Composition of the Mononuclear Aromatic Material in the Light Gas Oil Range, Low Refractive Index Portion, 230° to 305°C.

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The C_{13} to C_{15} alkylbenzenes from petroleum are principally di- and trisubstituted. The "average" disubstituted alkylbenzene has one methyl group and one long chain alkyl group attached to the benzene ring. In most of the molecules, the long chain alkyl group contains a methyl branch which is present, in some cases, as part of an isopropyl terminal. Most of the trisubstituted alkylbenzenes contain one methyl group substituent and two intermediate length alkyl side chains. A majority of the C_{13} to C_{15} monocyclanobenzene molecules contain a benzene ring condensed with a cycloparaffin ring with a methyl group attached to the benzene ring and with methyl or larger groups on the cycloparaffin ring. In a minority of the molecules, the benzene and cycloparaffin rings are joined through a single bond with a methyl group on the benzene ring and with methyl groups on the cycloparaffin ring.

SINCE 1927 the API Research Project 6 has been engaged in an investigation of the hydrocarbon components of petroleum. The greater part of the effort of the Project has been devoted to the examination of one reference petroleum from the Midcontinent area. Where possible, it is desirable to obtain the composition of petroleum in terms of the amounts of the individual components. This can be done for the lower part of the gasoline range, up to a boiling point of about 130° C.; here nearly all of the individual hydrocarbons have been isolated. However, for the higher boiling fractions because of the extreme complexity of the material, it is possible to isolate single hydrocarbons only in exceptional cases and one usually has to be content with the separation of the material, as completely as feasible, into groups of closely related isomers and the determination of the "average" molecular structure of the isomers within each group by spectroscopic methods.

The present investigation is concerned with the composition of one of the higher boiling fractions from the reference petroleum of Project 6; namely, the mononuclear aromatic portion of the light gas-oil fraction, 230° to 305° C.

PROCEDURE

The mononuclear aromatic material was prepared from the original light gas-oil fraction, 230° to 305° C., by adsorption fractionation with silica gel, as shown in Figure 1. The aromatic fractions resulting from this separation were blended accordingly to their refractive indices into four lots, *A*, *B*, *C*, and *D*. Lot *A*, from the blend of aromatic fractions with refractive indices, n^{25}_{D}, in the range 1.485 to 1.516 constituted the starting material. This was distilled in a column of high separating efficiency at a pressure of 30 mm. Hg (*14*). Results are shown in Figure 2. Twelve distillate fractions, as shown in Figure 2, were analyzed by low voltage mass spectrometry to determine the amounts of the several compound types as a function of the volume of distillate. Four portions of the distillate as indicated on the lower part of the figure were selected for a more detailed investigation. The procedure used to investigate Portion 4 is shown in Figure 3. Following the separation of distillate Portion 4 with a molecular sieve adsorbent into an adsorbed portion and an unadsorbed portion, each

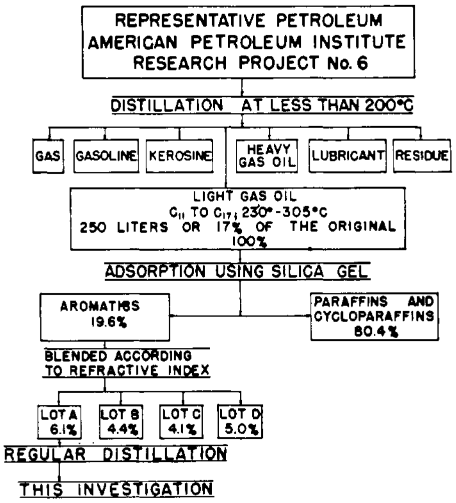


Figure 1. Schematic diagram showing the origin of the mononuclear aromatic material studied in this investigation

