Report Number BETC-001-3
Distribution Category UC-92b

MASTER

CHARACTERIZATION OF HIGH BOILING FOSSIL FUEL DISTILLATES VIA ^1H and ^{13}C NMR ANALYSIS

Quarterly Report III for the Period
January 1, 1979 through March 31, 1979

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Prepared for the United States
Department of Energy
Bartlesville Energy Technology Center

Under Contract EW-78-A-19-001

DISCLAIMER

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I. SUMMARY OF TASK OBJECTIVES AND SCOPE FOR THE QUARTER ENDING MARCH 31, 1979

The objective of this quarter was the completion of the ^{13}C NMR analysis of the diaromatic concentrates and fractions of the Wilmington (211-76; 16, 19 and 24) and Gach Saran (207-76; 15, 21 and 24) high boiling distillates (535-675°C). Data from this ^{13}C NMR investigation would then be combined with values obtained from the previously completed ^{1}H NMR analysis of these fractions. Attempts were to be made to calculate average molecular structures for each monoaromatic fraction. It was also an objective to obtain relative ratios of previously unreported specific signals of low intensity observed in the ^{13}C NMR spectra of these fractions.

II. ABSTRACT OF PROGRESS TO DATE

The main goal achieved this quarter was the successful completion of the ^{13}C NMR analysis of the diaromatic fractions of Wilmington (211-76; 16, 19 and 22) and Gach Saran (207-76; 15, 22 and 24) high boiling (535-675°C) distillates. The analysis of additional samples supplied by DOE at our request, as well as the remainder of the samples submitted under the original contract, is currently underway. We have found from initial observations of the polyaromatic-polar fractions that the analysis time per sample must be increased to 84 h in order to obtain reliable data.

III. DETAILED REPORT OF ACCOMPLISHMENTS TO DATE

a. Discussion and Evaluation of Data

Reported herein is the completed ^{13}C NMR analysis of the diaromatic fractions of the Wilmington crude (211-76) and Gach Saran (207-76) distillates. Also repeated in this report are the ^{1}H NMR data for the diaromatic fractions. All conclusions made in regard to the diaromatic fractions have been made based upon the combined ^{13}C and ^{1}H NMR analysis. Finally, a mathematical model system suggested by J. W. Vogh of the Department of Energy for the monoaromatic fractions is discussed.

(1) Analysis of Diaromatic Fractions

Table I lists the data and fundings from the spectra of the Wilmington Diaromatic (211-76) fractions. All values presented for the first time are given in italics.

Concentrate: Although several observations were made in Report II concerning the concentrate, a brief outline of the conclusions previously cited will be repeated here for clarity. It should be noted that the relative aromatic carbon content was determined from the ^{13}C NMR spectrum of the concentrate to be 37.1%. Not unexpectedly, this aromatic carbon content was found to be almost 10% greater than the aromatic carbon content found for the monoaromatic concentrate (27.4%). This is probably due to the presence of condensed ring aromatic compounds. An indication of this increase is found in the ^{1}H NMR spectra of the two concentrates. A distinct shift downfield in the overall aromatic envelope of signals was observed for the diaromatic concentrate relative to that observed for the monoaromatic concentrate. This shift was reflected in the diaromatic content in Table I. The content was estimated by integration of the signal pattern downfield

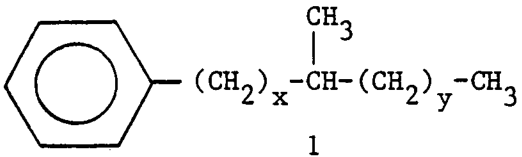
TABLE I
Wilmington Crude (535-675°C) Distillate
GPC 211-76 (Diaromatic Fractions)

		Mole % of Total H		
	Concentrate	#16	#19	#24
Ar-H	8.6	5.4	8.4	14.0
Al-H	91.4	94.6	91.6	86.0
Ar-H/Al-H	8.6/91.4 (1:10.6)	5.4/94.6 (1:17.5)	8.4/91.6 (1:10.9)	14.0/86.0 (1:6.1)
α-H(α to Ar)	17.0	9.9	17.8	18.9
β-H(β and greater to Ar)	74.4	80.8	73.8	67.1
Term CH_3	26.8	30.8	24.2	28.1
α-H(α to Ar)/ Total Al-H	17.0/91.4 (1:5.4)	9.9/94.6 (1:9.6)	17.8/91.6 (1:5.1)	18.9/86.0 (1:4.6)
Term CH_3/ Total Al-H	26.8/91.4 (1:3.4)	30.8/94.6 (1:3.1)	24.2/91.6 (1:3.8)	28.1/86.0 (1:3.1)
α-H(α to Ar)/ Term CH_3	17.0/26.8 (1:1.6)	9.9/30.8 (1:3.1)	17.8/24.2 (1:1.4)	18.9/28.1 (1:1.5)
Apparent Side Chain Length	>5	>9	>5	>4
Apparent Branches per Chain	0.0	1.1	-0.10	-0.01
Approx. Diaromatic (mole % of Total H)	5.0	3.17	4.0	9.0
Ar-C/Al-C (mole % of Total C)	37.1/62.9† (1:1.7)	*21.7/78.3*† *(1:3.6)*	39.1/60.9† (1:1.6)	*34.3/65.7*† *(1:1.9)*
Ar-H/Ar-C	1/4.3	*1/4.1*	1/4.6	*1/2.4*
Al-H/Al-C	1.5/1	*1.2/1*	1.5/1	*1.3/1*
Side Chain Length (from C peak ratios) estimated	C_9-C_{11}†	C_{12}-C_{14}†	C_{10}-C_{12}†	C_8-C_9†

† Sample contained 0.05 M $Cr(acac)_3$

from δ7.2 (the chloroform signal position)[1] to δ 9.0. A very broad but weak signal was observed at approximately δ 8.5 in the proton spectrum of the diaromatic concentrates (see page 35, Report I). This could possibly correspond to either protons on highly condensed aromatics or to protons on certain heteroaromatic compounds.

As outlined in Report II (page 18), prominent signals at 19.6 and 19.7 ppm in the ^{13}C spectrum could be attributed to methyl carbons *directly attached* to aromatic systems *in a hindered position*. It is also possible that these signals could, in part, arise from methyl carbons which branch from the main substituent chains as shown in **1**. Analysis of a variety of



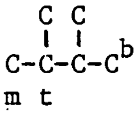
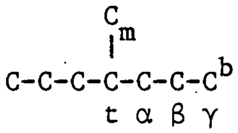
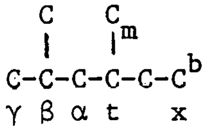
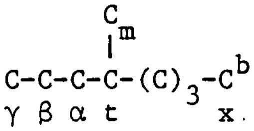
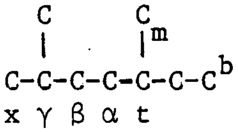
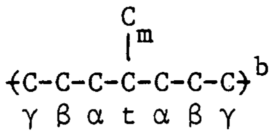
$C_6H_5-(CH_2)_x-\overset{CH_3}{\overset{|}{CH}}-(CH_2)_y-CH_3$

1

branch and unbranched alkanes has led to the development of additive substituent rules[2,3] which permit the calculation of ^{13}C chemical shifts for alkanes not previously investigated. A list of some of the model compounds used in these calculations and which may be relevant to this work are listed in Table II. In addition, it has been observed[4] that certain copolymers made from ethylene-propylene mixes should have isolated branch methyl groups. We reason that ^{13}C NMR signals from the polymers may have a resemblance to the types of compounds under investigation. An example is cited in Table II (cpd **7**). Unfortunately, the variety of monomethyl alkanes used in the previous cited studies[2,3] was limited and no methyl and plenyl substituted alkanes related to **1** have been revealed in our literature search to date. However, it is evident from the chemical shifts of a series of *n*-alkylbenzenes[5] that the effects of the phenyl ring on the ^{13}C NMR shifts of the alkyl side chain

