 56, 114–120.
Athabasca, Alberta, Canada; oil sand bitumen	Payzant, J. D.; Lown, E. M.; Strausz, O. P. <i>Energy Fuels</i> 1991 , 5, 445–453. Ritchie, R. G. S.; Roche, R. S.; Steedman, W. <i>Fuel</i> 1979 , 58, 523–530.
Douk Daka, Congo basin, West Africa; heavy oil	Jones, D. M.; Douglas, A. G.; Connan, J. <i>Energy Fuels</i> 1987 , 1, 468–476.
Boscan, Cerro Negro, Machete, Orucual, Venezuela; heavy oils	Cassani, F.; Eglinton, G. <i>Chem. Geol.</i> 1986 , 56, 167–183. Behar, F.; Pelet, R. J. <i>Anal. Appl. Pyrol.</i> 1984 , 7, 21–135.
Hassi Messaoud, Algeria; conventional oil	Huc, A.-Y.; Behar, F.; Roussel, J.-C. 1st Int. Symp. Heavy Crude Oils Petroleum Residues, Lyon, 1984, pp 438–443. Behar, F.; Pelet, R. J. <i>Anal. Appl. Pyrol.</i> 1984 , 7, 21–135. Huc, A.-Y.; Behar, F.; Roussel, J.-C. 1st Int. Symp. Heavy Crude Oils Petroleum Residues, Lyon, 1984, pp 438–443.
Anguille, Gabon; medium heavy oil. Bati-Raman, Turkey; heavy oil. Emeraude, Congo; heavy oil	Seifert, W. K.; Moldovan, J. M. <i>Geochim. Cosmochim. Acta</i> 1981 , 45, 783–794. Huc, A.-Y.; Behar, F.; Roussel, J.-C. 1st Int. Symp. Heavy Crude Oils Petroleum Residues, Lyon, 1984, pp 438–443.
Pematang, China	Huc, A.-Y.; Behar, F.; Roussel, J.-C. 1st Int. Symp. Heavy Crude Oils Petroleum Residues, Lyon, 1984, pp 438–443.
Duri, Indonesia; aromatic, intermediate	

selective one. Consequently RICO is a superior method, and its results are more representative of the distribution of alkyl moieties attached to the aromatic structures of asphaltene and petroleum than are pyrolysis results. Moreover, in most of the reported open-system pyrolysis studies, the light ends of the alkane products (C_1 – C_{6-10}) were lost completely and the middle portions (C_7 – C_{16}) may have been partially lost during handling and analysis. When the light end is recovered,^{8–10} methane is the most abundant hydrocarbon product or one of the most abundant products (in mole percent) followed by C_2 – C_4 hydrocarbons and the yields of higher n -alkanes (+ n -alk-1-enes) monotonically decline, not unlike in the case of RICO products. In fact, as mentioned before, there is surprisingly good agreement in the shapes of the distribution envelopes from RICO and pyrolysis.^{3b} The activation energies for the formation of individual n -alkanes are temperature dependent,^{8–10} signaling a complex mechanism and multiple sources of individual products. Despite all these complications, which were found to be absent in the closed-system pyrolysis of kerogen,¹¹ the n -alkane/ n -alk-1-ene distribution from the pyrolysis of asphaltene may be advantageously employed as a rapid comparative method for organic geochemical purposes.

(ii) *Determination of Methylene Bridges Connecting Two Aromatic Units.* A methylene chain which connects two aromatic units together is converted on RICO to a diacid. If the chain is *normal* then the resultant diacid will be an α,ω -di- n -acid:



Accordingly, the oxidation products from both samples contained homologous series of α,ω -di- n -acids, Figure 3 and Table 4. These diacids are partitioned between the organic and water phases of the reaction mixture. Almost all C_8 and higher acids are present in the organic phase, the C_7 and C_6 acids are in both phases, and the C_4 and C_5 acids are in the water phase. Lower acids such as oxalic and malonic acids, the expected products from the RICO of the biphenyl (diaryl) and diaryl methane linkages,



if formed, would be oxidized further⁵ by the Ru(VIII) ions, and therefore, RICO is not suitable for the determination of these functionalities. Nonetheless, the presence of diaryl linkages is proven by the appearance of certain isomers of the benzenetri- and tetracarboxylic

(8) Strausz, O. P.; Jha, K. N.; Montgomery, D. S. *Fuel* **1977**, 56, 114–120.

(9) Ritchie, R. G. S.; Roche, R. S.; Steedman, W. *Fuel* **1979**, 58, 523–530.

(10) Ekwenchi, M. M.; Lown, E. M.; Montgomery, D. S.; Strausz, O. P. *AOSTRA J. Res.* **1984**, 1, 127–137.

(11) Behar, F.; Vandenbroucke, M.; Tang, Y.; Marquis, F.; Espitalié, J. *Org. Geochem.* **1997**, 26, 321–339.

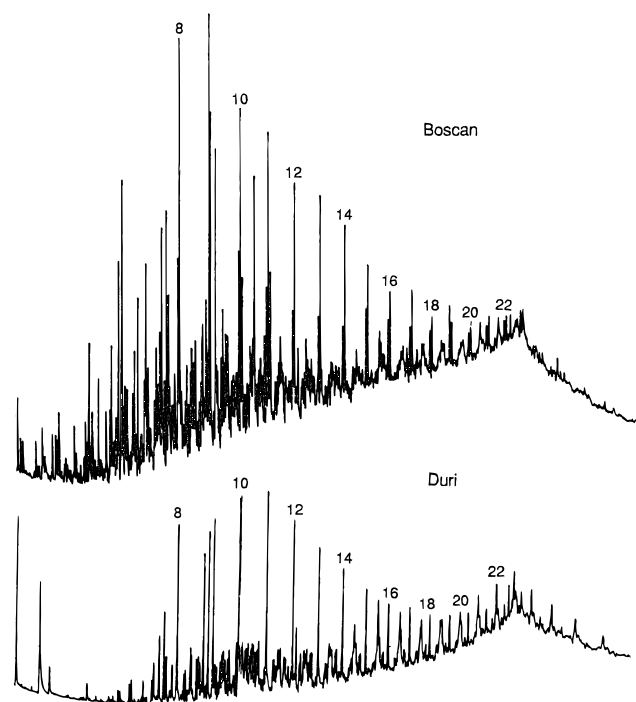


Figure 3. Gas chromatograms of α,ω -di-*n*-alkanoic acid methyl esters from the organic phase.

Table 4. Determination of Methylene Bridges between Aromatic Moieties in Boscan and Duri Asphaltene

bridge length	no. of bridges per 100 C atoms in asphaltene		no. of C atoms per 100 C atoms in asphaltene	
	Boscan	Duri	Boscan	Duri
C ₂	0.076	0.084	0.152	0.168
C ₃	0.083	0.120	0.249	0.360
C ₄	0.063	0.102	0.252	0.408
C ₅	0.061	0.097	0.305	0.485
C ₆	0.060	0.093	0.360	0.558
C ₇	0.058	0.081	0.406	0.567
C ₈	0.041	0.092	0.328	0.736
C ₉	0.035	0.086	0.315	0.774
C ₁₀	0.026	0.069	0.260	0.690
C ₁₁	0.023	0.054	0.253	0.594
C ₁₂	0.018	0.042	0.216	0.504
C ₁₃	0.012	0.030	0.156	0.390
C ₁₄	0.008	0.022	0.112	0.308
C ₁₅	0.005	0.018	0.075	0.270
C ₁₆	0.004	0.013	0.064	0.208
C ₁₇	0.005	0.011	0.085	0.187
C ₁₈	0.002	0.009	0.036	0.162
C ₁₉	0.001	0.007	0.019	0.133
C ₂₀	0.001	0.004	0.020	0.080
C ₂₁₋₂₃			~0.100	
C ₂₁₋₂₆				~0.200
total	0.58	1.03	3.76	7.78

acids among the benzenepolycarboxylic acid products, as discussed later.

The length of the polymethylene bridges connecting two aromatic units extends from C₀ to C₂₃₋₂₆. As found in the case of Alberta oil sand asphaltenes, the concentration of the C₂ unit is somewhat less than that of the C₃ unit but from C₃ on the concentration decreases monotonically within experimental error. The strength of the benzylic C–C bond in diarylethane is considerably weaker than the C–C bond in more extended bridges, and therefore, its reactivity would be considerably higher. Thus, it could be argued that the low concentration of the C₂ bridge is due to its elevated reactivity in

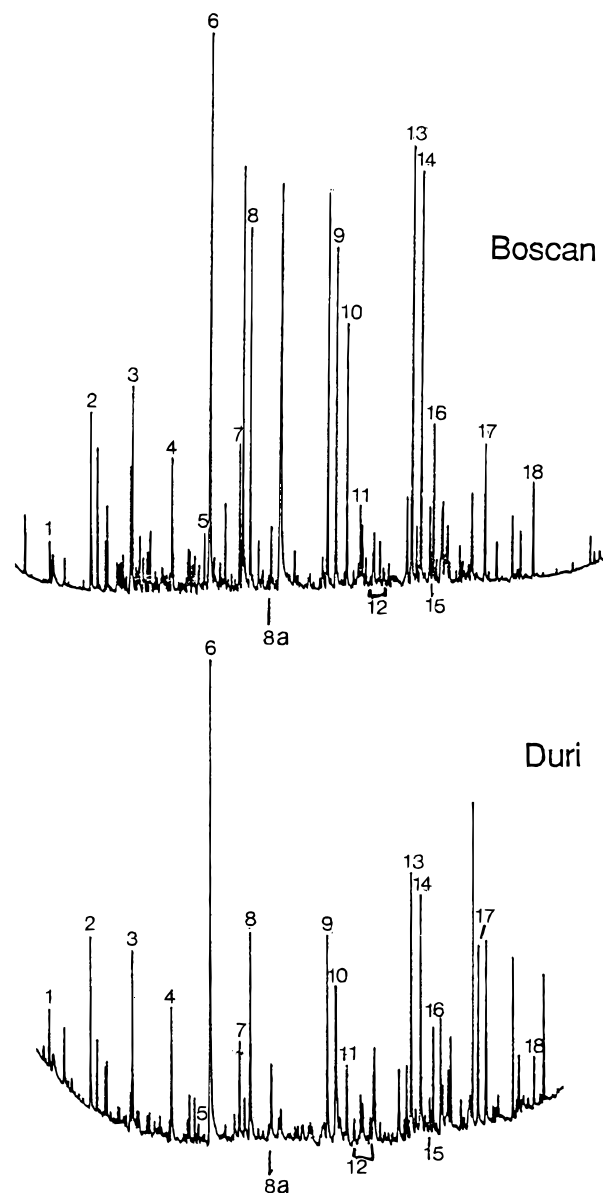


Figure 4. Gas chromatograms of the benzenepolycarboxylic acid methyl esters. For peak assignments see Table 5.

undergoing thermal C–C cleavage to form two benzylic radicals or in donating hydrogen atoms to free radicals. For similar reasons, the concentration of C₁ bridges would be expected to be low as well.