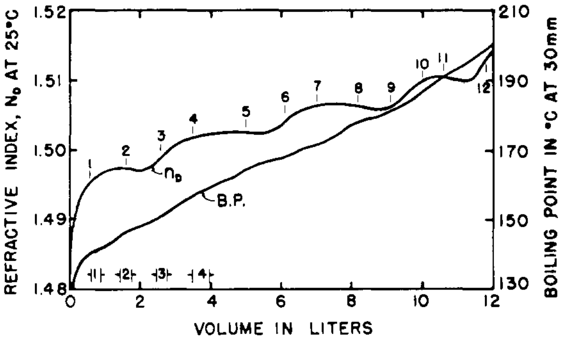


Figure 2. Results of distillation, at 30 mm. of Hg. of the mononuclear aromatic material. The numbers on the curve show the positions of the fractions examined by mass spectroscopy. The numbers at the bottom of the figure refer to the portions which were investigated more completely

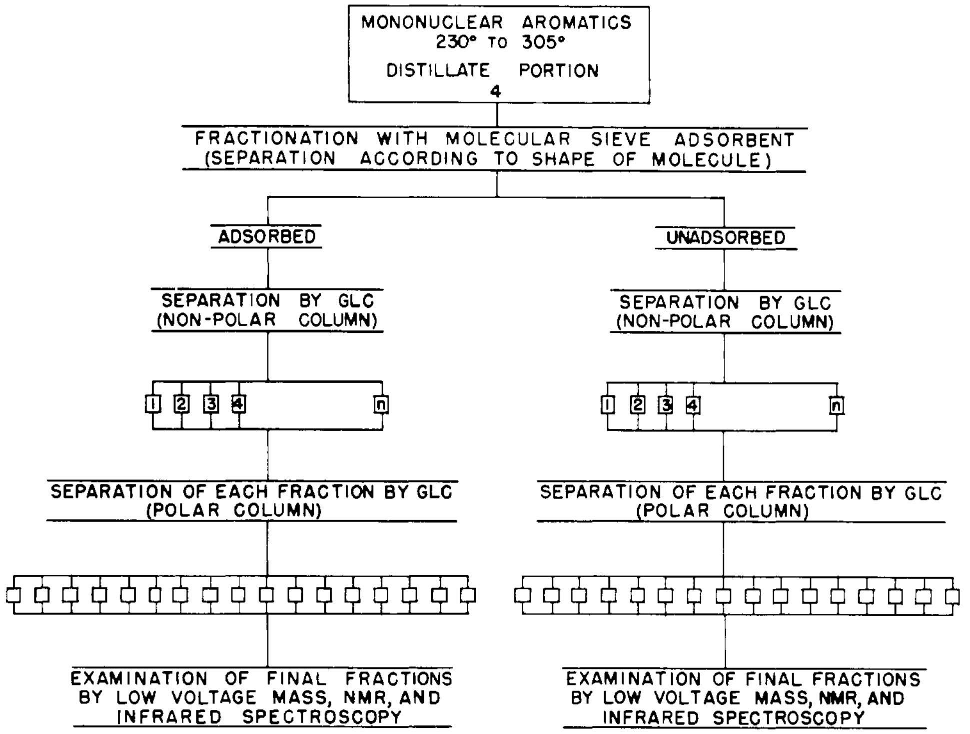


Figure 3. Schematic diagram showing the procedure for processing distillate Portion 4. The procedure with distillate Portions 1, 2, and 3 was the same except that the fractionation with the non-polar columns was omitted

of these portions was processed by preparative scale gas-liquid chromatography with a nonpolar column to give a series of chromatographic fractions. Each chromatographic fraction was processed additionally on a polar column to give a final series of fractions. Each final fraction was examined by low voltage mass, infrared, and nuclear magnetic resonance spectroscopy to determine the structure of the "average" molecule. The same procedure was used to investigate distillate Portions 1, 2, and 3 except that the step involving the separation with the nonpolar column was omitted.

Separation with Molecular Sieve Adsorbents. Aromatic hydrocarbons can be separated according to the size and shape of the molecules by the use of molecular sieve adsorbents. For example, from a solution in 2,2,4-trimethylpentane, *n*-decylbenzene can be completely adsorbed, whereas, 1,3,5-triethylbenzene is only slightly adsorbed on Linde Molecular Sieve 10X (*11*).