TABLE II

^{13}C NMR Data for Select Alkanes from the Literature

			Chemical Shifts[a]				
Compound	C_m	C_t	C_α	C_β	C_γ	C_x	Ref.
 $\underset{m}{\text{C}}-\underset{t}{\overset{\text{C}}{\text{C}}}-\overset{\text{C}}{\text{C}}-\text{C}^b$ 2	19.2	34.0	-	-	-	-	3
 $\text{C}-\text{C}-\text{C}-\underset{t}{\overset{\text{C}_m}{\text{C}}}-\underset{\alpha}{\text{C}}-\underset{\beta}{\text{C}}-\underset{\gamma}{\text{C}}^b$ 3	19.3	32.3	39.5	20.2	14.1	-	3
 $\underset{\gamma}{\text{C}}-\underset{\beta}{\overset{\text{C}}{\text{C}}}-\underset{\alpha}{\text{C}}-\underset{t}{\overset{\text{C}_m}{\text{C}}}-\text{C}-\underset{x}{\text{C}}^b$ 4	19.0	32.1	46.6	25.4	22.2	11.0	3
 $\underset{\gamma}{\text{C}}-\underset{\beta}{\text{C}}-\underset{\alpha}{\text{C}}-\underset{t}{\overset{\text{C}_m}{\text{C}}}-(\text{C})_3-\underset{x}{\text{C}}^b$ 5	20.2	32.6	39.6	19.4	14.0	13.7	3
 $\underset{x}{\text{C}}-\underset{\gamma}{\overset{\text{C}}{\text{C}}}-\underset{\beta}{\text{C}}-\underset{\alpha}{\text{C}}-\underset{t}{\overset{\text{C}_m}{\text{C}}}-\text{C}-\text{C}^b$ 6	19.0	34.8	34.4	36.5	28.4	22.3	3
 $(\underset{\gamma}{\text{C}}-\underset{\beta}{\text{C}}-\underset{\alpha}{\text{C}}-\underset{t}{\overset{\text{C}_m}{\text{C}}}-\underset{\alpha}{\text{C}}-\underset{\beta}{\text{C}}-\underset{\gamma}{\text{C}})^b$ 7	19.9	33.2	37.5	27.4	30.3	-	4

[a] In ppm calculated from TMS. [b] Obtained as a 50% solution in dioxane.
[c] Obtained as a solution of o-dichlorobenzene-benzene.

are no longer detectable individually after C(4) from the ring. Thus, methyl groups on carbons further than C(4) from the ring may exhibit signals for branch methyls in the same range as observed for similarly branched alkanes.

Inspection of Table II reveals that the methyl branch signals (C̲m) in the ^{13}C NMR spectra only roughly agree with the signals at δ 19.6 and 19.7 observed in the diaromatic fractions. This could, in part, be due to a difference in solvents used as indicated in the footnotes. In our case, all of the spectra of the oil fractions which we have recorded to date have been with samples in $DCCl_3$ as a solvent. We are currently trying to obtain several model compounds which we believe will help in the assignment of the signal at $\sim \delta$ 19.7.

Fraction #16: The ^{13}C NMR data for this fraction is reported for the first time in Table I. The ^{1}H NMR data was recorded previously in Report II (see pages 20 and 41). From the Table, it is evident that this fraction showed a sharp drop in the relative amount of aromatic carbon (21.7%) and hydrogen (5.4%) when compared to the levels observed in the concentrate. A corresponding drop had been observed in the Wilmington monoaromatic fractions (Report II, Table I, page 9); hence the drop was not unexpected in this case. Using the relative peak intensities of signals at δ 14.1, 22.7, 32.7, 29.4, 29.7, 37.3, 31.9 and 30.0 and applying the equation for calculation of side chain lengths (see page 10, Report I), an average side chain length of C_{12}-C_{14} was determined for fraction #16. However, it was evident from the ^{13}C spectrum that there was a low, broad envelope of high signal density which also contributed to the aliphatic portion of the spectrum. Perhaps more significant, several small but distinct ^{13}C signals were observed in the spectrum of fraction 16 which could <u>not</u> be attributed to simple, unsubstituted alkyl side chains. These signals were located at 19.7, 24.4

27.9 and 39.3 ppm, all being downfield from the TMS standard. Examination of Table I revealed that the ^{13}C signals at 27.4 (probably $^{13}CH_2$ or ^{13}CH) and 19.7 could be attributed to side chain substitution. However, alternatives exist which we feel may also play a role. It was noted that ^{13}C shifts reported[6] for several hydroaromatic hydrocarbons might also account for these signals. Examples of several model compounds and the chemical shifts of the pertinent carbons are given in Table III. Of special interest were shifts in structures 8, 9, 11 and 14 at or near 24.4 ppm. These types of structures could be considered to contribute to the signals observed in the ^{13}C NMR spectrum of fraction #16. However, it is speculative at the moment as to how alkyl substitution on structures such as 8-14 (Table III) would affect the shifts of these representative carbons. The effect of substitution would, of course, be expected to diminish with increasing distance from the point of substitution. We are currently searching the literature for more representative models. There exists the distinct likelihood that the signals in the carbon spectra cited above arise from a combination of all of these possible structural features (Tables II and III). The broadness seen in the signals centered at 37.4 and 19.7 ppm in the ^{13}C spectrum of #16 certainly hints strongly that this is the case.

Fraction # 19: The complete ^{1}H and ^{13}C NMR analysis of this fraction was given previously (see Report I, page 17), but the data are reproduced in Table I for comparison purposes. The most notable feature present in the data is the rather large increase in the relative aromatic carbon content of fraction 19 when compared to that of fraction 16. The same type of increase was noted between the first two fractions (209-76, fractions #15 and 19) of the Wilmington monoaromatic series (see page 11, Report II). This could be explained by assuming an overall decrease in the average side chain lengths in addition to a possible increase in the condensed ring

TABLE III

^{13}C Shifts in Select Hydroaromatic Model Compounds[6]

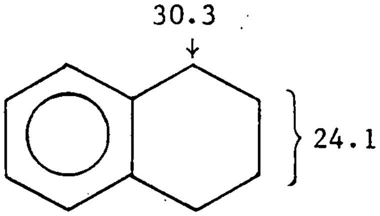
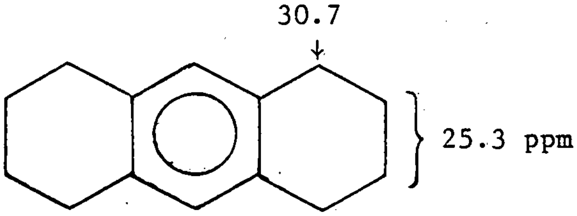
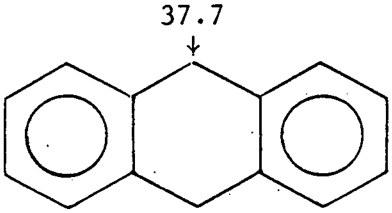
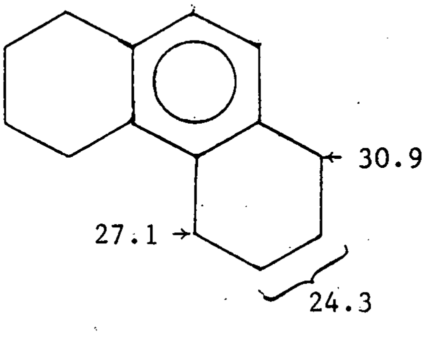
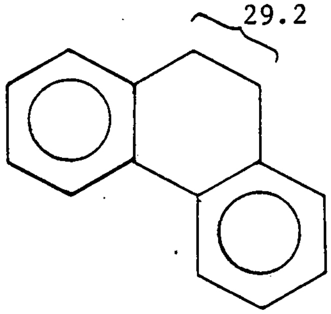
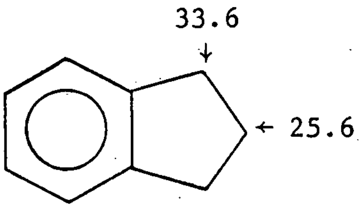
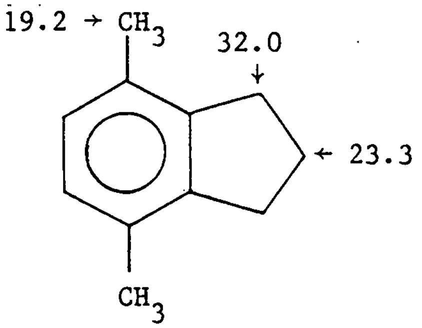
Compound	Structure and Shifts[a]
8	
9	
10	
11	

TABLE III (con't)

Compound	Structure and Shifts[a]
12	
13	
14	

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[a] Shifts reported in ppm downfield from TMS.

chain lengths in addition to a possible increase in the condensed ring aromatic content.