The total number of bridges per 100 C in the asphaltene, 1.0 and 0.58 in the Duri and Boscan sample, respectively, is less than the total number of *n*-alkyl side chains, and the number of carbon atoms in the bridges is also less, 7.8 and 3.8 per 100 C in the asphaltene. The corresponding values for Athabasca asphaltene are 0.61 and 3.8. These features appear to be characteristic properties of all asphaltenes from thermally mature crude oils studied by RICO thus far. As previously noted, the Boscan and Athabasca asphaltenes derived from Type II source rocks show similar values for the length of their *n*-alkyl side chains, which on the average is somewhat shorter than the length in the Duri asphaltene, obtained from Type I source rocks. In the case of polymethylene bridge substituents, the former two asphaltenes feature a nearly identical number of bridges and carbon atoms whereas the latter asphaltene

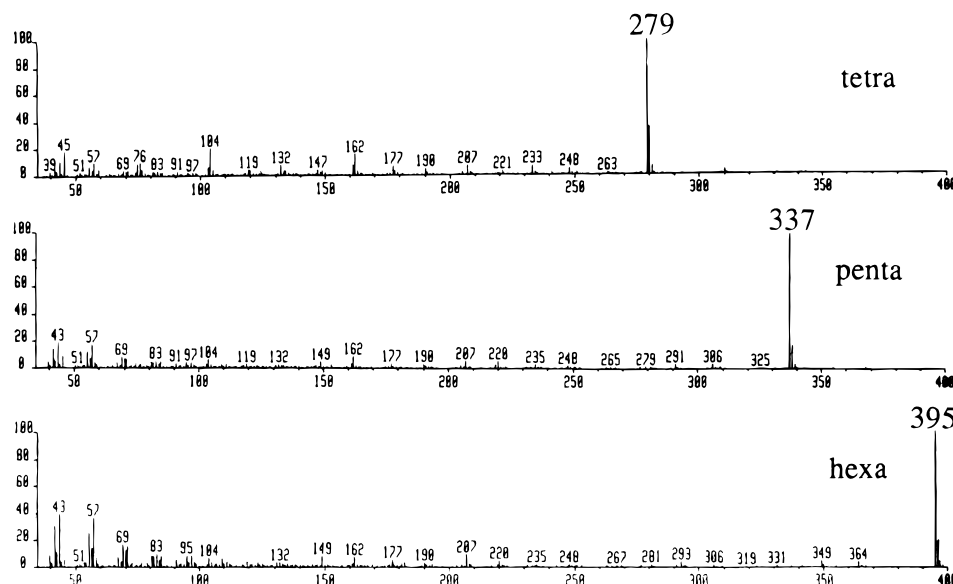
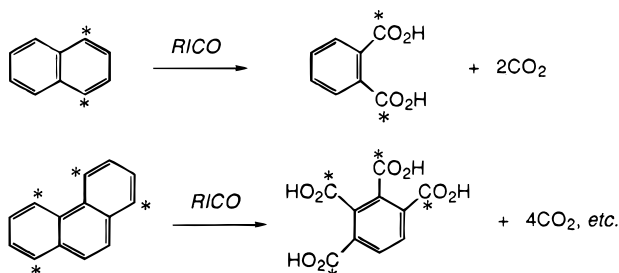


Figure 5. Mass spectra of the methyl esters of benzenetetra-, benzenepenta-, and benzenehexacarboxylic acids.

is again different, having nearly twice as many bridges and carbon atoms in them. Whether these trends reflect characteristic attributes of Type I and Type II source rock-derived asphaltenes cannot be assessed with any certainty in the absence of a more extensive database.

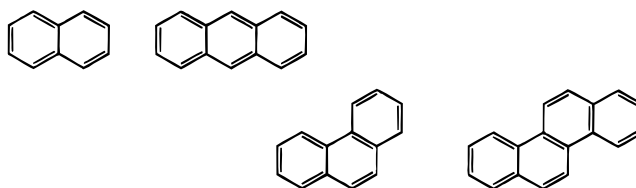
The smaller peaks appearing in the gas chromatograms between the diacid ester peaks are *n*-monocarboxylic acid and branched carboxylic acid esters. These are relatively more important in the Boscan products, Figure 3.

(iii) *Benzenecarboxylic Acids.* A third group of acids produced in the RICO of petroleum asphaltenes comprises benzenedi- through hexacarboxylic acids and their monomethyl derivatives, Figures 4 and 5. The structural assignments are listed in Table 5. The combined yield of these products is small, of the order of 0.6–2% of the asphaltene. These acids are the oxidized residues of condensed aromatic nuclei which were present in the asphaltene:



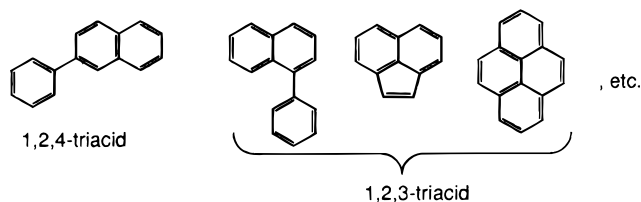
The carboxylic group has a tendency to deactivate the benzene ring against further oxidative attack by the ruthenium ion, resulting in the accumulation of these acids in the final products of the reaction. The distribution of the benzenepolycarboxylic acids provides a unique tool to probe into the mode of aromatic condensation in the asphaltene molecule.

The diacids result from the RICO of naphthalene and the unsubstituted terminal ring of linearly condensed segments of polycondensed aromatic hydrocarbons, e.g.

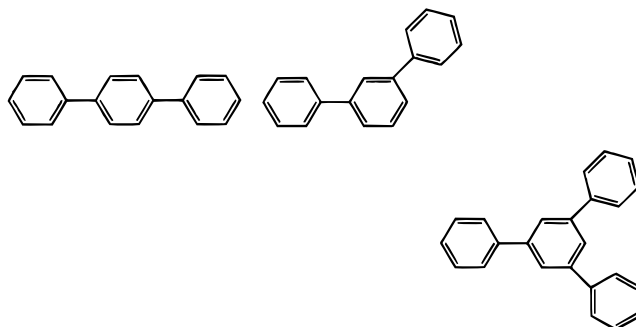


These appear to be the most abundant structural types in mature native asphaltenes. In addition to diacids, they may also afford tetraacids (with the exception of naphthalene). So far only the 1,2-diacid isomer has been found.

Triacids result from diaryl and condensed structures:
















The absence of 1,3- and 1,4-diacids and 1,3,5-triacids is noteworthy and implies that triaryl and tetraaryl structures, e.g.



are not likely significant structural elements of petroleum asphaltene.

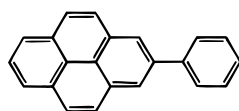
Among the tetraacids, the major isomers are 1,2,3,4- and 1,2,4,5- species from the phenanthrene- and anthracene-type structural units. The 1,2,3,5-isomer, prob-

Table 5. Structural Assignments of the Peaks in Figure 4

Peak no.	Structure ^a	Peak no.	Structure
1	MeO ₂ C(CH ₂) ₂ CO ₂ Me	10	
2	MeO ₂ C(CH ₂) ₃ CO ₂ Me	11,12	
3	MeO ₂ C(CH ₂) ₄ CO ₂ Me	13	
4	MeO ₂ C(CH ₂) ₅ CO ₂ Me	14	
5	MeO ₂ C(CH ₂) ₆ CO ₂ Me	15	
6		16	
7		17	
8		18	
8a			
9			

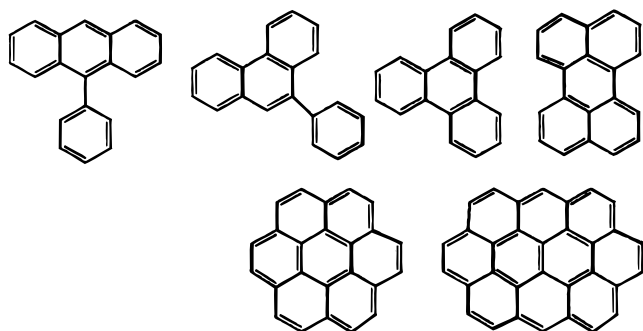
^a R = CO₂CH₃.

ably coming from a diaryl structure, e.g.



is also present in the oxidation products but in a much smaller concentration than the above isomers.

Penta- and hexa acids may arise from the structural types



The similarity in the benzenepolycarboxylic acid products of the various mature native asphaltene samples studied thus far is close, if not striking. In their RICO products, asphaltene samples from as diverse crude oils as oil sand bitumen, carbonate bitumen, heavy oil, light oil, high-sulfur/low-sulfur oil from different parts of the world display benzene di- through hexacarboxylic acid distributions that would hardly exceed the expected random scatter in multiple analyses of asphaltene samples from a given reservoir. This finding provides an argument in favor of similar alkyl substitutions on the aromatic moieties in most, but probably not all, native petroleum

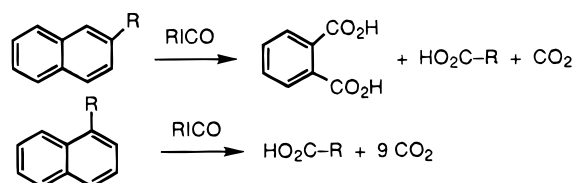
Table 6. Relative Percentage Yields of Benzenepolycarboxylic Acids

acid	sample (% yield)						
	Athabasca		Duri		Boscan		Chinese
di	34.7 ^a	31.4 ^b	43.8 ^a	39.6 ^c	41.9 ^a	37.9 ^c	9.4 ^d
tri	29.5 ^a	20.7 ^b	26.8 ^a	18.8 ^c	29.5 ^a	20.7 ^c	39.9 ^d
tetra	28.8 ^a	26.1 ^b	22.7 ^a	20.6 ^c	23.4 ^a	21.2 ^c	40.6 ^d
penta	5.7 ^a	14.6 ^b	5.4 ^a	13.8 ^c	3.3 ^a	8.5 ^c	5.7 ^d
hexa	1.3 ^a	7.2 ^b	1.3 ^a	7.2 ^c	1.8 ^a	10.0 ^c	4.4 ^d
total	100	100	100	100	99.9	98.3	100

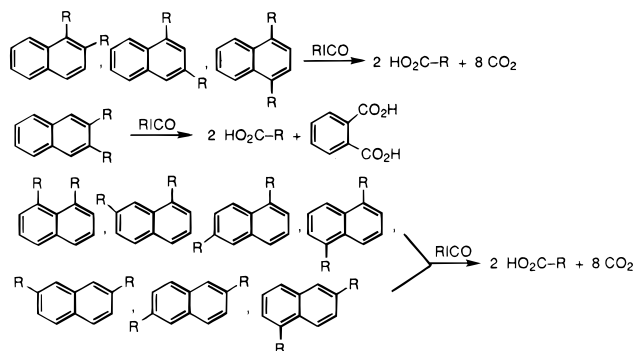
^a Old method of analysis. ^b New method of analysis 1. ^c Recalculated values. ^d New method of analysis 2. See text for details.

asphaltenes regardless of their origin. The immature, saline lake asphaltene in Table 6 shows considerable departure in distribution from the rest, and this may be attributed to its immaturity.¹²