Experiments were performed to determine whether molecular sieve adsorbents could be used advantageously to effect a separation in the gas phase. For these investigations a column ¼ in diameter and five feet in length, packed with 14 grams of crushed molecular sieve 10X was used. In contrast to the liquid phase experiments it was found that both *n*-decylbenzene and 1,3,5-triethylbenzene were completely adsorbed and could not be brought out of the column at temperatures in the range 260° C. to 350° C. Evidently, the greater kinetic energy resulting from the higher temperatures involved in the gas phase operations make it possible for the molecules of 1,3,5-triethylbenzene to enter the pores of the adsorbent and become adsorbed. The compound, 1,3,5-triisopropylbenzene, with a large bulky molecule, was swept out of the column in a relatively short time at temperatures in the 260° to 350° C. range which indicated that it was not significantly adsorbed. All of the selected distillate fractions were completely adsorbed. Thus, it was not possible to use molecular sieve adsorbent 10X in a gas phase process to bring about a separation of the molecules in these fractions. The liquid phase procedure adopted was a modification of that described previously (*11*). Briefly, it consisted in forcing 50 ml. of a 50–50 mixture of the aromatic hydrocarbon and 2,2,4-trimethylpentane upward through a packed column, one meter in length and 1.6 cm. in diameter, at a rate of 30 cm. per day. After the charge was introduced additional solvent was passed through the column at the same rate to sweep out the unadsorbed portion. The adsorbed material was desorbed and recovered by removing the molecular sieve from the column and boiling with ethanol for three hours. The per cent by volume of the adsorbed and unadsorbed portions obtained from distillate Portions 1 to 4 (Figure 1) are:

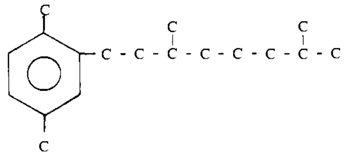
Distillate Portion	Adsorbed Portion, %	Unadsorbed Portion, %
1	34	66
2	44	56
3	40	60
4	42	58

Separation by gas-liquid chromatography. For the separation by gas-liquid chromatography a Beckman Megachrom preparative scale instrument was used with two 24-foot columns in parallel. For separations with the nonpolar partitioning liquid, 20% Apiezon "L" on 42-60 mesh fire brick, at a temperature of 240° C. was used. For separations with the polar partitioning liquid, 25% diethylene glycol succinate or ethylene orthophthalic polyester on 42–60 mesh fire brick at a temperature of 180° to 200° C. was used. In both cases, helium, the carrier gas, was passed through the column at a rate of 15 liters per minute. Experiments performed using various sample sizes showed that, for optimum resolution, a 0.4 ml. sample was the most satisfactory. In an experiment performed with Apiezon "L" with a sample from distillate Portion 4(adsorbed part), the chromatogram showed eight peaks or shoulders which were designated in order of their retention times as *A*, *B*, *C*, *D*, *E*, *F*, *G*, and *H*. Since the Megachrom provides for the collection of only four fractions, the material represented by peaks A and E was combined and collected as a single fraction. Similarly, peaks B plus F, C plus G, and D plus H were combined for collection. Fractions A-E, B-F, C-G, and D-H were reprocessed with Apiezon column to give eight fractions. Each of these fractions, A, B, C, D, E, F, G, and H was separated with a polar column to give 27 final fractions. Chromatograms deposited with the ADI illustrate the procedure. Figure 4 gives the results of the low voltage mass spectrometric analysis of Fraction E and the three final fractions, E-a, E-b, and E-c. The unshaded areas give the amounts of compounds of the series C_nH_{2n-6}; these are alkylbenzenes. The shaded areas give the amounts of compounds of the series C_nH_{2n-8}, these are monocyclanobenzenes, for example, tetrahydronaphthalenes and indanes.