It was noted again that certain signals which did not match the expected ^{13}C NMR shifts of simple, unbranched side chains were discernable in the ^{13}C spectrum of fraction #19. In particular, signals at 11.4, 19.6, 24.4, 27.8 and 39.2 ppm could be seen, although the noise present in the spectrum made additional assignments difficult. Referring to Tables II and III, it is evident that some of these signals could arise from structural types similar to those given. A brief discussion of the over-all importance of these signals appears at the end of this section.

Fraction #24: The ^{13}C NMR data for this fraction appears for the first time in Table I along with the ^{1}H NMR data reported previously (see pages 19, 20, and 42, Report II). The most notable feature of this fraction was the drop in aromatic carbon content (34.3%) and the rise in the aromatic proton content (14.0%) when compared to those data for fraction 19. The broad bands evident in the alkyl portions of both the ^{13}C and ^{1}H NMR spectra of this fraction suggest increased levels of short, highly-branched side chains and an increase in the amount of naphthenic material (e.g. structures similar to compounds **8**-**14**, Table III). Although it was possible to calculate a side chain length (see page 10, Report I) from the relative signal intensities of specific carbons in the longer side chains, the value obtained (C_8-C_9) can not be considered representative of the entire sample due to the presence of the broad, alkyl band of signals. An increase in the amount of naphthenic material, especially in the number of naphthenic rings per molecule, might be expected to result in a decline in the relative amount of aromatic carbon. Such an increase could also account for a rise in the relative aromatic proton contents, since the average number of protons per alkyl carbon would be expected to decline. We are presently investigating the possibility of deriving average molecular structures which would account for these trends.

We were not able to discern in the ^{13}C NMR spectrum of fraction #24 any of the minor signals (such as at 24.5 ppm) observed in the earlier fractions (such as cited for fractions 16 and 19) of this series. This was due to the dramatic increase in signal density in the alkyl portion of the ^{13}C NMR spectrum when compared to the analogous areas in the spectra of fractions 16 and 19. A further discussion of the overall trends observed in this series will be reserved for the end of this section.

Table IV lists for the first time the completed ^{13}C and ^{1}H NMR data for the diaromatic fractions of the Gach Saran distillate (535-675°C). All new entries in the Table are in italics and underlined. A detailed description of each fraction follows.

Fraction #15: The relative aromatic carbon content (as determined from the ^{13}C NMR spectrum) was found to be considerably higher (23.0% Ar-C) than that observed in the corresponding monoaromatic Gach Saran fraction (14.2%) (page 14, Report II). From previously observed trends, this was somewhat expected. As was pointed out for the Wilmington fractions, several low intensity signals were observed in the alkyl region of the ^{13}C NMR spectrum of this fraction. These were recorded at 19.6, 24.4, 27.0, 30.3 and 37.0 ppm. The significance of these signals may be inferred from the possible structural types with similar chemical shifts given in Tables II and III. A further comparison will be given at the end of this section.

Fraction #21: The relative aromatic carbon content of this fraction was found to be considerably higher (37.4% Ar-C) than that found in the previous fraction 15[7] (23.0% Ar-C). A much broader, more intense band for aliphatic

TABLE IV
Gach Saran (535-675°C) Distillate
GPC 207-76 (Diaromatic Fractions)

		Mole % of Total H	
	#15	#21	#24
Ar-H	5.8	9.6	11.9
Al-H	94.2	90.4	88.1
Ar-H/Al-H	5.8/94.2 (1:16.2)	9.6/90.4 (1:9.4)	11.9/88.1 (1:7.4)
α-H(α to Ar)	10.2	17.2	19.6
β-H(β and greater to Ar)	84.0	73.2	68.5
Term CH_3	20.7	23.9	23.6
α-H(α to Ar)/ Total Al-H	10.2/94.2 (1:9.2)	17.2/90.4 (1:5.2)	19.6/88.1 (1:4.5)
Term CH_3/ Total Al-H	20.7/94.2 (1:4.6)	23.9/90.4 (1:3.8)	23.6/88.1 (1:3.7)
α-H(α to Ar)/ Term CH_3	10.2/20.7 (1:2.0)	17.2/23.9 (1:1.4)	19.6/23.6 (1:1.2)
Apparent Side Chain Length	>9	>5	>4
Apparent Branches per Chain	0.3	-0.1	-0.2
Approx. Diaromatic (mole % of Total H)	3.3	6.1	8.7
Ar-C/Al-C (mole % of Total C)	23.0/77.0† (1:3.4)	37.4/62.6† (1:1.7)	32.3/67.7† (1:2.1)
Ar-H/Ar-C	1/4.0	1/4.0	1/2.7
Al-H/Al-C	1.2/1	1.4/1	1.3/1
Side Chain Length (from C peak ratios) estimated	C_{14}-C_{16}†	C_9-C_{10}†	C_8-C_9†

† Sample contained 0.05 M $Cr(acac)_3$

carbon signals was evident in this fraction 21. This broad band obscured the low, sharp signals (such as δ 24.5) seen in the ^{13}C spectrum of fraction 15. One exception was a peak at ∿ 19.7 ppm (from TMS), which, as outlined previously, may be due to methyl carbons attached to an aromatic system but in a hindered position (see pages 12 and 13, Report II). In addition, signals arising from methyl groups branching from the main alkyl side chain may have contributed to this signal (see Table II).

Fraction #24: The relative aromatic carbon content of this fraction 24 was lower (32.3% Ar-C) than that observed for the previous fraction 21 (37.4% Ar-C). This trend has been paralleled in every series of fractions investigated to date. To ascertain the reliability of these measurements, we are currently analyzing additional fractions from the series which will bracket the samples obtained under the original contract.

(2) Summary of the Analysis of the Diaromatic Fractions

A distinct maxima was observed in the relative aromatic carbon content in both the Wilmington and Gach Saran diaromatic fraction series. This maxima is displayed graphically in Figure 1. Also shown in Figure 1 is the steady increase in the aromatic proton content observed in each series of diaromatic fractions. Both of these trends were observed in the monoaromatic fractions as well (see page 35, Report II). At present, we believe this maxima (or rather the sharp decline in relative aromatic carbon content between the second and third fractions in each series) most likely stems from an increase in the naphthenic and saturated fused ring content. Such an increase would be predicted to influence the Al-H/Al-C ratio, with a maxima being observed for the center fraction in each case. This indeed was observed. However, conclusions drawn from the Al-H/Al-C ratio must be considered with caution, since, without another form of analysis (e.g. elemental