Having said all this, it must be emphasized that with the exception of the hexaacid product, the yields of the benzene acids are not numerically correlatable with the relative distributions of their progenitor aromatic structural types. As the very low total yields of the benzene acids suggest, the chances of them forming have quite low probabilities. This is because of the profound influence the aliphatic substituents exert on the outcome of the RICO reaction and the relatively high concentration of aliphatic carbon in the asphaltene ($C_{\text{aliph}}/C_{\text{arom}} \approx 1.5$). The effect of aliphatic substituents on the benzene acid yields can be understood from the following examples:



Thus, the statistical value for the yield of benzene diacid from singly substituted naphthalene is 0.5. From di-substituted naphthalenes,



the statistical value is 1/11 (one diacid from 11 different possible substitution patterns) or 0.09. Since R can be a single methyl and since for one naphthalene molecule there are 15 aliphatic carbons, triple or even quadruple substitution should be dominant and the expected yield of benzenedicarboxylic acid from triply substituted naphthalene would be zero. But even from statistically

Table 7. Elemental Composition of Boscan and Duri Nondistillable Oxidized Residue^a

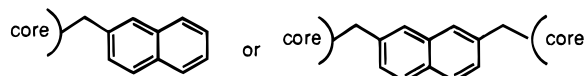
	% composition			
	Boscan	Duri	Boscan ^c	Duri ^c
C	64.78	69.44	23.32	13.89
H	7.44	8.62	2.68	1.72
N	1.28	0.95	0.46	0.19
S	4.30	0.34	1.55	0.07
O	17.25	16.85	6.21	3.37
(H/C) _a	1.38	1.49		
average MW	1960 ^b	1670 ^b		

^a Yields: Boscan 36%, Duri 20%. ^b g mol⁻¹ (VPO). ^c In terms of feed asphaltene.

disubstituted naphthalene with the 0.09 value, $11 \times 10 = 110$ carbon atoms would yield only one diacid. Per weight, this would correspond to

$$110 \times 12 \times \frac{100}{80 (\%C \text{ in asph})} = 1650 \text{ g of asph}$$

yielding one diacid. Consequently, the numerical values of the relative or absolute yields of the benzenedithrough-pentaacids depend not only on the abundance of the aromatic structural type but also on the amount and position of aliphatic substituents on it. In the case of naphthalene, all the diacids originate from singly and doubly substituted species since higher-substituted species should not yield diacids. In the singly (and doubly) substituted naphthalene species, the substitution is (or can be) the linkage to the asphaltene molecular core, e.g.



For hexaacids, different considerations apply. In this case, the yield should not depend on substitution and, as discussed in an accompanying article in this issue,¹³ the absolute yield gives an upper limit for the number of fully pericondensed aromatic structures in the asphaltene. In the present instances, this upper limit can be estimated¹³ to be less than one fully pericondensed aromatic system per four asphaltene molecules.

Table 6 lists the percentage yields of the di- through hexaacids in terms of the total acids. As seen from the data, the distributions of the benzenepolycarboxylic acids from the two samples are similar and in effect their distributions are also similar to those of the previously studied Athabasca, Peace River, Lloydminster, and Cold Lake asphaltenes.⁵ As in the present case, Table 6, the most abundant benzenepolycarboxylic acids were the diacids, followed by the tetra- > tri- > penta- > hexacarboxylic acids. A different distribution was found in the asphaltene from an immature saline lake deposit in China, where the order was tetra- ≥ tri- > di- > penta- > hexacarboxylic acids.¹²

Returning to Table 6, the data are listed according to the old method of analysis employing methylation in the aqueous phase, a new method 1 reported in 1997¹⁴ employing methylation of the dry acids, approximate

(13) Strausz, O. P.; Mojelsky, T. W.; Faraji, F.; Lown, E. M.; Peng, P. *Energy Fuels* **1999**, *13*, 207.

(14) Wang, Z.; Liang, W.; Que, G.; Qian, J. *Petrol. Sci. Technol.* **1997**, *15*, 559–577.

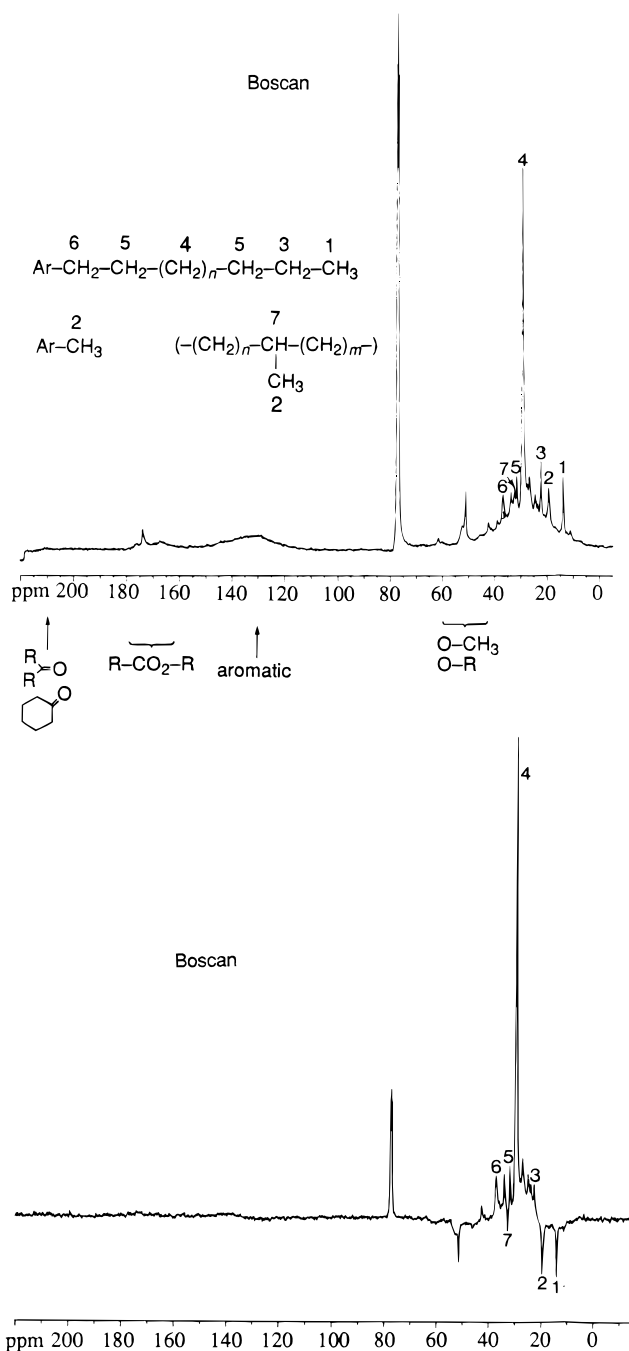


Figure 6. 500 MHz ¹³C (top) and attached proton test (APT, bottom) NMR spectra of the Boscan oxidized residue. In APT, CH₂ and quaternary carbon give positive signals while CH₃ and CH give negative signals.

recalculated values obtained by correcting the old measurements, using the ratio of the values from new measurements to old measurements and a new method 2 developed by us in 1996¹² involving extraction of the dry acids with acetone and methylation of the acetone extract. The new methods are superior to the old ones and afford higher recoveries of the higher acids.

In summary, the presence of a benzenepolycarboxylic acid species in the RICO products proves the presence of the progenitor aromatic condensation types in the asphaltene structure, and the absence of a given benzenepolycarboxylic acid may be taken as proof for the absence of the corresponding types of progenitor aromatic condensation. But with the exception of the

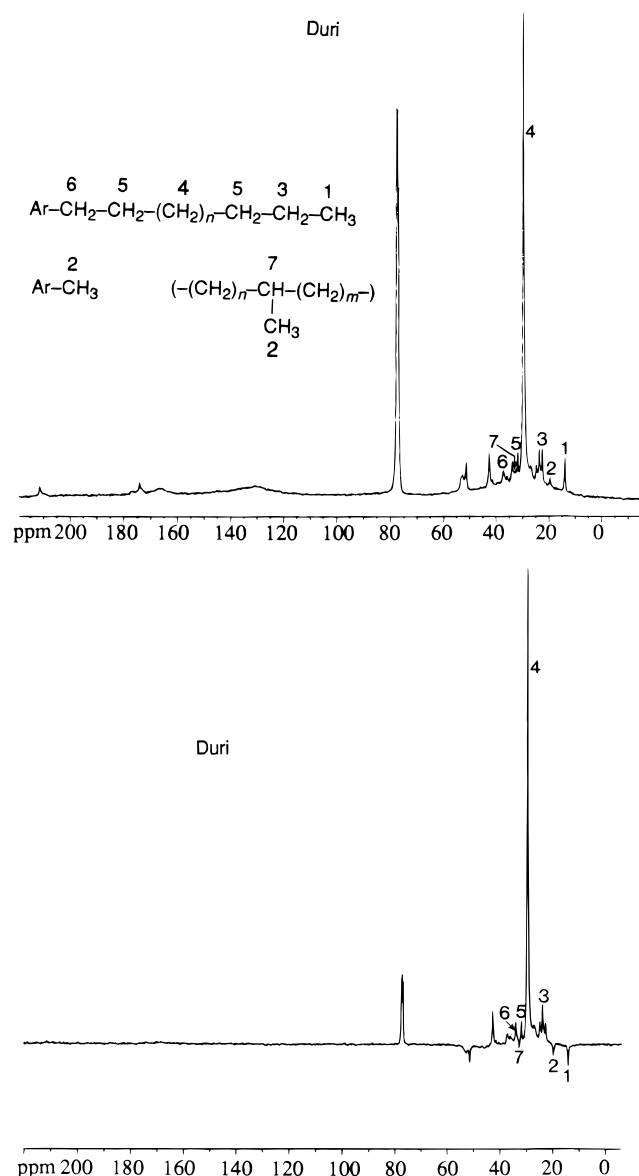


Figure 7. 500 MHz ^{13}C (top) and APT (bottom) NMR spectra of Duri oxidized residue.

Table 8. Carbon Functionalities from the 500 MHz ^{13}C NMR Spectra of Oxidized Residues^a

sample	CO (ketone)	CO ₂ (ester)	C _{arom}	C _{saturate}
Boscan	trace	5.2	13.9	80.9
Duri	1.0	6.0	11.8	81.8

^a C % of total carbon.

hexa acids, the numerical values of the benzene acids cannot be directly related to the abundances of the types of aromatic structures in the asphaltene, and therefore, the numerical values in Table 6 should be viewed with this in mind.