Analyses by Low Voltage Mass Spectrometry. The total concentration of each species, principally members of the C_nH_{2n-6} and C_nH_{2n-8} series, was computed from the principal parent ion only, that is the molecular ion containing the most abundant isotopes of carbon and hydrogen. Several investigators (*3, 6, 7*) have determined sensitivities of pure hydrocarbons of the series encountered in this investigation and have discussed the application of these sensitivity values to the analysis of petroleum fractions. Crable, Kearns, and Norris (*3*) have shown that the sensitivities of the alkylbenzenes depend markedly on the extent of substitution with the sensitivity increasing as the substitution in increased. In this investigation it was found that the "average" monocyclanobenzene contains a methyl group attached to the benzene ring. Thus, the monocyclanobenzenes of the series C_nH_{2n-8} may be regarded as approximately equivalent in sensitivity to trisubstituted alkylbenzenes. This investigation also showed that the alkylbenzenes in this fraction of petroleum were di- and trisubstituted. For this reason, the sensitivities of the alkylbenzenes and cyclanobenzenes were taken as equal. Computations based on the assumption that the alkylbenzenes in this fraction are monosubstituted, with the use of the corresponding sensitivities, lead to a serious overestimation of the alkylbenzene content.

Nuclear Magnetic Resonance Analyses. These analyses were peformed on a Varian V4203 high resolution spectrometer at a constant oscillator frequency of 60 Mc. and a magnetic field of 14,600 gauss. Chemical shifts were measured by the audio side band method. The samples were prepared in five mm. glass tubing about eight inches in length. Fifty mg. of samples, 400-500 mg. of carbon tetrachloride solvent, and a drop of tetramethylsilane was introduced to the glass tube and the sample sealed under vacuum. The tetramethylsilane provided a reference standard at 10τ units on the chemical shift scale (*12*).

Figure 5 shows an NMR spectrum of pure (99 + mole percent) 1-4-dimethyl-2-(3,7-dimethyloctyl)-benzene.



The various peaks are attributable to several different types of protons. The peak assignments are as follows:

The peak at 3.1τ units is attributable to benzenoid type protons; at 7.5τ units the alpha methylene or methine peaks occur. Methyl protons alpha to the benzene ring resonate at 7.7-7.8τ units. In the range from 8.4 to 8.8τ units beta methyl, and methylene and methine protons which are beta or farther from the aromatic ring resonate. The peak at 9.0 to 9.2τ units is attributable to methyl protons in the gamma position or farther from the benzene ring.

The area under each peak is proportional to the number of protons responsible for the given peak (*2, 5*). The areas under the peaks were determined with a planimeter and are an average of three measurements. The number of protons given for each peak is an average of two separate NMR experiments. In the case of the 1,4-dimethyl-2-(3,7-dimethyloctyl)-benzene in the following results were obtained using this method:

	Number of Protons	
Type of Proton	From measured areas	From the structural formula
Aromatic (benzenoid)	3.1	3.0
Methylene or methine alpha to aromatic ring	2.0	2.0
Methyl alpha to aromatic ring	6.2	6.0
Methylene or methine beta or farther removed from the aromatic ring plus methyl beta to the aromatic ring	9.9	10.0
Methyl gamma or farther removed from the aromatic ring	8.8	9.0

When the peaks representing the different types of protons do not seriously overlap, as in the foregoing case, it is possible to determine the number of each kind of proton within ±5 per cent.

The data for the pure compound shows three protons on the ring, thus the benzene is trisubstituted. There are six