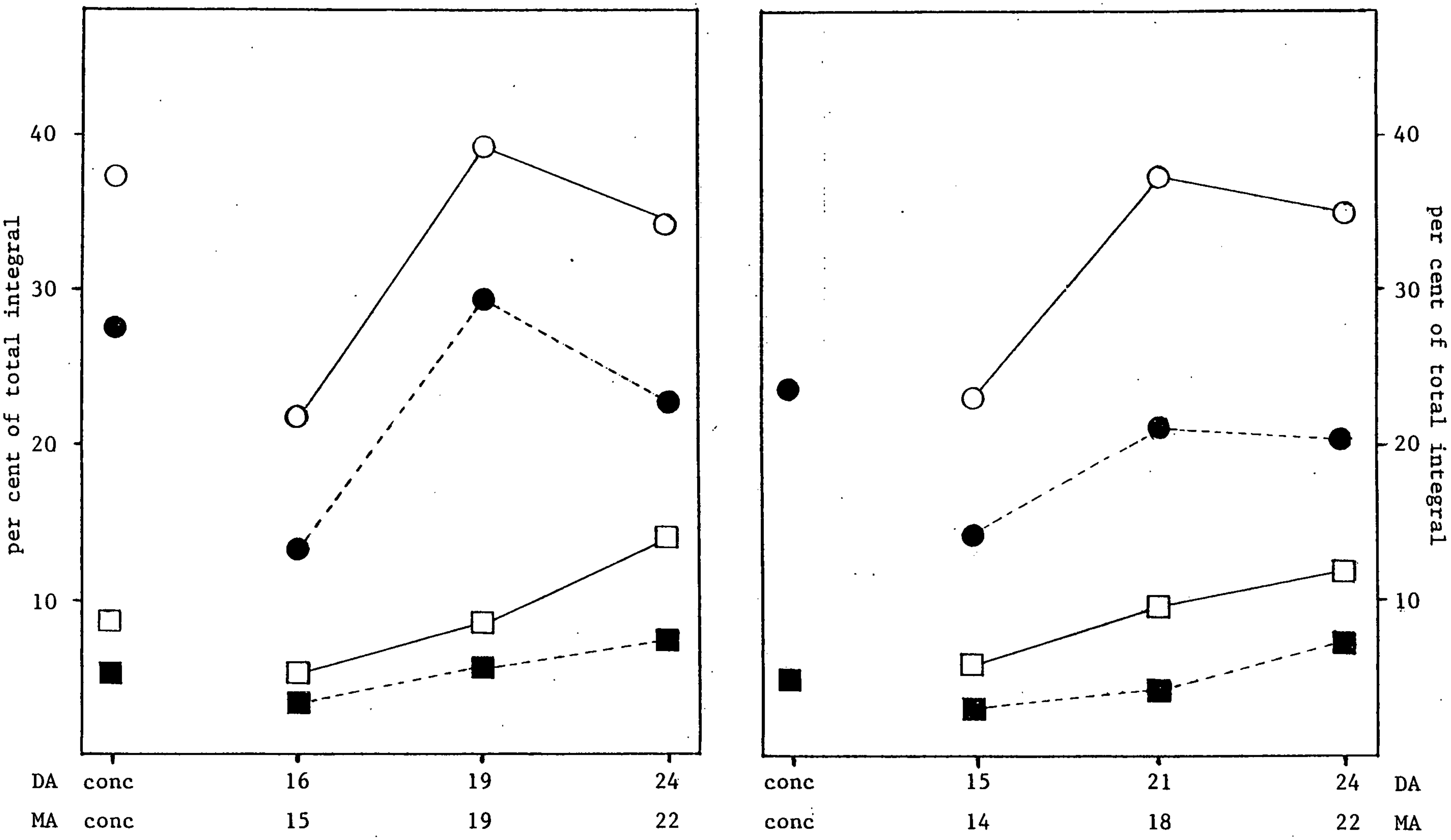


Figure 1. Aromatic carbon (DA- ○ ; MA- ●) and proton (DA- □ ; MA- ■) content of the diaromatic (DA) and monoaromatic (MA) fractions of Wilmington (left) and Gach Saran (right) distillates expressed as per cent of the total carbon or proton integrated areas of the respective NMR spectra.

or mass spectral analysis) for each fraction, there is no simple means of normalizing the ^{1}H to ^{13}C NMR spectra. Table V summarizes the findings from the low intensity signals observed in the alkyl carbon region of the ^{13}C NMR spectra. Each chemical shift is reported in ppm relative to TMS with the signal intensity normalized to the 14.1 ppm signal in each spectrum given in parenthesis. Each signal could arise from systems like those shown in the several different model compounds (Tables II and III). The limited number of models precludes any definitive conclusions at this time. It is tempting to assume that the presence of certain signals (e.g. at ∿ 24.5 ppm) supports one structural feature type over another. Further analysis must await the acquisition of additional spectra of model compounds.

(3) Comments on a Mathematically Constructed Structural Model

Recently a mathematical treatment[7] of our data from the monoaromatic GPC fractions was used to predict an average molecular structure. The fundamental assumptions involved were: 1) only normal and branched alkyl substituents on monoaromatic ring systems were considered; 2) no saturate rings or olefinic material were permitted; and 3) that branching on carbons alpha to the aromatic rings was not allowed. The fundamental structure assumed was:

$$C_6H_y-(CH_2)_{6-y}-(C_zH_{2z+1})_{6-y}$$

A series of simultaneous equations were then developed which used the relative ratios of aromatic and aliphatic proton content:

$$\text{Ar-}\underline{H}/\text{Total } \underline{H} = a = \frac{y}{18-2y+12z-2zy}$$

$$\text{Ar-}\underline{H}/\text{Total } \underline{H} = b = 1-y$$

$$\alpha - \underline{H}(\alpha \text{ to Ar})/\text{Total } \underline{H} = c = \frac{12-2y}{18-2y+12z-2zy}$$

TABLE V

Comparison of Select ^{13}C NMR Signals from Spectra of the Diaromatic Fractions to Model Compounds

Approx. Chemical Shift[a]	Wilmington Diaromatic 211-76[b]			Gach Saran DA 207-76[b]		Relevant Model Compounds from Tables II and III
	Conc.	16	19	15	21	
∿11.0	11.4 (c)	-	-	-	-	4
19.6	19.7 (1.01)	19.7 (1.09)	19.6[e] (0.62)	19.7 (0.53)	19.6 (0.48)	2-5, 7, 14; also comp'ds 1-5, in Report II
24.5	-	24.4 (0.77)	-	24.4 (0.30)	-	4, 8, 9, 11, 13 and 14
27.5	27.9 (0.72)	27.9 (0.67)	27.9 (0.56)	27.0 (0.40)	-	7 and 11
37.0	36.9 (0.68)	37.1 (0.59)	-	37.0 (0.44)	-	6, 7 and 10
37.5	37.6 (0.64)	37.4 (1.12)	37.4 (0.52)	37.4 (0.52)	-	7 and 10
39.0	39.2 (0.59)	39.3 (0.58)	-	-	-	3 and 5

[a] Approximate shifts in ppm from TMS.

[b] Recorded chemical shifts in ppm from TMS (and peak intensities normalized to the 14.1 ppm terminal methyl signal in each spectrum.

[c] Signal intensity not recorded.

These equations were then solved by an iterative method and the values we obtained experimentally for these ratios were inserted to obtain values for $\underline{y}$ and $\underline{z}$. The value of $\underline{y}$ (the degree of substitution on the aromatic ring) could then be used in conjunction with the value of $\underline{z}$ to give an average carbon number per molecule. The calculations were completed for the Gach Saran monoaromatic (206-76) fractions which yielded the following values:

	#14	#18	#22
y	3.00	2.38	2.82
average carbon number per molecule	51.4	32.0	22.6

The other values (branching, side chain length, etc.) calculated, of course, agreed with our previous calculations, since they were determined using the same ratios and assumptions found experimentally. It was noted that the average carbon number per molecule for the first fraction 14 (and possibly fraction 18) would be sufficiently high to place these fractions in the proper boiling range (535-675°C).[8] However, the value of 22.6 carbons per molecule could be considered too low to be in this boiling range. Other models which permitted saturate rings also predicted a carbon number for fraction 22 of 20 carbons per molecule, much too low for this boiling range. If, however, one considered possible diaromatic contamination, a carbon number in the correct size can be estimated. Consider the ratio of alkyl to aromatic carbons as obtained from the ^{13}C NMR spectrum. If $\underline{n}$ is the number of alkyl carbons and if we assume a naphthalene aromatic structure, the following equation is pertinent:

$$\frac{n}{10} = \text{Al-}\underline{C}/\text{Ar-}\underline{C}$$

$$n = (10)(\text{Al-}\underline{C}/\text{Ar-}\underline{C})$$

From the carbon ratios given in Report II (page 14), we obtained a value of n $\sim$ 39. Adding the ten aromatic carbons (from a naphthalene type system), an average carbon number of 49 is obtained. This is well within the mark expected for compounds in this boiling range. However, this presupposes that such diaromatic species predominate in this fraction. The extension of the aromatic proton band to almost δ 8 (see page 34, Report I and page 14, Report II) suggested that over one-half of this fraction 22 could actually be composed of diaromatic species.[9]

(4) Test of Minimum Detectability

The very low level of aromatic carbon signals detected in the spectra of the saturate fractions of the Wilmington ("H" 9-29-76) and Gach Saran ("A" 9-29-76) distillates (see page 30, Report II) demands an evaluation of instrumental sensitivity. Simply, a limit is needed with respect to the determinable lower level of aromatic carbon signals which are detectable by the NMR unit within a reasonable time. Moreover, the accuracy of the integration of such small signals must also be evaluated. Normally, analyses of several standard solutions of a specific model compound would be used to test the limits of detectability as well as the accuracy of the measurements. Unfortunately, such a simple test system employing one compound is not proper in this instance since the complexity of the mixture renders a comparison of an analysis with that of a single, standard reagent untenable.