(iv) *Nondistillable Oxidized Residue.* Another major product of the RICO reaction of asphaltene is a nondistillable residue containing ca. 17% oxygen, Table 7, showing that this residue is in a highly oxidized state. The 500 MHz ^{13}C NMR spectra of the methylated residues, Figures 6 and 7, gave the data listed in Table 8. The spectra reveal the presence of fairly long *n*-alkyl moieties (peak 4) which must be attached mainly to naphthenic carbons since the aromatic carbon contents of the residues are relatively low, estimated to be 13.9%

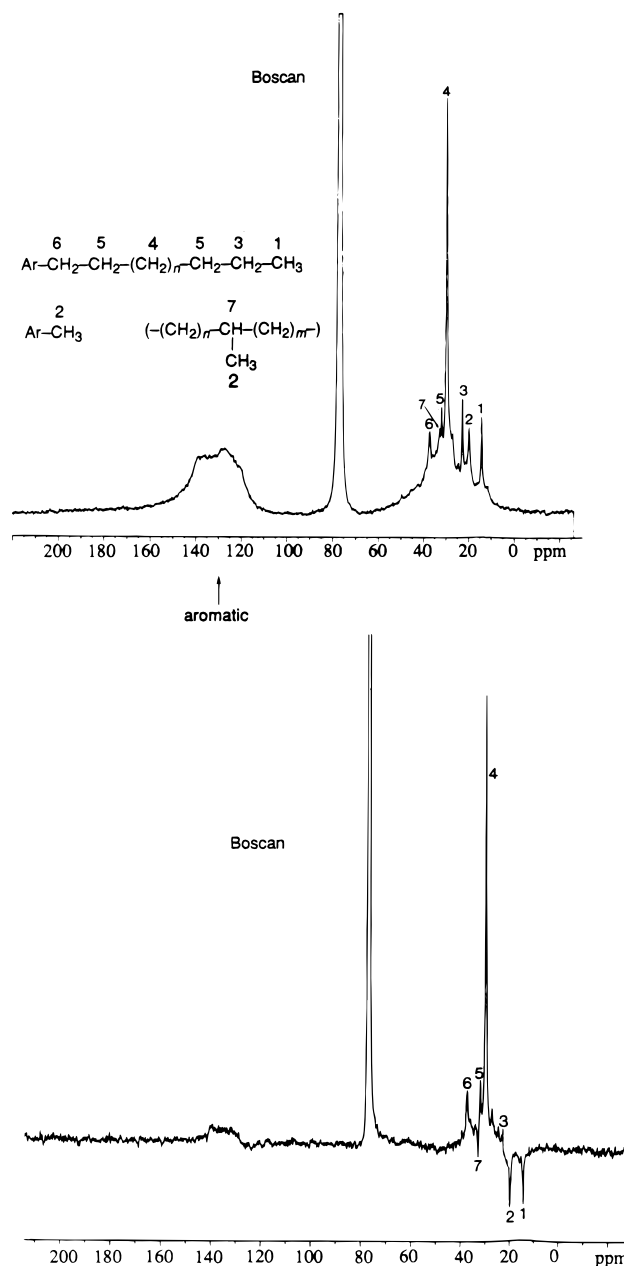


Figure 8. 500 MHz ^{13}C (top) and APT (bottom) NMR spectra of Boscan asphaltene. The spectrum is fully relaxed, without nuclear Overhauser effect.

and 11.8% of the total carbon in the Boscan and Duri residues. The 0–40 ppm regions of the spectra are quite similar to the corresponding regions of the unoxidized asphaltene spectra, Figures 8 and 9. For comparison, a 400 MHz ^{13}C NMR spectrum of Athabasca asphaltene is displayed in Figure 10. The resemblance among the three asphaltene spectra and that between the two oxidized residues is a remarkable further validation of the proposal that native asphaltenes have closely similar molecular structures. The attached proton test spectra also shown in Figures 6–9 serve as aids to the assignment of the resonances in the NMR absorption spectra. In the APT spectra, positive absorptions are due to secondary and quaternary carbons whereas negative absorptions are due to primary and tertiary carbons.

Quantitative data for various carbon functionalities derived from the ^{13}C NMR studies are tabulated in Tables 8 and 9. As seen from the data in Table 9, the

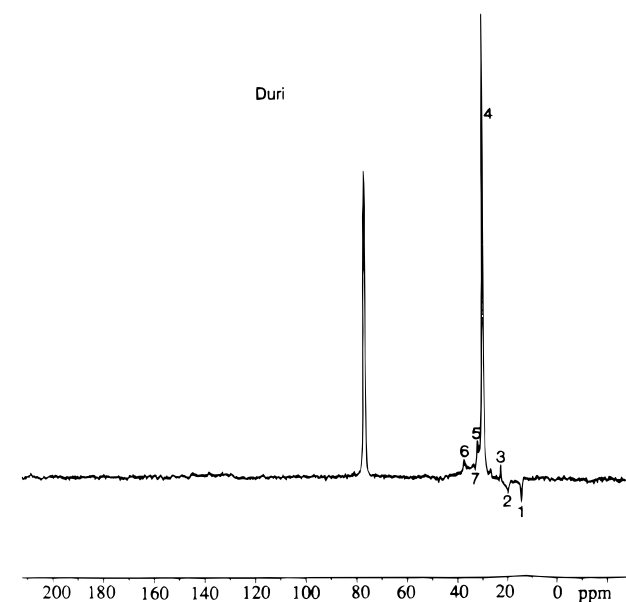
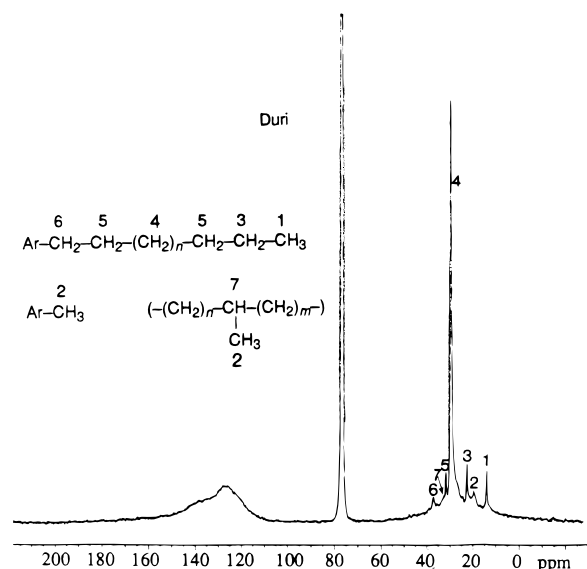


Figure 9. 500 MHz ^{13}C (top) and APT (bottom) NMR spectrum of Duri asphaltene. The spectrum is fully relaxed, without nuclear Overhauser effect.

aromatic carbon contents of the three asphaltenes listed fall in the narrow range ($42.0 \pm 0.7\%$). Moreover, the residual aromatic carbon in the oxidized material comprises about 9.1% and 4.6% of the aromatic carbon in the Boscan and Duri feed asphaltenes. The molecular weights of the residues, 1960 and 1670 g mol^{-1} (VPO) for the Boscan and Duri samples, are significantly reduced compared to the starting asphaltenes but are still relatively high, suggesting the possibility of molecular association. Most of the oxygen in the oxidized residue is present in sulfones and perhaps sulfinic and sulfonic methyl esters and carboxyl groups of methyl esters, which tend not to associate extensively. However, as shown below, RICO generates alcoholic OH groups which can cause molecular association.

From the elemental compositional data it is seen that most of the sulfur and nitrogen is removed during RICO and 25.4% of the sulfur originally present in the Boscan and 17.4% in the Duri remains in the oxidized residue.

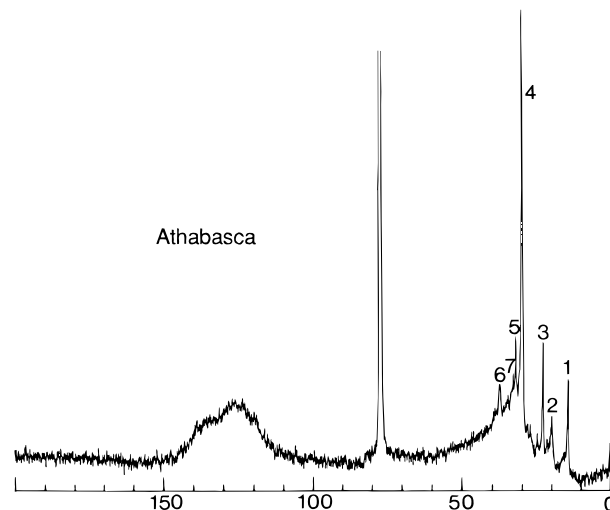


Figure 10. 400 MHz ^{13}C NMR spectrum of Athabasca asphaltene.

Table 9. Aromatic and Aliphatic Carbon in Asphaltenes^a

	C_{ar}	C_{aliph}
Boscan	42.7	57.3
Duri	41.2	58.8
Athabasca	42.0	58.0

^a All spectra were fully relaxed without nuclear Overhauser effect.

Also, 41.5% of the nitrogen is retained in the Boscan and 12.9% in the Duri residue.

The ^1H NMR spectra of the oxidized residues, Figure 11, also show the presence of long *n*-alkyl moieties, esters, and other structural features, and Table 10 summarizes the structural elements detected by NMR spectroscopy.

The FTIR spectra of the oxidized residues, Figure 12, are similar and show intense absorptions at $\sim 1720\text{ cm}^{-1}$ due to the ester carbonyl stretch, a broad absorption centered around 3400 cm^{-1} attributable to polymeric OH stretch in alcohols, strong CH_2 and CH_3 bendings at 1470 and 1380 cm^{-1} , and weak aromatic absorptions at ~ 1600 , 1980, 2060, and $\sim 3070\text{ cm}^{-1}$. The shape of the combination/overtone bands at 1980 and 2060 cm^{-1} is consistent with a polysubstituted aromatic structure (1,3,5-tri-, 1,2,4,5-tetra-, penta-, and hexa- substitution), and the $\sim 3070\text{ cm}^{-1}$ aromatic C-H stretch corresponds to the 3030 cm^{-1} aromatic stretch in the asphaltene. The Boscan sample also features saturated sulfone band absorptions at ~ 1120 and $\sim 1300\text{ cm}^{-1}$ corresponding to the prominent 1120 and 1270 cm^{-1} absorptions in the model compound 2-*n*-dodecylthiane-1,1-dioxide, also shown in Figure 12. These absorptions appear to be much weaker, and the $\sim 750\text{ cm}^{-1}$ absorption, which may correspond to the $\sim 730\text{ cm}^{-1}$ absorption in the model compound, also appears weaker in the Duri than in the Boscan sample, in agreement with the higher sulfur content of the latter. For the Duri sample, H_{arom} was determined by 500 MHz NMR to be 4.1%, which translates to an $H_{\text{arom}}/C_{\text{arom}}$ ratio of about 0.5.