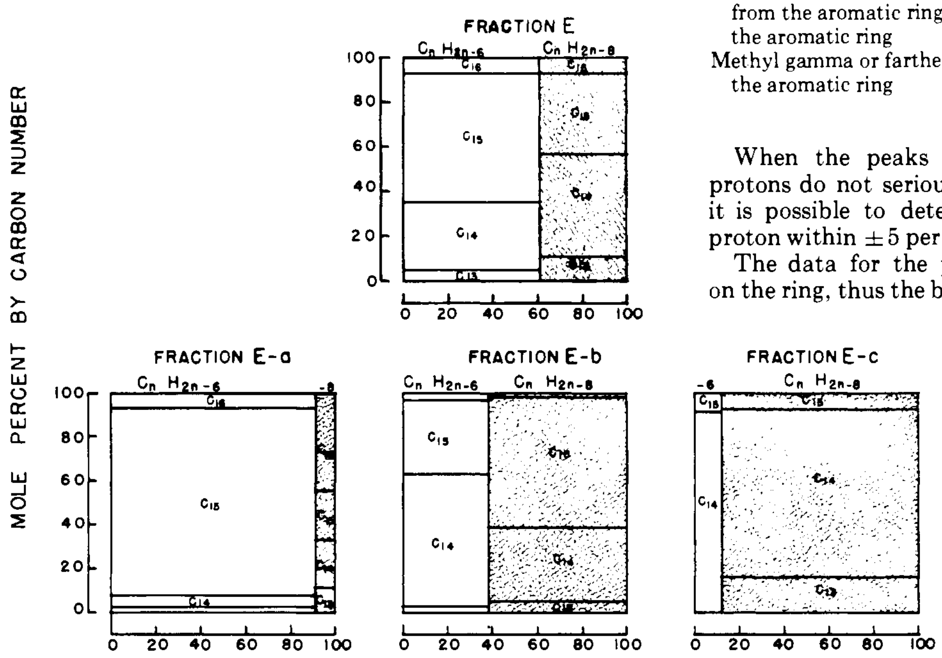


Figure 4. Results of low voltage mass spectrometric analysis of Fraction E and the three final fractions E-a, E-b, and E-c

methyl hydrogens alpha to the ring; therefore, two of the substituents are methyl groups. The value for methylene or methine-type hydrogens alpha to the ring (2 instead of 1) shows that, for the third substituent, a methylene group is alpha to the ring; Also these methylene protons show splitting (a triplet) resembling that due to an adjacent methylene group. There are 10 hydrogens attributable to beta methyls or to methylene and methine groups at positions beta or farther removed from the ring. The presence of an alpha methylene which is split by a beta methylene confirms the fact that there are no beta methyl groups. The peak attibutable to methyls gamma or farther removed from the ring accounts for nine protons or three methyl groups. From this information it is determined that the compound is a dimethyl decyl benzene. The C_{10} chain is branched having three methyls attached at positions gamma or farther from the ring. The NMR peaks at 9.07 and 9.17 show splitting of these methyls by an adjacent methine hydrogen. This pronounced splitting is characteristic of molecules with isopropyl terminals.

In the case of complicated aromatic hydrocarbon structures NMR spectroscopy cannot completely determine the structures of the side chains. Furthermore, in the case of mixtures of these hydrocarbons the difficulty of analysis is obviously increased. Since the final fractions are mixtures of closely related isomers only the structure of the "average" molecule can be ascertained.

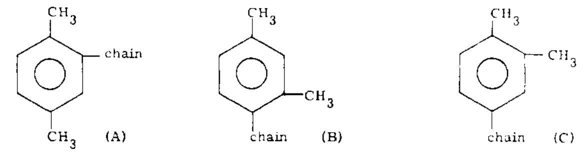
Infrared analysis. Infrared spectra of the final fractions were obtained on either a Perkin Elmer 21, or Perkin Elmer Infracord, Model 137B and Infracord Model NIR 137G spectrometer. Pure liquid samples were used in rock salt cells having a thickness of 0.20 mm., and a film thickness of sample. Spectra were obtained in the 2 to 15 micron range.

From studies with pure alkylbenzenes Young, Duvall, and Wright (*17, 16*) have shown that spectral patterns in the 5 to 6 micron range are characteristic of the positions of the substituent groups on the benzene ring and are independent of the nature of the substituent groups. This pattern together with other correlations as described by McMurray and Thornton (*8*) aids in ascertaining the positions of the substituent groups on the benzene ring. The studies of McMurray and Thornton (*8, 16*) show that a doublet in the 7.225–7.320 micron region indicates the presence of gem dimethyl branches on alkyl chains or isopropyl terminals. A band at 13.4 to 13.8 microns indicates the presence of a sequence of unbranched methylene groups on side chains four or more carbon atoms in length (*15*). However, aromatic absorption bands due to out-of-plane vibrations also occur in this region, so that the band is not generally useful for aromatic hydrocarbons.