It was decided to determine the sensitivity of the instrument using a specific combination of two chromatographic fractions in a ratio chosen to give a low level of aromatic carbon signals in the NMR spectrum. Since the ^{13}C NMR spectrum of Sil-Al fraction 355 from motor oil displayed no detectable aromatic signals for 110,000 acquisitions, it was chosen as the standard test system. A small amount of Wilmington MA concentrate was added to give a low concentration of aromatic material. Because the level of aromatic material in the MA concentrate was determined to be high (27.4% of the total carbon integral), it was reasoned that any error associated with the analysis of this concentrate would be relatively small. Thus a dilute solution of this component would be expected to give reasonably accurate measure of the percentage of aromatic carbon in the standard test solution.

A test solution of 0.1678 g of Sil-Al fraction 355, 3.3 mg of Wilmington MA concentrate, and 8.7 mg of $Cr(acac)_3$ (to act as a relaxation agent) in 0.33 mL of $DCCl_3$ was placed in a 5 mm sample tube for analysis by PFT NMR techniques. A total of 110,000 pulses were made over a 63-h period, using a pulse angle of ∿ 45° (8.8 μs; P2 value), an acquisition time of 1.36 s and a delay (D5 value) between acquisitions of 0.7 s. The decoupler was gated off during the 0.7 s delay to suppress NOE effects (see Report I for definitions). The spectrum was integrated electronically using the TT-100 computer.

The amount of aromatic material present was calculated to be 0.9 mg, based upon a value of 27.4% aromatic material for the Wilmington MA concentrate. The total amount of sample weighed was 0.1711 g. Thus, the quantity of aromatic material present was calculated to be 0.53% of the total carbon. Integration of the spectrum yielded a value of 1.16% of the total carbon integral for the amount of aromatic carbons. A broad, low intensity band of signals was definitely observed, even though the accuracy of the integration was in error by 100%. However, it should be noted that the level of detectability is on the order of 1 mg/0.5 mL of aromatic carbon, and that this level of aromatic carbon can be observed and can be determined by normal integration procedures. Nevertheless, a very large number of accumulations is required in order for the percent error to be reduced significantly.

Finally, a summary of the data obtained to date is given in Table VI.

b. References

1. N. F. Chamberlain, *The Practice of NMR Spectroscopy*, Plenum Press, New York, 1974. pp. 56-57.

2. D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).

3. L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).

4. F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, Heyden and Son, Philadelphia, PA, 1978, pp. 225, 295-296.

5. J. B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972, p. 98.

6. H. L. Retcofsky and R. A. Friedel in *Spectrometry of Fuels* (R. A. Friedel, ed.), Plenum Press, New York, 1970, p. 90.

7. J. Vogh, Bartlesville Energy Technology Center, Bartlesville, OK, private communication.

8. N. F. Chamberlain, *The Practice of NMR Spectroscopy*, Plenum Press, New York, 1974, p. 61.

9. One must assign a demarcation line between monoaromatic and diaromatic proton signals in the ^{1}H NMR spectrum. Typically, this is taken to be δ 7.2, the point at which the solvent signal, $HCCl_3$, occurs. See N. F. Chamberlain, *Ibid*., Plenum Press, New York, 1974, p. 57.

TABLE VI

Summary of Data to Date

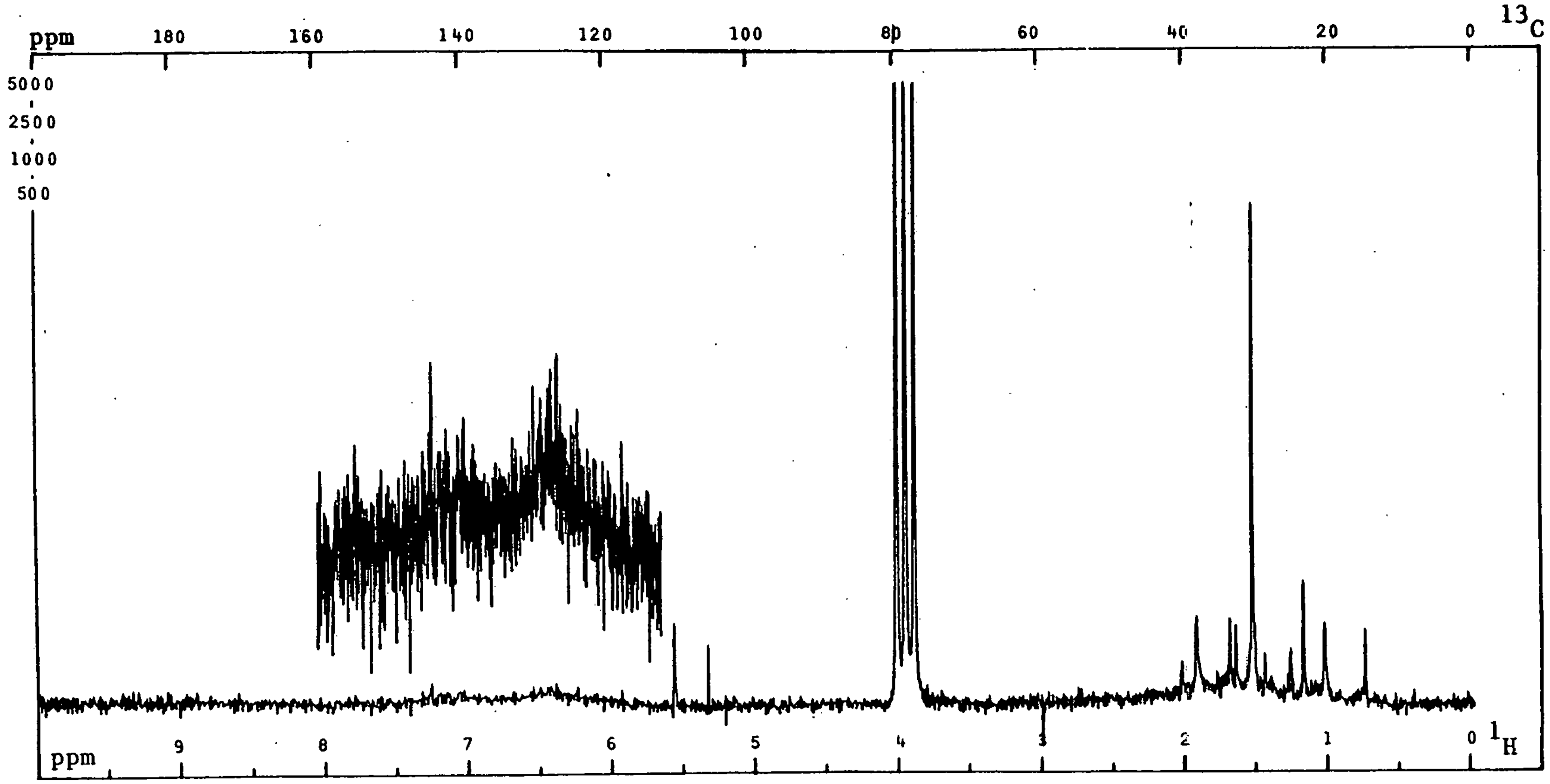
Source	Ar-H^a	Al-H^a	Ar-H/Al-H	α-H^{a,b}	β-H^{a,c}	Term. CH$_3$^{a}	α-H^b/Tot. Al-H	Term. CH$_3$/Tot. Al-H	α-H^b/Term. CH$_3$	Appar. side ch. len.	Appar. br./ch.	Approx. Diar.	Ar-C^{d,f}/Al-C	Ar-H^{e,f}/Ar-C	Al-H^{e,f}/Al-C
Wilmington Crude															
Monoaromatic															
Concentrate	5.3	94.7	1/17.9	12.4	82.3	28.1	1/7.6	1/3.4	1/2.3	7	0.5	2.0	1/2.6	1/5.2	1.3/1
GPC 209-76 #15	3.4	96.6	1/28.4	7.8	88.8	23.6	1/12.4	1/4.1	1/3.0	12	1.0	0.3	1/6.6	1/3.9	1.1/1
GPC 209-76 #19	5.4	94.6	1/17.5	13.8	80.8	27.7	1/6.8	1/3.4	1/2.0	6	0.33	1.7	1/2.4	1/5.4	1.3/1
GPC 209-76 #23	8.3	91.7	1/11.0	15.9	75.8	30.7	1/5.8	1/3.0	1/1.9	5	0.29	4.1	1/3.4	1/3.1	1.2/1
Diaromatic															
Concentrate	8.6	91.4	1/10.6	17.0	74.4	26.8	1/5.4	1/3.4	1/1.6	5	0.00	5.0	1/1.7	1/4.3	1.5/1
GPC 211-76 #16	5.4	94.6	1/17.5	9.9	80.8	30.8	1/9.6	1/3.1	1/3.1	9	1.10	3.2	*1/3.6*	*1/4.1*	*1.2/1*
GPC 211-76 #19	8.4	91.6	1/10.9	17.8	73.8	24.2	1/5.1	1/3.8	1/1.4	5	-0.10	4.0	1/1.6	1/4.6	1.5/1
GPC 211-76 #24	14.0	86.0	1/6.1	18.9	67.1	28.1	1/4.6	1/3.1	1/1.5	4	-0.01	9.0	*1/1.9*	*1/2.4*	*1.3/1*
Polyaromatic-Polar															
Concentrate	5.7	94.3	1/16.5	13.0	81.3	29.9	1/7.2	1/3.2	1/2.3	7	0.53	3.3	1/2.5	1/5.0	1.3/1
GPC 210-76 #16	2.5	97.5	1/39.0	7.7	89.8	32.3	1/12.7	1/3.0	1/4.2	13	1.8	1.1			
GPC 210-76 #21	5.2	94.8	1/18.2	12.2	82.7	27.8	1/7.8	1/3.4	1/2.3	8	0.53				
GPC 210-76 #26	9.5	90.5	1.9.6	17.4	73.2	28.3	1/5.2	1/3.2	1/1.6	5	0.10				
Saturate Fraction	0.9	99.1	1/105	2.6	96.4	33.6	1/37.5	1/2.9	1/12.7	37	0.0	0.0	1/16.0	1/6.6	1.05/1
ch Saran Crude															
Monoaromatic															
Concentrate	5.0	95.0	1/19.0	11.2	83.8	23.1	1/8.5	1/4.1	1/2.1	8	0.4	1.6	1/3.3	1/4.7	1.24/1
GPC 206-76 #14	3.1	96.9	1/31.2	6.2	90.7	20.3	1/15.6	1/4.8	1/3.3	15	1.2	0.0	1/6.0	1/4.6	1.13/1
GPC 206-76 #18	4.1	95.9	1/23.4	12.5	83.4	19.4	1/7.7	1/4.9	1/1.6	7	0.0	2.1	1/3.7	1/5.2	1.22/1
GPC 206-76 #22	7.2	92.8	1/12.9	16.2	76.6	23.7	1/5.7	1/3.9	1/1.5	5	0.0	3.6	1/3.9	1/2.8	1.16/1
Diaromatic															
GPC 207-76 #15	5.8	94.2	1/16.2	10.2	84.0	20.7	1/9.2	1/4.6	1/2.0	9	0.3	3.3	*1/3.4*	*1/4.0*	*1.22/1*
GPC 207-76 #21	9.6	90.4	1/9.4	17.2	73.2	23.9	1/5.2	1/3.8	1/1.4	5	-0.1	6.1	*1/1.7*	*1/3.9*	*1.44/1*
GPC 207-76 #24	11.9	88.1	1/7.4	19.6	68.5	23.6	1/4.5	1/3.7	1/1.2	4	-0.2	8.7	*1/2.1*	*1/2.7*	*1.30/1*