In saturated sulfides the sulfur is known to be oxidized in RICO to the sulfone whereas thiophenes are destroyed. Therefore, the residual sulfur (4.3% and 0.34% in Boscan and Duri residues) may be assumed

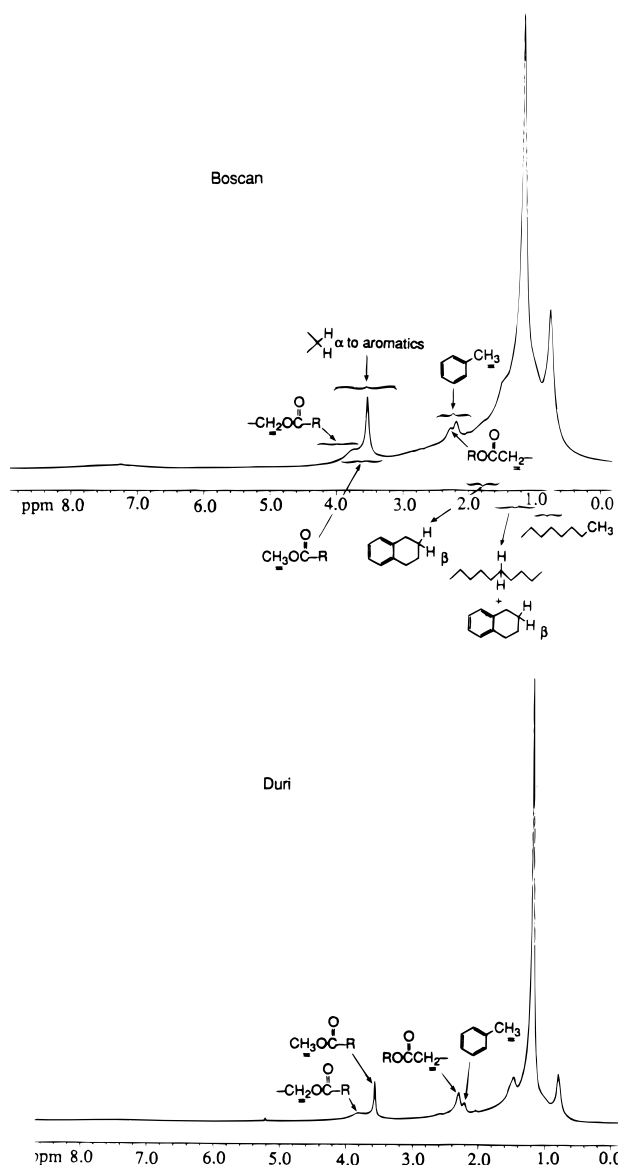
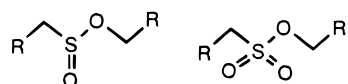


Figure 11. 500 MHz ^1H NMR spectra of Boscan and Duri oxidized residues.

Table 10. Structural Elements Detected in the Oxidized Residues by NMR Spectroscopy

$\text{R}-\text{C}(=\text{O})-\text{R}$; $\text{R}-\text{CO}_2-\text{R}$; C_{arom} ; C_{naph} ; $\text{R}-\text{CH}_2-\text{CH}_2-\text{R}$; $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$; $-\text{O}-\text{CH}_3$; $-\text{O}-\text{R}$; C_6H_5 ; $-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R}$; $\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{R}$; $\text{R}-\text{O}-\text{C}(=\text{O})-\text{CH}_2-$; C_{10}H_7 ; C_{10}H_8
--

to be present as sulfones (sulfinic and sulfonic acid esters).



With this in mind the oxygen in the oxidized Boscan

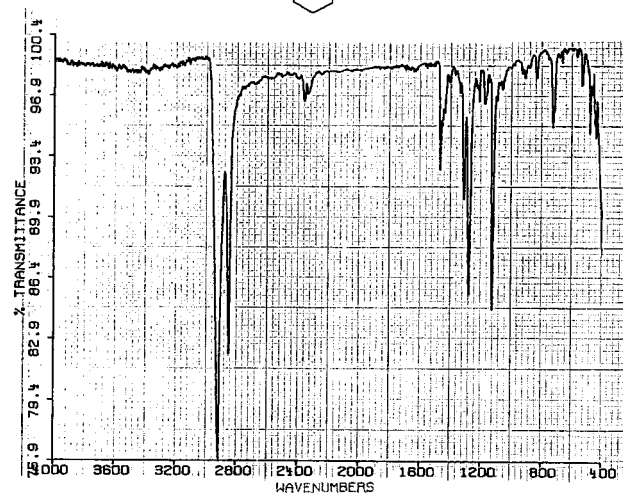
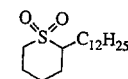
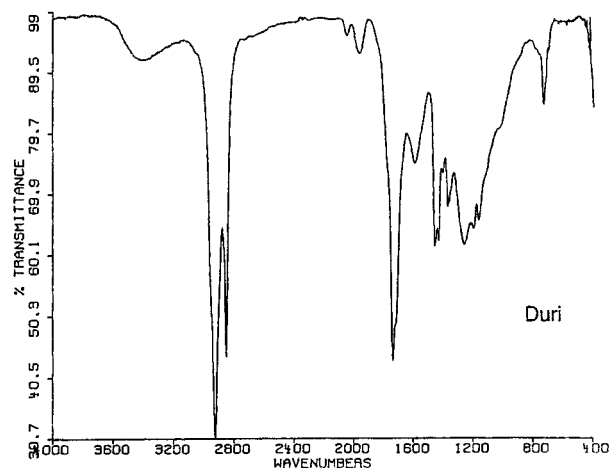
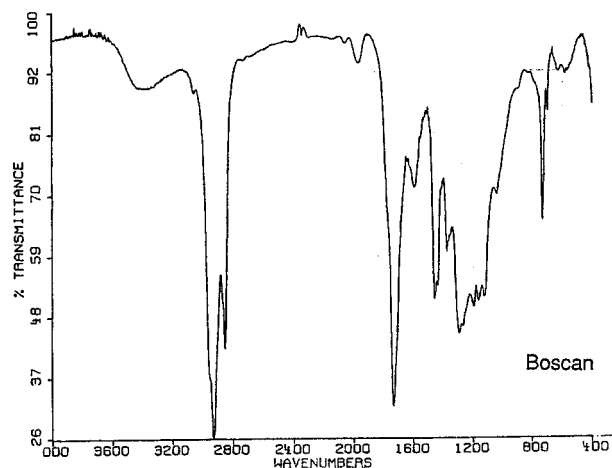
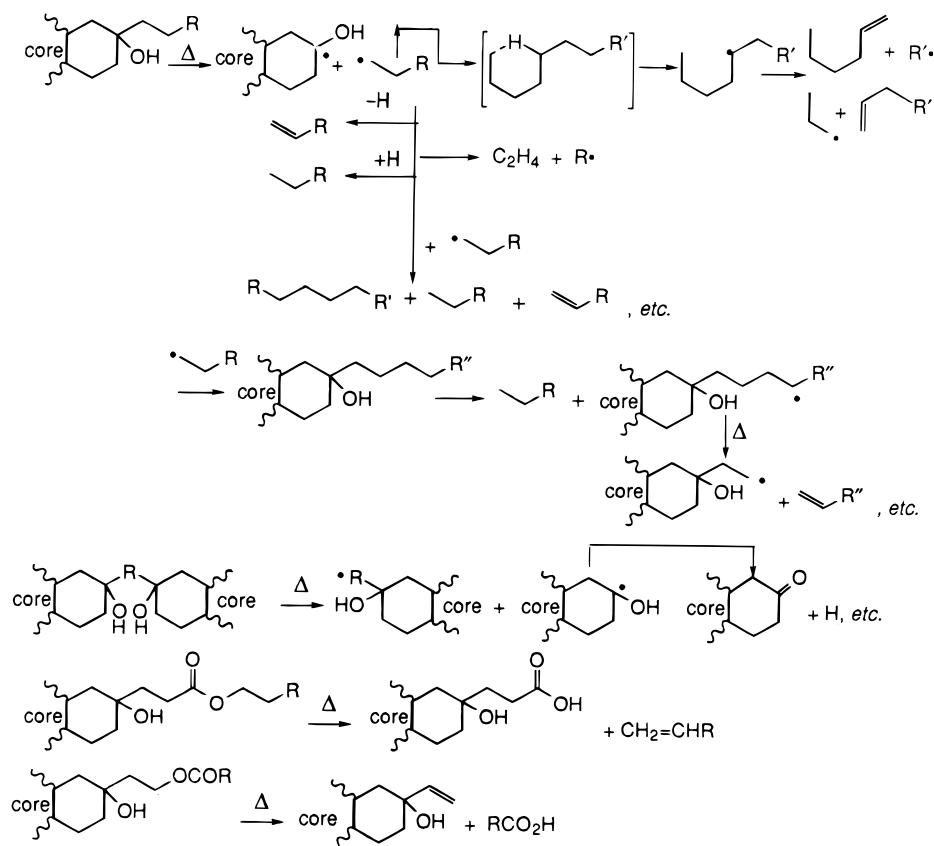


Figure 12. FTIR spectra of Boscan and Duri oxidized residues and 2-*n*-dodecylthiane-1,1-dioxide.

sample can be accounted for as follows:

originally present in asphaltene	1.4%
in $\text{R}-\text{SO}_2-\text{R}$	4.3%
in $\text{R}-\text{CO}_2-\text{CH}_3$: $\frac{5.2 \times 64.78}{100} \times \frac{32}{12}$	9.0%
total	14.7%

From elemental analysis the value found was 17.3%,

Scheme 1^a

^a Elimination of water followed by allylic C–C bond cleavages is also a plausible reaction path leading to similar end products (vide infra).

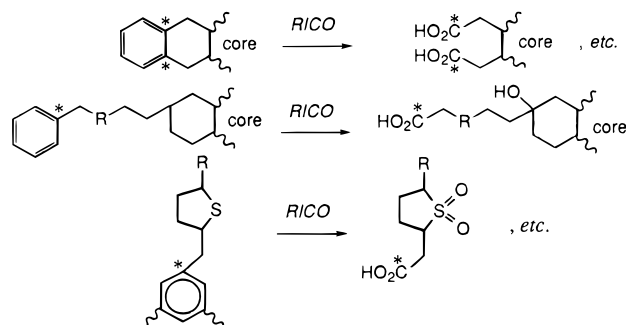
and the difference, 2.6%, too large to be attributable to experimental error, may be assumed to be present as alcohols, as indicated by the FTIR spectra, Figure 12. The ¹³C NMR spectra of all the oxidized and nonoxidized asphaltenes feature the characteristic tertiary ¹³C absorption around 32 ppm, and tertiary carbons have been shown to be oxidized to alcohols in RICO under conditions similar to those employed here. The broad absorption in the FTIR spectra maximizing around 3400 cm⁻¹ is then probably due to the tertiary alcohols formed from the oxidation of tertiary carbons. However, as clearly evidenced in the ¹³C NMR spectra, not all the tertiary carbons are oxidized to alcohols because both the oxidized Boscan and Duri spectra show tertiary ¹³C absorption.

Similarly, for the oxidized Duri sample, the oxygen balance is as follows:

originally present in asphaltene	2.1%
in R–SO ₂ –R	0.68%
in R–CO ₂ –CH ₃	11.11%
in R–CO–R	0.93%
total	14.8%

Elemental analysis gave 16.9%, and again the difference, 2.1%, must represent alcohols which arose from the RICO of tertiary C–H bonds (vide infra). RICO is also known to oxidize ethers to esters. This reaction may have some relevance because ether bonds have been shown to be present in Athabasca asphaltene¹⁵ and also in some kerogens.¹⁶

(v) *Pyrolysis of the Oxidized Residue.* The RICO residue is essentially the naphthenic/aliphatic core of the asphaltene. Aromatic-attached naphthenic rings and alkyl chains are oxidized at the site of attachment to the carboxylic group:



More can be learned about the structure of the asphaltene molecule by pyrolyzing the oxidized residue after esterification with diazomethane treatment. The pyrolysis was carried out at 375 °C in a flow reactor. As before with Athabasca asphaltene, three sets of products were separated by chromatography on a silica gel column: (1) series of *n*-alkanes + *n*-alk-1-enes with *n*-pentane elution; (2) series of *n*-alkanoic + 1-*n*-alkenoic acid methyl esters with methylene chloride elution and, after removal of a more complex ester mixture with 10%

(15) Peng, P.; Morales-Izquierdo, A.; Hogg, A.; Strausz, O. P. *Energy Fuels* **1997**, *11*, 1171–1187.