TABLE VI (con't)

Source	Ar-H[a]	Al-H[a]	Ar-H / Al-H	α-H[a,b]	β-H[a,c]	Term CH_3[a]	α-H[b] / Tot. Al-H	Term. CH_3 / Tot. Al-H	α-H[b] / Term. CH_3	Appar. side ch. len.	Appar. br./ch.	Approx. Diar.	Ar-C[d,f] / Al-C	Ar-H[e,f] / Ar-C	Al-H[e,f] / Al-C
Gach Saran Crude															
Polyaromatic-Polar Concentrate	7.4	92.6	1/12.5	14.8	77.8	22.5	1/6.2	1/4.1	1/1.5	6	0.0	5.1	1/2.2	1/4.2	1.34/1
GPC 208-76 #15	2.9	97.1	1/33.2	9.4	87.6	20.5	1/10.3	1/4.7	1/2.2	10	0.4				
GPC 208-76 #20	6.1	93.9	1/15.4	14.8	79.0	23.2	1/6.3	1/4.0	1/1.6	6	0.04				
GPC 208-76 #25	12.6	87.4	1/6.9	19.8	67.6	23.0	1/4.4	1/3.8	1/1.2	4	-0.22				
Saturate Fraction	0.9	99.1	1/106	2.5	96.5	26.0	38.8	1/3.8	1/10.2	39	6.0	0.0	1/12.2	1/8.4	1.07/1
t. Frac. Fr. Oil															
#1465	0.6	99.4	1/166	3.3	96.1	27.3	1/30	1/3.6							
#1480	0.5	99.5	1/199	2.1	97.4	27.8	1/47.4	1/3.6							
#1498	0.6	99.4	1/166	0.8	98.6	33.1	1/165	1/3.0							
#1570	0.5	99.5	1/199	1.9	97.6	28.8	1/52.4	1/3.4							
#1553	0.6	99.4	1/166	0.6	98.8	33.1	1/165	1/3.0					1/18.6	1/10.2	1.05/1
#1553-HPLC	0.0	100.0	0.0	0.0	100.0	32.7	0.0	1/3.1					1/24.6	1/7.8	1.03/1
#39-1484	0.0	100.0	0.0	0.0	100.0	30.4	0.0	1/3.3					0.0	0.0	1.0
Sil-Al #355	0.0	100.0	0.0	0.0	100.0	30.5	0.0	1/3.3					0.0	0.0	1.0
													0.0	0.0	1.0

[a] Mole % of total proton integral. [b] Protons on carbons α to arenes. [c] Protons on carbons β or greater to arenes. [d] Expressed in mole % of total carbon integral. [e] Ratio of mole % of the total proton integral vs mole % of total carbon integral. [f] All carbon spectra were recorded using gated decoupling techniques. Cr(acac)$_3$ was used as a relaxation agent when sample size dictated it.

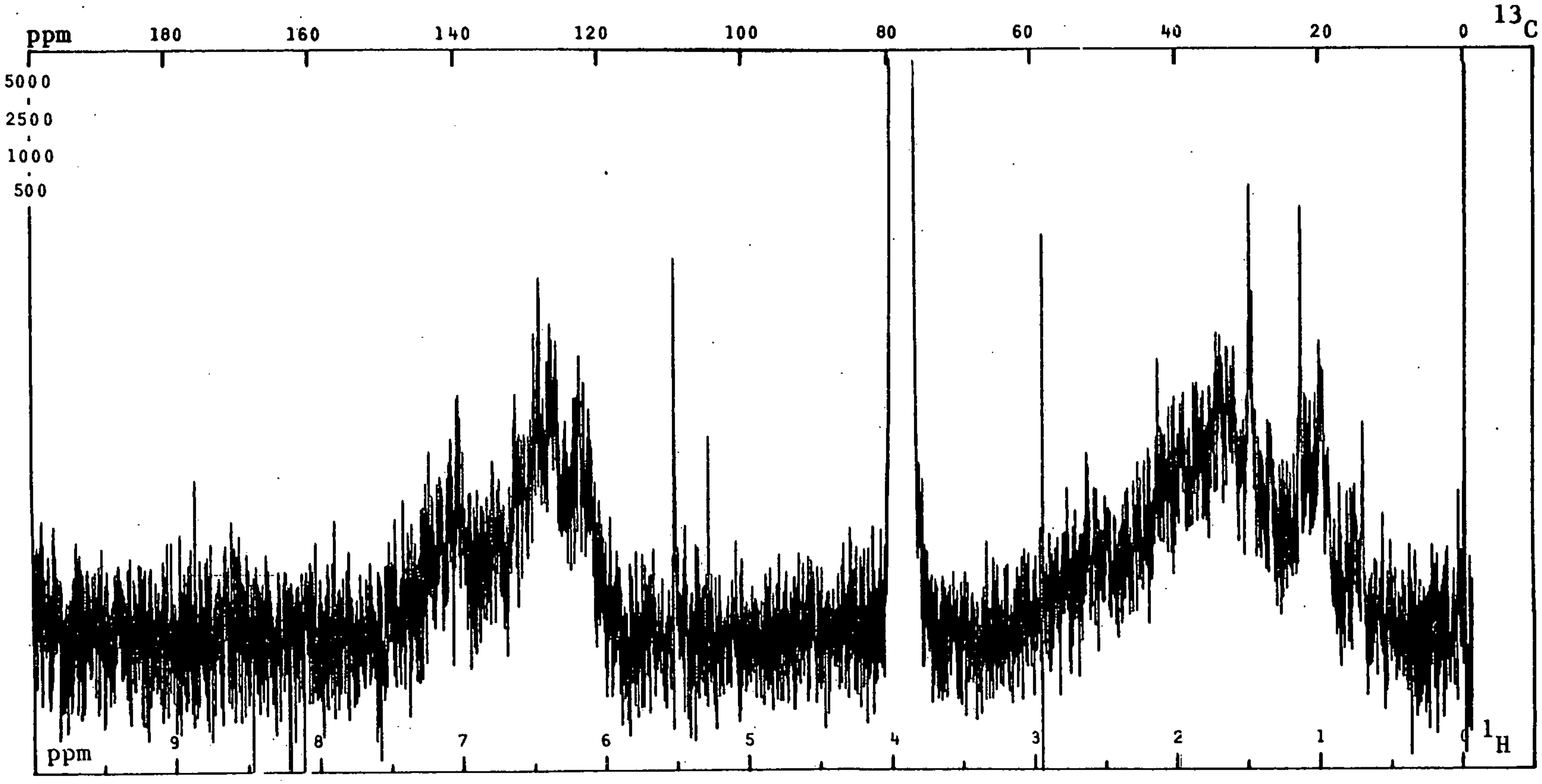
^{13}C NMR Spectrum of Oil. Wilmington DA GPC 211-76 #15 (see Table I)



Sample doped with 0.05 M $Cr(acac)_3$

PFT X CW _ ; Solvent. . . $DCCl_3$; SO. . 35101 Hz; PW. . 3000 Hz; T. . . 37 °C; Acq/SA. . 110,000
Size. . 8 K; P2/RF. . 8.8 µs/dB; SF. . 25.2 M Hz; FB. . ±3 K Hz; Lock. . ^{2}H ; D5/ST. . 0.7 s s
DC. . ^{1}H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq. Wv. 100 Hz

^{13}C NMR Spectrum of Oil, Wilmington DA GPC 211-76 #24 (see Table I)



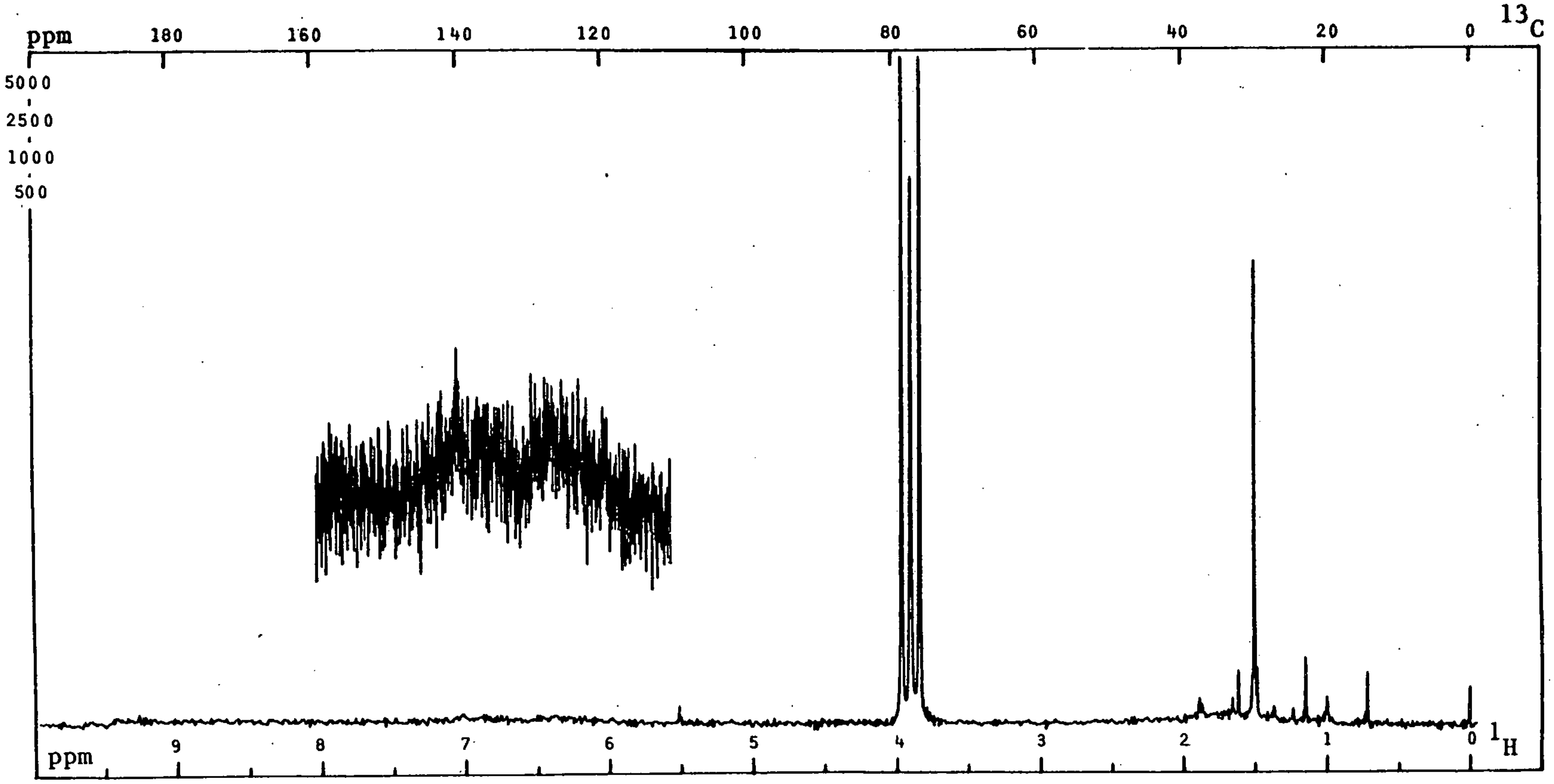
Sample doped with 0.05 M $Cr(acac)_3$

PFT X CW _ ; Solvent. . $DCCl_3$; SO. . 35101 Hz; PW. . 5000 Hz; T. . 37 °C; Acq/SA. . 149,600

Size. . 8K; P2/RF. . 8.4 µs/dB; SF. . 25.2M Hz; FB. . ±3 K Hz; Lock. . ^{2}H ; D5/ST. . . 0.7 s

DC. . ^{1}H ; Gated Off. .Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

^{13}C NMR Spectrum of Oil, Gach Saran DA GPC 207-76 #15 (see Table IV)