(16) Behar, F.; Vandenbroucke, M. *Org. Geochem.* **1987**, *11*, 15–24.

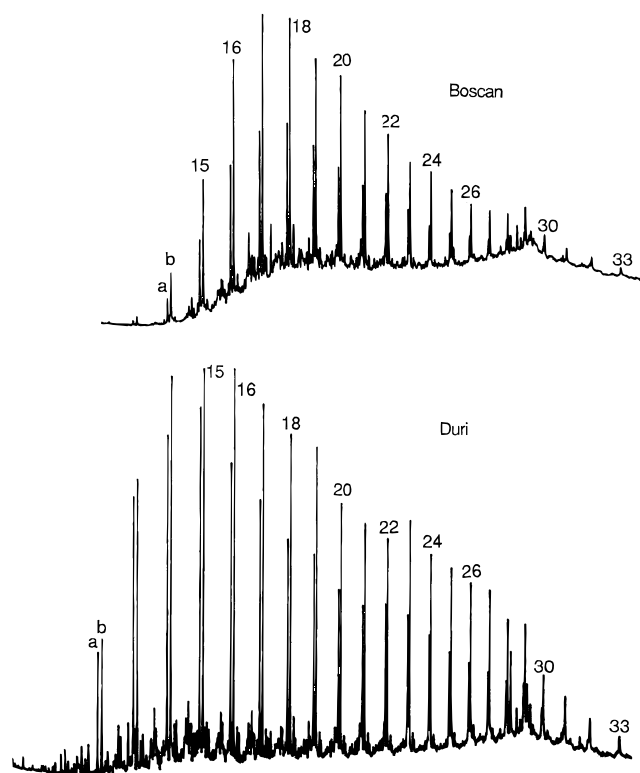


Figure 13. Gas chromatograms of *n*-alkanes and *n*-alk-1-enes from the pyrolysis of the oxidized residues: a = alkene, b = alkane.

EtAc/CH₂Cl₂ elution, (3) series of free *n*-alkanoic acids with 10% CH₃OH/CH₂Cl₂ elution.

These products arose as shown in Scheme 1.^{17,18}

(1) The distribution of *n*-alkanes/*n*-alkenes is shown in Figure 13. In both cases, the carbon chain of the products extends to at least C₃₃, the upper end of the detection limit of the GC employed. The distribution in the two samples shows only some differences: the alkane/alkene envelopes from the Boscan material are smoother and the alkane/alkene ratios are somewhat higher, especially at the higher end of the chromatogram. The alkane/alkene ratio is not a molecular parameter, and its value depends on the experimental conditions employed, such as the availability of hydrogen donor molecules, length of reaction time, radical steady-state concentrations, etc. The sample size of the Boscan oxidized residue used in the thermolysis experiment was nearly twice as high as the Duri residue, and this could explain the difference in the *n*-alkane/*n*-alkene ratio. The apparent maxima in the concentration distributions are very likely due to material losses at the low molecular weight end of the chromatogram. Another notable feature of the hydrocarbon distribution is the more rapid concentration drop with increasing chain length above C₁₈ in the case of the Boscan material—a trend that evidently follows the one seen in the distribution of the *n*-alkanoic acids (representing the aromatic-attached *n*-alkyl side chain distributions) from the RICO of the asphaltenes, Figure 2. Analogous trends can be seen in the *n*-alkane/*n*-alk-1-ene distribu-

tion from the direct pyrolysis of the whole Boscan and Duri asphaltenes as well. It is also noted that the contribution of the penultimate reaction in the above reaction sequence to the yield of the *n*-alk-1-enes is negligible.

The appearance of the *n*-alkane/*n*-alk-1-ene series in the thermolysis products suggests the presence of *n*-alkyl side chains and bridges attached to naphthenic rings in the asphaltene. An approximate estimation of the amount of naphthenic-attached alkyl carbons can be obtained if it is assumed that their concentration distribution is similar to that of aromatic-attached alkyls. The approximate number of carbon atoms in naphthenic-attached alkyls then will be given by the expression

$$(\text{no. of C in } C_{16+} \text{ } n\text{-alkyl})_{\text{naphth}} (\%) \times \left(\frac{\text{no. of C in all } n\text{-alkyls}}{\text{no. of C in } C_{16+} \text{ } n\text{-alkyls}} \right)_{\text{arom}}$$

From the measured yields of the *n*-alkane + *n*-alk-1-ene products and the data in Figure 13 and Tables 1 and 2, one can then calculate for Boscan asphaltene the number of carbon atoms in naphthenic-attached alkyl moieties as follows:

$$\frac{\sum_{\text{total}} C = 7.14 + 3.76}{1.0(\%)} = 1.0 \times \frac{10.90}{1.110} = 9.8 \text{ carbon atoms per 100 C in asphaltene}$$

This is comparable with the number of carbon atoms in *n*-alkyl moieties attached to aromatics, 7.14 + 3.76 = 10.9 per 100 C atoms. Similarly, for the Duri sample,

$$\frac{\sum_{\text{total}} C = 10.7 + 7.78}{1.2(\%)} = 1.2 \times \frac{18.48}{4.143} = 5.4 \text{ carbon atoms per 100 C in the asphaltene}$$

compared to 18.5 carbon atoms attached to aromatic rings.

These results reveal that the number of carbon atoms in *n*-alkyl moieties is larger in the Duri asphaltene, 23.9, where a larger proportion, 77%, is attached to aromatic systems compared to the Boscan asphaltene, where the corresponding values are 20.7 and 53.0%. Here, however, we should keep in mind that the Duri asphaltene yielded an insoluble residue up to 16 wt % of the asphaltene, containing 14% organic material. The FTIR spectrum of this residue suggests that the main components present are



like materials with a possible minor contribution from

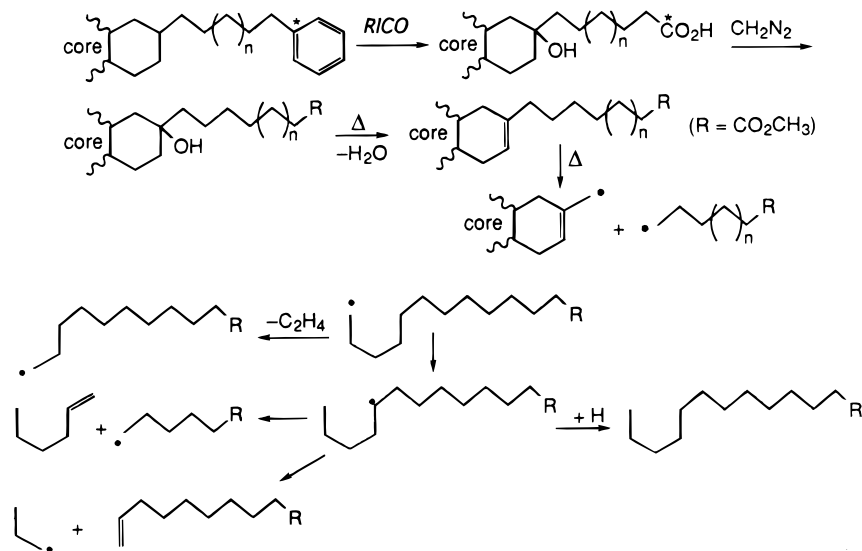


like materials. Thus, some ring-attached *n*-alkyl moi-

(17) Safarik, I.; Strausz, O. P. *Res. Chem. Intermed.* **1996**, *22*, 275–314.

(18) Safarik, I.; Strausz, O. P. *Res. Chem. Intermed.* **1997**, *23*, 63–99.

Scheme 2

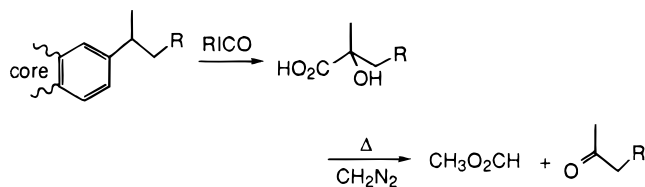


eties not included in the 23.9% value given above could have been present in the Duri asphaltene. The presence of *n*-alkyl side chains on the naphthenic rings is also clearly evident from the ^{13}C NMR spectra of the oxidized residues (vide supra).

Tertiary C–H bonds, depending on molecular geometry, electronic, and steric effects, may be oxidized in RICO to tertiary hydroxyl groups,¹⁹ and the resultant tertiary alcohols may resist further oxidation. The presence of alcohols is clearly evident from the FTIR spectra of the oxidized residues of both asphaltenes. From the oxygen balance estimate, at least 2.6 and 2.1 wt % oxygen can be assigned to tertiary alcohols in the Boscan and Duri oxidized residues, respectively. Primary and secondary alcohols are oxidized to carboxylic acids and ketones in RICO and would not be expected to be present in the oxidized residue. The oxidation of some of the tertiary C–H bonds in the RICO reaction is indicated in the above reactions schemes. However, it is stressed again that as shown by the presence of the tertiary carbon resonance peaks in the ^{13}C NMR and attached proton test NMR spectra (Figures 6 and 7) and the tertiary proton resonance around 1.5 ppm in the ^1H NMR spectra (Figure 11), not all tertiary C–H bonds are oxidized in the RICO reaction.

(2) The formation of *n*-alkanoic and *n*-alkenoic acid methyl esters is unambiguous proof of the existence of methylene bridges connecting an aromatic to a naphthenic ring system, Scheme 2. The total ion current mass chromatograms of the methyl esters are shown in Figure 14. The two asphaltenes yielded similar chromatograms of the esters which ranged from $\sim\text{C}_8$ to $\sim\text{C}_{25}$, and there are apparently more esters in Boscan than in Duri. Here again the lower molecular weight end was lost. Three different series can be recognized. One comprises the methyl esters of *n*-alkanoic acids, another *n*-alkyl methyl ketones, and the third could be ω -*n*-alkenoic acid methyl esters. Representative mass spectra of the pentadecanoic acid methyl ester member of the *n*-alkanoic acid ester series (scan 524), the methyl tetradecyl ketone member of the *n*-alkyl methyl ketones

(scan 514), and the tetradecenyl acid methyl ester member of the ω -*n*-alkenoic acid methyl esters (scan 503) are shown in Figure 15 for the case of Boscan asphaltene. The latter two assignments are tentative. The ketones could conceivably form via reactions of the type



ene structure from which they were formed would be one carbon atom shorter (assuming no chain length change upon thermolysis) than the length of the acids in the esters. The total amount of methyl esters and ketones recovered is low, $\sim 2.0\%$ of the asphaltene, but the losses in the chromatographic separation are high, and below C_{14} most of the esters are lost. If we again assume that the carbon number distribution in the bridges between an aromatic and a naphthenic ring is similar to that between two aromatics, then from the Boscan yield of methyl esters, 1.8 wt %, it is possible to obtain a rough estimate for the total number of carbons in the bridges between an aromatic and a naphthenic system. First we convert 1.8% ester, assuming an average chain length of C_{15} for the acids, to number of carbons/100 C in asphaltene, which is given by

$$1.8\% \times \frac{197}{256} \times \frac{12}{14} \times \frac{1}{0.811} = 1.5 \text{ C in bridges/100 C}$$

in asphaltene in the C_{11+} range

From this, the total number of C in bridges between an aromatic and a naphthenic ring/100 C in asphaltene is given as

(19) Bakke, J. M.; Lundquist, M. *Acta Chem. Scand.* **1986**, B40, 430–433.