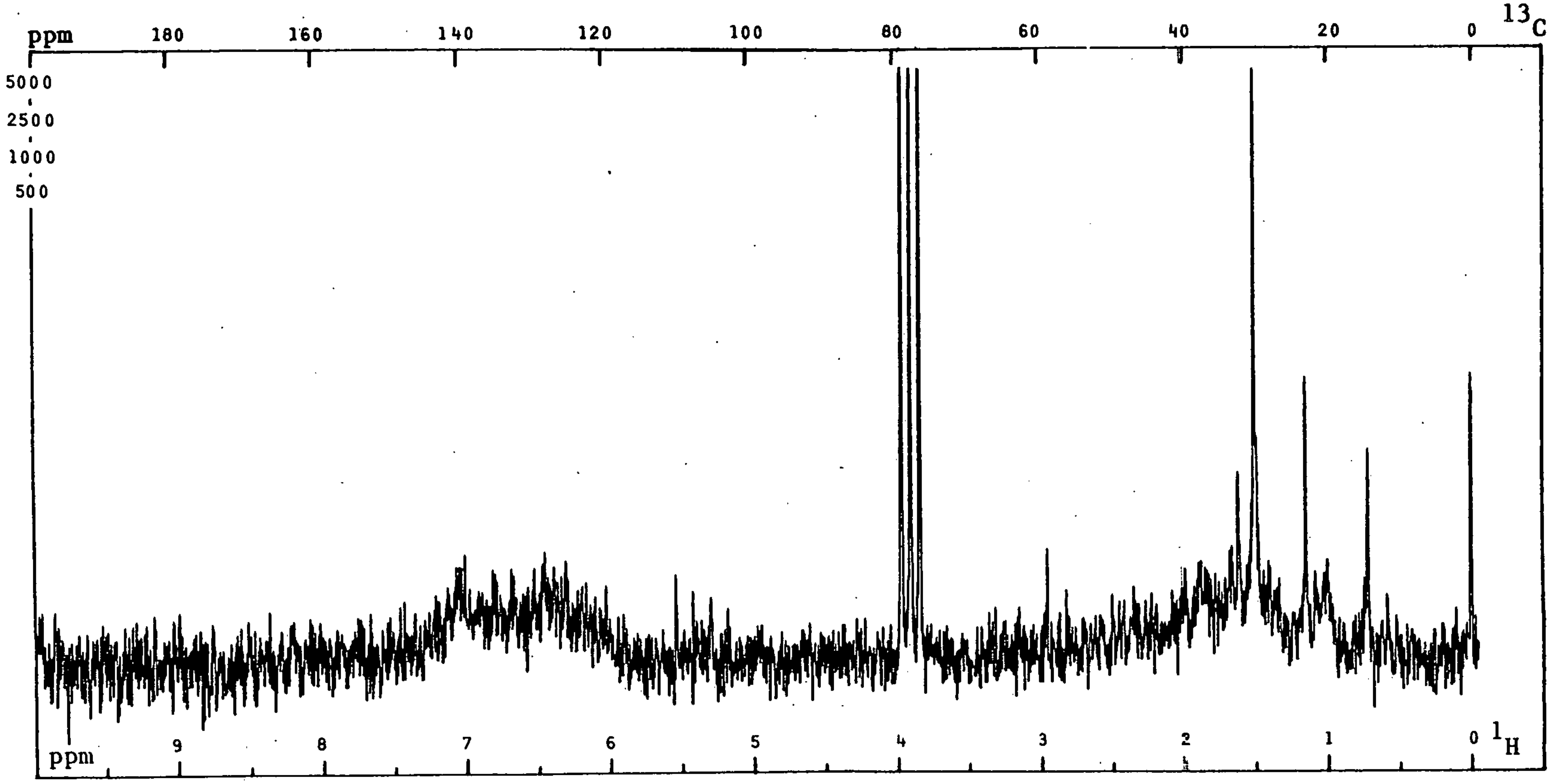
Sample doped with 0.05 M Cr(acac)$_3$

PFT X CW _ ; Solvent. . DCCl$_3$; SO. . 35101 Hz; PW. . 5000 Hz; T. . 37 °C; Acq/SA. . 122,600

Size. . 8K; P2/RF. . 8.8 μs/dB; SF. . 25.2 M Hz; FB. . ±3 K Hz; Lock. . ^{2}H ; D5/ST. . 0.7 s

DC. . ^{1}H; Gated Off. .Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

^{13}C NMR Spectrum of Oil, Gach Saran DA GPC 207-76 #21 (see Table IV)



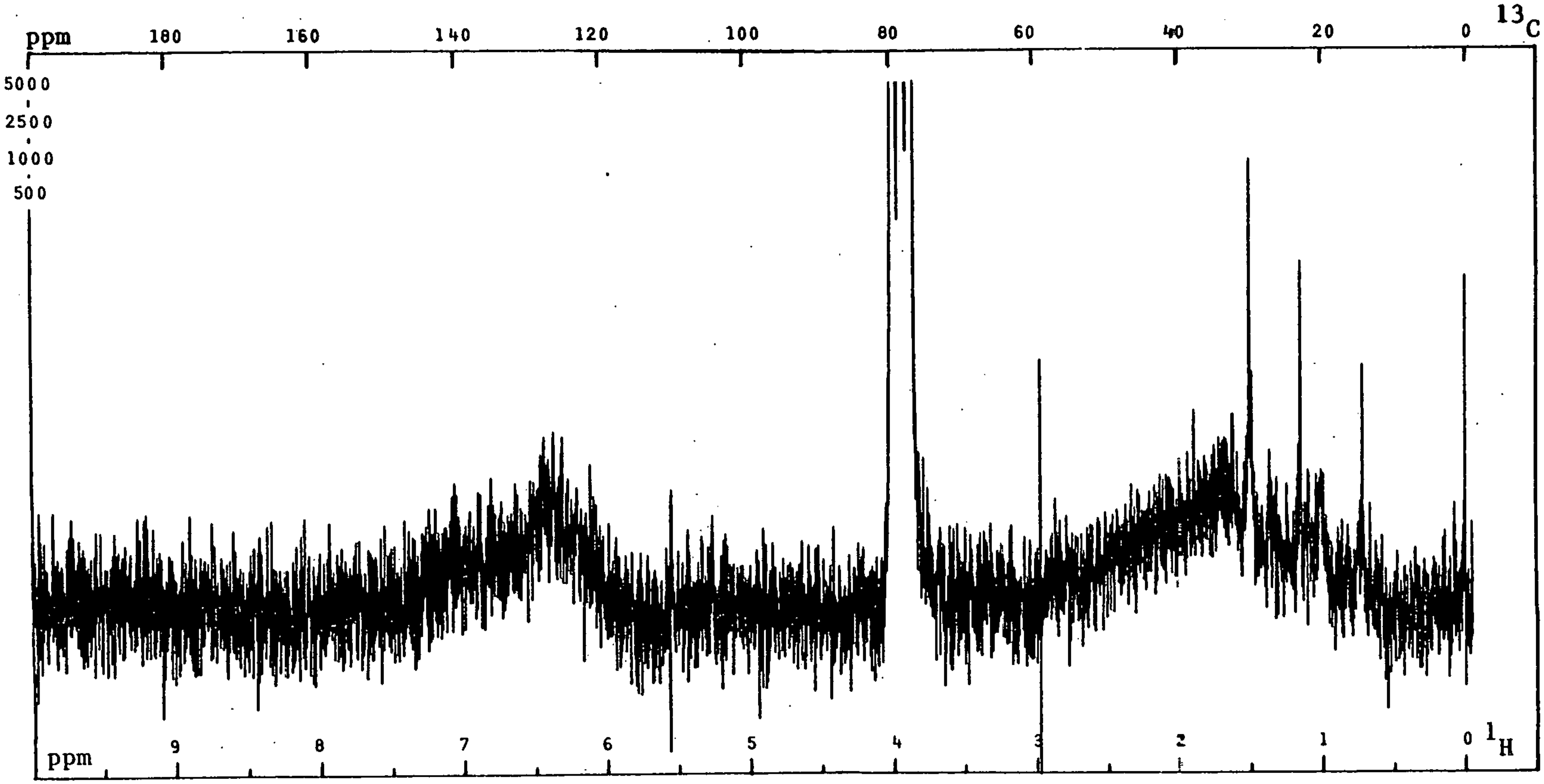
Sample was not doped. A 12 mm sample tube was used.

PFT X CW _ ; Solvent. . DCCl$_3$; SO. . 35101 Hz; PW. . 5000 Hz; T. . 37 °C; Acq/SA. . 8,600

Size. . 8K; P2/RF. . 8.8 μs/dB; SF. . 25.2 M Hz; FB. . ±3 KHz; Lock. . ^{2}H ; D5/ST. . 5.0 s

DC. . ^{1}H; Gated Off. .Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. .Sq Wv 100 Hz

^{13}C NMR Spectrum of Oil, Gach Saran DA GPC 207-76 #24 (see Table IV)



Sample doped with 0.05 M Cr(acac)$_3$

PFT X CW _ ; Solvent. . DCCl$_3$; SO. . 35101 Hz; PW. . 5000 Hz; T. . 37 °C; Acq/SA. . 114,500

Size. . 8 K; P2/RF. . 8.8 µs/dB; SF. . 25.2 M Hz; FB. . ±3K Hz; Lock. . ^{2}H ; D5/ST. . 0.7 s

DC. . ^{1}H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

IV. WORK PLANNED FOR NEXT QUARTER

During the fourth quarter we anticipate the completion of the contract, with the polyaromatic-polar fractions of both the Wilmington (210-76) and Gach Saran (208-76) distillates to be analyzed. In addition we have requested a few specific samples from DOE which we believe will aid in the overall ^{1}H and ^{13}C analysis. These samples will be used primarily to more clearly discern the trends in total aromatic content observed in specific series. Finally, upon completion of the entire analytical scheme, an overall summary of our findings will be drawn together for publication.

V. ACKNOWLEDGMENTS

We gratefully acknowledge the encouragement and support by Dr. Gene P. Sturm and J. W. Vogh at the Bartlesville Energy Research Center. We are also grateful to the Office of Research, College of Arts and Sciences, for aid in preparing this report.