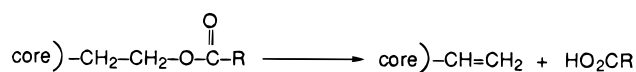
$$1.5 \frac{\sum_{\text{total}} 3.76}{\sum_{C_{11+}} 1.14} = 5.0$$

Similarly, for the Duri asphaltene

$$2.0 \times \frac{197}{256} \times \frac{12}{14} \times \frac{1}{0.874} \times \frac{\sum_{\text{total}} 7.78}{\sum_{C_{11+}} 3.04} = 3.9$$

i.e., 5.0 and 3.9 carbons in bridges between an aromatic and a naphthenic ring per 100 C atom in the two asphaltenes.

(3) The third class of compounds isolated from the thermolysis products was a series of *n*-alkanoic acids in the C₆–C₂₂ range showing a distinct preference for the C_{even} members; C₁₀ or C₁₆ are the predominant members, Figure 16. The formation of these products is explained in terms of the molecular decomposition of their esters



which are present apparently in all native petroleum asphaltenes.^{5,15} (A portion of those esters could have come from the corresponding ethers since in RICO, ethers are known to be oxidized to esters.) Because of their high even-to-odd carbon preference, these acids must be of a relatively recent origin, as discussed before,^{20,21} and are the remnants of microbiological activities in the deposit. The yields of the acid fraction were 1.8% and 1.6% in terms of the asphaltene for the Boscan and Duri samples, respectively.

A summary of the total amount of *n*-alkyl moieties identified is given in Table 11. The values obtained for the Boscan and Athabasca asphaltenes—both being Type II-derived asphaltenes—are identical, within experimental error, and the value for the Athabasca sample agrees with the value obtained from ¹³C NMR spectroscopic measurements.²² The value for the Type I-derived Duri asphaltene is about 9% higher, mainly because of the higher abundance of aromatic-attached alkyl carbons. The true value should be even higher by the amount lost in the insoluble oxidation residue. The higher yield from the Duri asphaltene is in qualitative agreement with the higher yield of saturates in its pyrolysis oil, 16 wt %, than from Boscan asphaltene, 11 wt %. This is also in line with expectation since Type I kerogens are known to contain more alkyl groups than Type II kerogens.²³

Thermal Decomposition of Asphaltenes: Sulfur Compounds in the Pyrolysate. Only the Boscan sample was subjected to pyrolysis. Under our pyrolytic

(20) Mackenzie, A. S.; Wolff, G. A.; Maxwell, J. R. *Advances in Organic Geochemistry 1981*; Bjoroy, M., et al., Eds.; Wiley Heyden: London, 1983; pp 637–649.

(21) Cyr, T. D.; Strausz, O. P. *Org. Geochem.* **1984**, 7, 127–140.

(22) Cyr, N.; McIntyre, D. D.; Toth, G.; Strausz, O. P. *Fuel* **1987**, 66, 1709–1714.

(23) Tissot, B.; Welte, D. *Petroleum Formation and Occurrence*, 2nd ed.; Springer: Germany, 1984; pp 131–159.

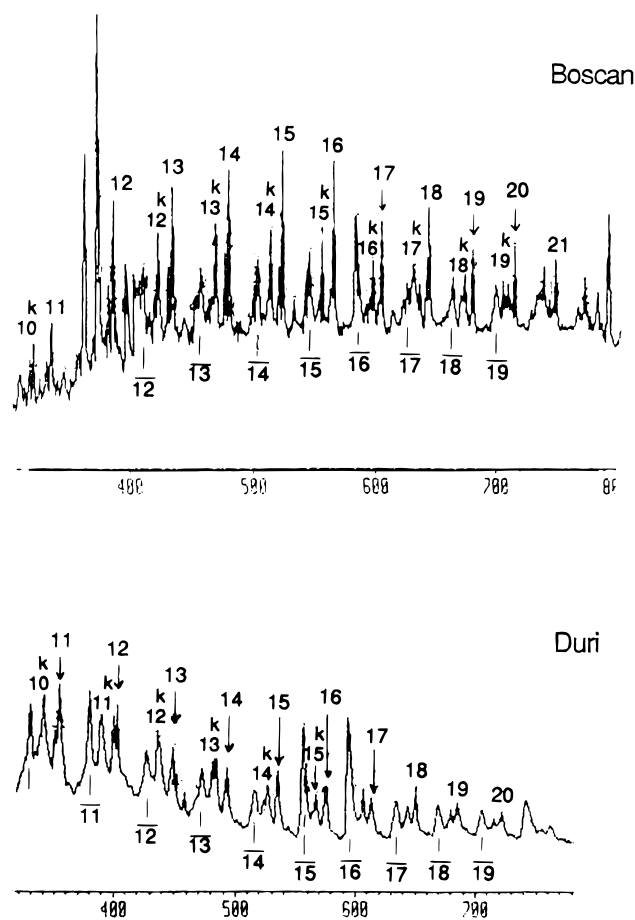


Figure 14. Total ion current mass chromatograms of *n*-alkanoic and alkenoic acid methyl esters from the pyrolysis of the oxidized residues. The numbers above the peaks refer to the carbon numbers of the acids, the horizontal bars correspond to monounsaturations, and the letter k refers to methyl *n*-alkyl ketones.

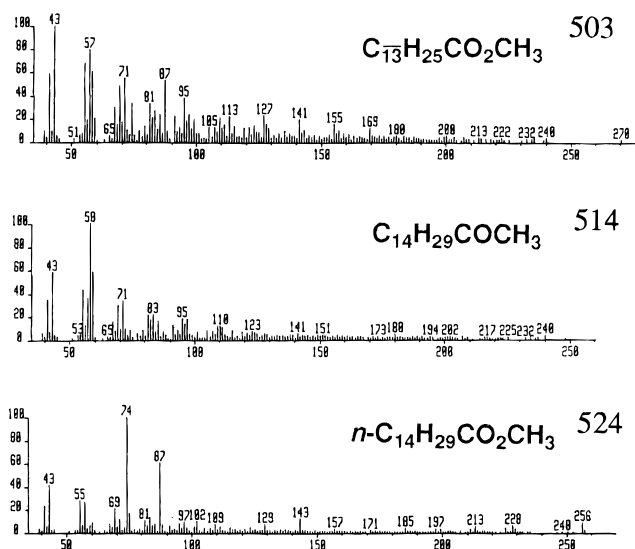


Figure 15. Mass spectra of pentadecanoic acid methyl ester, methyl tetradecyl ketone, and tetradecenyl acid methyl ester from selected scans of the Boscan residue, Figure 14. Identification of the latter two compounds is tentative.

conditions (430 °C, ~15 s residence time), Boscan asphaltene yielded 30% pyrolysate. The pyrolysis oil was composed primarily of alkenes, alkanes, aromatics, and sulfur compounds, as found for Athabasca asphaltene.

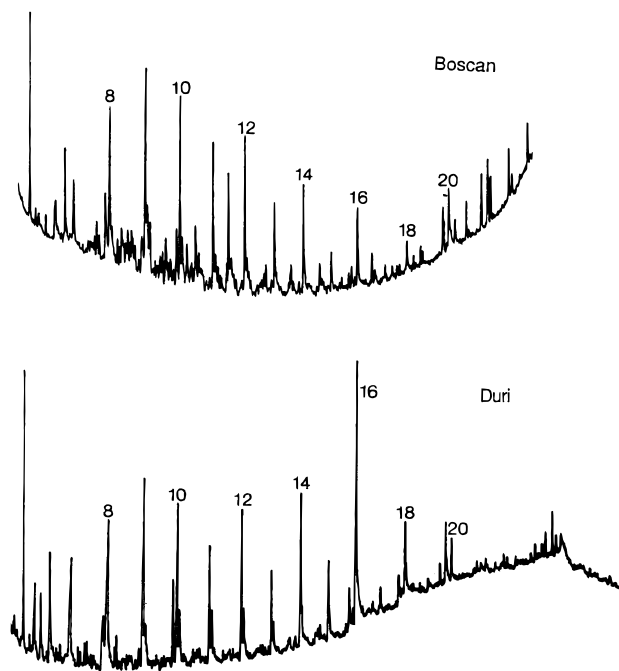


Figure 16. Gas chromatograms of the free *n*-alkanoic acids from the pyrolysis of the oxidized residues.

Table 11. Estimate of the Total *n*-Alkyl Carbons in the Asphaltenes

Type	Duri	Boscan	Athabasca
C per 100C in the asphaltene			
	10.7	7.1	9.2
	7.8	3.8	3.8
	5.4	9.8	4.5
	3.9	5.0	5.1
	1.6	1.8	3.9
Total	29.4	27.5	26.5

For the analysis of the Boscan asphaltene pyrolysate, we have employed the same procedure as that reported previously.¹ The initial step is to remove selectively the alkenes from the reaction mixture to prevent any interference with the oxidative–reductive reactions used in subsequent steps. The hydroboration with the reagents $\text{BH}_3 \cdot \text{THF}$, H_2O_2 , and NaOH efficiently convert nonpolar alkenes to polar alcohols, which can be cleanly separated from the other nonpolar pyrolysis oil components.

After removal of the alkenes, the sulfides in the sample are oxidized selectively to the sulfoxides with *tert*-butylammonium periodate and the polar sulfoxides are isolated by chromatography. The sulfoxides are reduced back to sulfides by LiAlH_4 at the reflux temperature of dioxane. Next, the thiophenes are oxidized to the sulfones with *m*-chloroperbenzoic acid in the presence of NaHCO_3 . As before, the polar sulfones are separated by column chromatography and reduced back

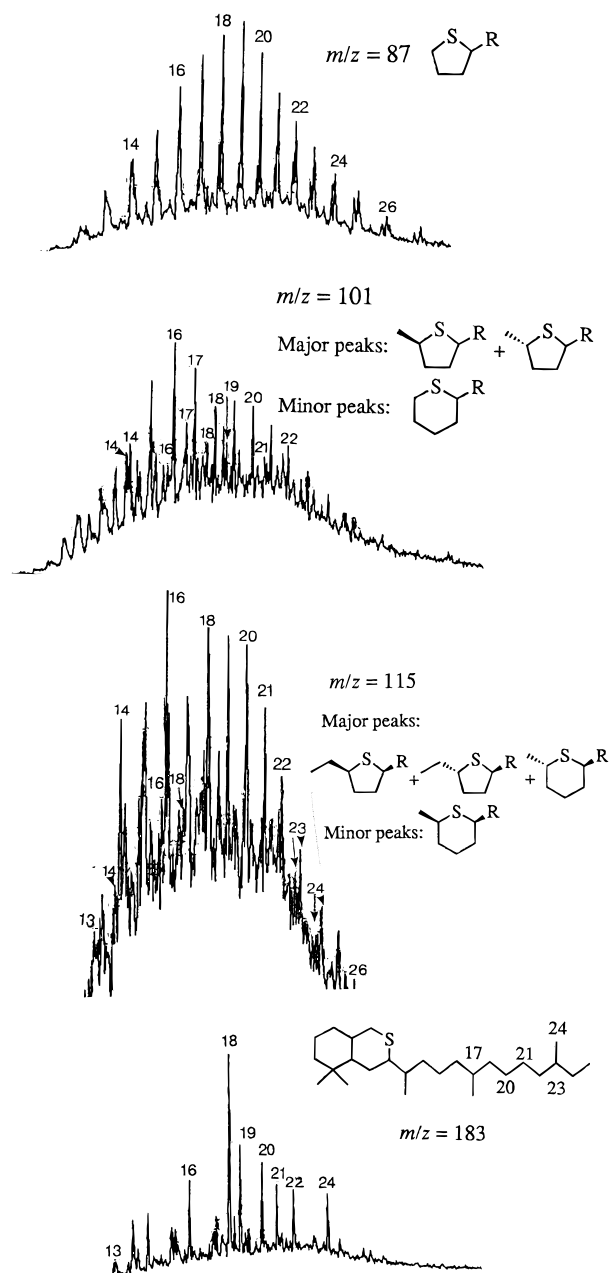


Figure 17. $m/z = 87$, 101, 115, and 183 cross-scan chromatograms of the Boscan asphaltene pyrolysate sulfide fraction.

to the nonpolar thiophenes with LiAlH_4 in dioxane.

From the Boscan pyrolysis oil, 1% sulfides and 1.5% thiophenes were isolated. This corresponds to only a small portion of the total sulfides and thiophenes and of the sulfur content (6.10%) of Boscan asphaltene. The low recovery is due to the combined losses arising from the low yield of the pyrolysis oil from too small quantities of sample material and the complexity of the analytical procedure.

Figure 17 shows cross scans for $m/z = 87$, 101, 115, and 183, respectively, of the sulfides isolated from Boscan pyrolysis oil. With cyclic sulfides a major mass fragmentation mode is cleavage of the alkyl group at the position of attachment to the cyclic system. Thus, the cross scan for $m/z = 87$ corresponds to monoalkylthiolanes with the substituent at position 2, as found before in nonbiodegraded petroleum²⁴ and in Atha-

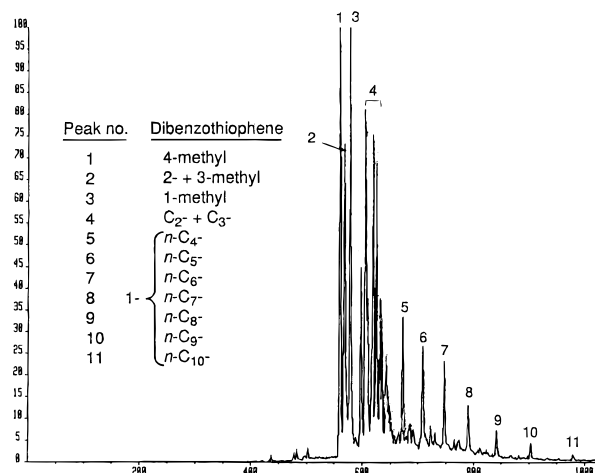
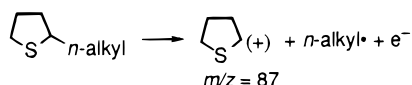


Figure 18. $m/z = 197$ cross-scan chromatogram of the thiophene fraction of the Boscan asphaltene pyrolysate. The assignments are tentative.

basca asphaltene pyrolysate.²⁵



The $m/z = 101$ cross scan corresponds to 2- n -alkyl-5-methylthiolanes and/or 2- n -alkylthianes; both series give the fragment ion in question:

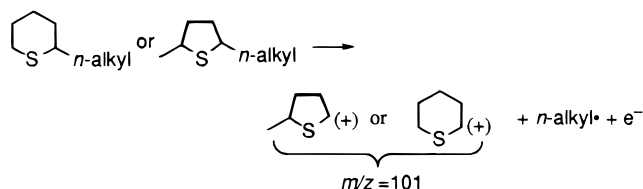
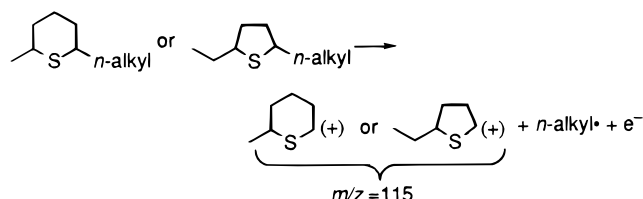


Figure 18 shows that both series are present. In Athabasca asphaltene pyrolysate,²⁰ the thiolanes were the major series and the thianes the minor series. The distribution here appears to be very similar to that in Alberta asphaltenes²⁵ as well as in the maltene fractions of most nonbiodegraded oils studied so far.²⁴

The $m/z = 115$ cross scan in Figure 17 corresponds to 2-alkyl-6-methylthianes (two isomers) and 2-alkyl-5-ethylthiolanes (two isomers):



Both series have been seen in Athabasca asphaltene pyrolysate.

Last, the $m/z = 183$ cross scan corresponds to dicyclic terpenoid sulfides:

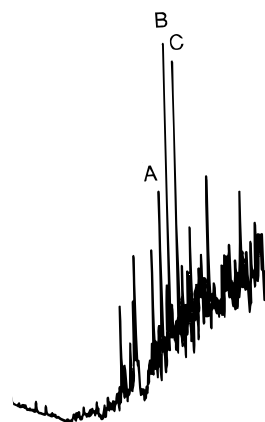
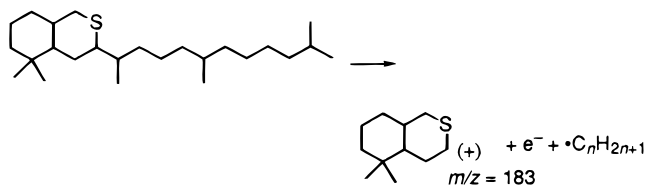


Figure 19. Gas chromatogram of the thiophene fraction of the Boscan asphaltene pyrolysate. A = 4-methyl, B = 2- and 3-methyl, and C = 1-methyldibenzothiophene.

The major dicyclic compound corresponds to the one having 18 carbon atoms, corresponding to a seven-carbon alkyl chain. In Athabasca maltene, the major components were the C₁₃ and C₂₀ members, but in the asphaltene, the C₁₈ member predominated, as in the present case. In our experience, dicyclic terpenoid compounds occur primarily in the maltene component and not in asphaltene. It is possible that the dicyclic sulfides detected here are not genuine asphaltene pyrolysis products of the high molar mass asphaltene; they either had been occluded in the asphaltene and were freed only on pyrolysis or arose from the thermal decomposition of the acetone-extractable lower mass asphaltene.²⁶

The thiophene fraction isolated was subjected to GC-MS analysis. The dominant compound classes present were alkylbenzothiophenes and dibenzothiophenes in similar distributions, as found in the pyrolysis oil of Athabasca asphaltene and some oil sand maltenes.¹ From the $m/z = 197$ cross scan analysis, Figure 18, it was determined that the major series of n -alkyldibenzothiophenes was the 1- n -alkyldibenzothiophene series, as found before.¹ The 1-, 2-, 3-monomethyldibenzothiophene isomers were measured quantitatively from the gas chromatogram, Figure 19, and the calculated dibenzothiophene maturity index (DBTI)²⁷

$$\text{DBTI} = \frac{2\text{-methyl} + 3\text{-methyl}}{2(1\text{-methyl})}$$

was 0.72. The DBTI index has been correlated²⁷ with the depth of burial of crude oil deposits, and from previous experience,⁷ the value 0.72 corresponds to a depth of about 500 m for the Boscan sample.

Conclusions

The present study has brought to light useful information on the covalent molecular structure of two vastly different asphaltenes, the Duri low-sulfur, paraffinic oil asphaltene and the Boscan high-sulfur aromatic im-

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mature asphaltene. Both asphaltenes, like their Alberta counterparts, the high-sulfur Athabasca, Cold Lake, Peace River and Carbonate bitumen asphaltenes and Lloydminster heavy oil asphaltenes, contain *n*-alkyl groups attached to aromatic and naphthenic rings as side chains and bridges connecting aromatic and naphthenic rings. *n*-Alkyl groups are also present in the form of long-chain ester- and probably ether-bound side chains attached to naphthenic (and possibly aromatic) rings. The distribution of alkyl, naphthenic, and aromatic carbons is remarkably constant, around $(28 \pm 1.0):(30 \pm 1.7):(42 \pm 0.7)$, in all the asphaltenes studied. This result should be taken with the caveat that the Duri asphaltene produced a significant amount of an organic material containing insoluble residue which, if it were taken into consideration, could weaken this correlation. The same can be said for the distribution of aromatic condensations as judged on the basis of the yields of benzenepolycarboxylic acid products from the ruthenium ion-catalyzed oxidation. Apparently, phenanthrene-type condensation is more abundant than anthracene-type condensation; biaryl structures are present and pericyclic condensed structures are sparse. The nondistillable oxidized residue has a high molecular mass, indicating the presence of fairly large aliphatic domains in the asphaltene, although the intervention of alcoholic association in the residue, contributing to the apparent high molar mass, is a likely possibility.

The FTIR and ^{13}C NMR spectra of the Duri, Boscan, and all Alberta asphaltenes as well as of their oxidized residues are also quite similar. Pyrolysis of the Boscan

asphaltene yielded the same types of sulfur compounds found before in Alberta asphaltenes, namely, 2-*n*-alkylthiolanes and thianes, dicyclic terpenoid sulfides, and 1-*n*-alkyldibenzothiophenes, as principal homologous series.

All of the major homologous series of compounds obtained from asphaltene by chemolysis or pyrolysis have structures which can be formally derived by the cyclization, aromatization, and condensation of a linear carbon chain—a fatty acid or alcohol—precursor. The specificity of substitution in the molecular building blocks—into which is encoded information on the nature of the biotic source material and evolutionary history of the asphaltene—points to the high degree of order underlying the apparent surface randomness of asphaltene. Also, the fact that the molecular building blocks of vastly different asphaltenes are nearly identical dictates that petroleum asphaltenes are not merely a solubility class fraction of petroleum but macromolecular components with closely similar covalent structures.

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