The infrared spectrum of 1,4-dimethyl-2-(3,7-dimethyloctyl)-benzene is depositied with the ADI. The 5–6 micron region shows a pattern characteristic of 1,2,4-trisubstitution. The doublet in the 7.225 to 7.320 region shows the presence of gem dimethyl side chain branching or isopropyl terminals.

The foregoing spectroscopic analyses can be used to obtain some information about the structure, assuming it to be unknown, of the compound 1,4-dimethyl-2-(3,7-dimethyloctyl)-benzene.

From low voltage mass spectrometry its general formula is $C_{18}H_{30}$. From the previous discussion of the NMR and infrared spectra the compound is a 1,2,4-trisubstituted benzene. Two side chains are methyl, and the third side chain contains ten carbon atoms. This side chain has three methyl groups, two of which constitute an isopropyl terminal. The first two carbon atoms adjacent to the benzene ring are methylene carbon atoms, so that the other methyl group is gamma or farther from the ring. It is to be noticed that there are three possible structural isomers of the 1,2,4-trisubstituted molecule discussed. These structures are as follows:



Which particular isomer cannot be determined from the analysis.

Thus, using physical methods of analysis, the 1,4-dimethyl-2-(3,7-dimethyloctyl)-benzene could only be described as a dimethyl-(X,7-dimethyloctyl)-benzene where the X indicated a methyl branch attached at a position gamma or farther from the ring.

For the final fractions the spectroscopic analysis yields the following information:

Amount of each hydrocarbon type and the carbon numbers of those types.

Average number of substituents on the benzene ring and some information concerning the positions of these substituents.

Number of methyl groups on the benzene ring of the "average" molecule.

Number of methylene or methine protons alpha to the aromatic ring of the "average" molecule.

Number of methylene or methine protons beta or farther from the ring plus beta methyl protons in the "average" molecule.

Number of methyl groups gamma or farther from the aromatic ring of the "average" molecule.

Some information concerning the extent of branching of the side chains of the "average" molecule.

Analysis of a Typical Final Fraction. A detailed description of a typical final fraction is given in the following example. The final fraction C-b from the adsorbed part of Portion 4 is composed of 92% alkylbenzenes and 79% of the material has a carbon number of 14. Figure 6 shows an NMR spectrum of this final fraction. Using the peak area method, as described earlier, of determining the number of hydrogens

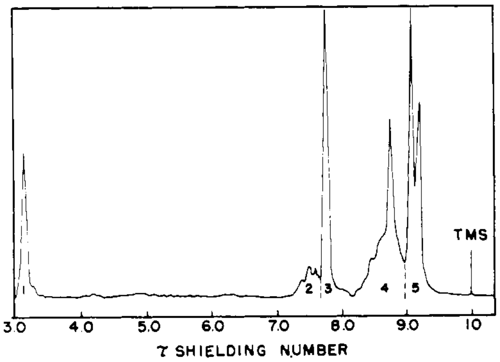


Figure 5. Nuclear magnetic resonance spectrum of 1,4-dimethyl-2-(3,7-dimethyloctyl)-benzene

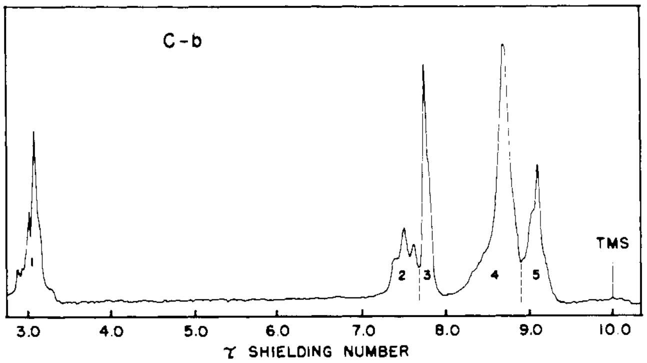


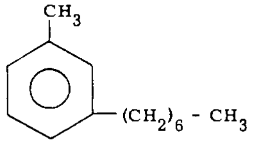
Figure 6. Nuclear magnetic resonance spectrum of a final fraction from Portion 4 (adsorbed part) fraction C-b

attributable to each peak the following results were obtained:

Type of Proton	Number of Protons (from measured areas)
Aromatic Benzenoid	3.7
Methylene or methine alpha to aromatic ring	2.7
Methyl alpha to aromatic ring	3.1
Methylene or mething beta or farther removed from the aromatic ring plus methyl beta to the aromatic ring	9.4
Methyl gamma or farther removed from the aromatic ring	3.5

The above data show that the benzene ring contains 3.7 protons; thus the benzenes are principally disubstituted. Since there are three alpha methyl protons, one of the substituents is a methyl group and the other is a long chain. The value of 2.7 for methylene or methine type hydrogens alpha to the ring indicates that the second substituent has a methylene group alpha to the ring. (The somewhat high value, 2.7 instead of 2.0, may be attributed to the presence of some trisubstituted components.) The NMR spectrum shows this methylene to be split into a triplet due to an adjacent methylene group. The presence of an alpha methylene split by beta methylene indicates that there are no beta methyl groups. There are 9.4 protons attributable to methylenes or methines beta or farther removed from the ring. The peak at 8.7τ units is characteristic of a long chain or methylenes since between the 8.8 to 8.9 region no peaks attributable to beta methyl protons are evident. Thus the 9.4 protons account for approximately 5 methylene groups. The value of 3.5 for methyl protons gamma or farther removed from the benzene ring indicates a long unbranched alkyl chain having a terminal methyl group. Thus, since there is one methylene alpha and five more beta and farther removed giving six methylenes on the chain and there is one terminal methyl group, the chain is a normal heptyl group attached to the ring. Thus, the main component of this final fraction is a methylheptylbenzene.

The infrared spectrum of this fraction is deposited with the ADI. The pattern in the 5.0-6.0 micron region is charcteristic of 1,3-disubstitution on the benzene ring. Other characteristic bands as mentioned in the previous section confirm that most of the material in this fraction is 1,3-disubstituted. Furthermore, the band in the 7.2-7.3 micron region indicates that there are no terminal isopropyl groups. Thus, the main component in the final fraction of Portion 4 (adsorbed part) C-b is 1-methyl-3-*n*-heptylbenzene having the structure:



RESULTS

Results in terms of the amounts of the several compound types (present in Lot *A*) as a function of the volume of distillate are given in Figure 7. The total material is composed of 41% of the series C_nC_{2n-6} (alkylbenzenes), 40% of the series C_nH_{2n-8} (monocycloanobenzenes), 16% of the series C_nH_{2n-10} (dicyclanobenzenes), 3% of the series C_nH_{2n-12} (tricyclanobenzenes or naphthalenes), and a trace of the series C_nH_{2n-14}.

Also given in Figure 7 is the distribution according to carbon number. The relative amounts according to carbon number for the alkylbenzenes, monocyclanobenzenes and dicyclanobenzenes are:

Compound Type	Percent of Total Distillate						
	C-13	C-14	C-15	C-16	C-17	C-18	C-19
C_nH_{2n-6}	4	12	10	7	5	2	1
C_nH_{2n-8}	2	10	11	8	6	2	1
C_nH_{2n-10}	...	1	3	5	4	2	1

Mononuclear aromatics are also present in Lot *B* (Figure 1). The total amounts of the different series are as follows:

Compound Type	Mole Percent of Light Gas-Oil Fraction, 230-305° C.		
	Lot *A*	Lot *B*	Total
C_nH_{2n-6}	2.50	0.71	3.21
C_nH_{2n-8}	2.44	2.11	4.55
C_nH_{2n-10}	0.98	0.84	1.82
C_nH_{2n-12}	0.18	0.66	0.84
C_nH_{2n-14}	...	0.07	0.07
Total	6.10	4.40	10.50

Lots *A* and *B* probably contain substantially all the mononuclear aromatic material belonging to the C_nH_{2n-6} and C_nH_{2n-8} series. It is believed that significant amounts of the C_nH_{2n-10} and C_nH_{2n-12} series will be found in Lot *C*.

The results of mass spectral analysis of typical final fractions from the adsorbed and unadsorbed parts of Portions 1, 2, 3, and 4 are given in Table I. This table gives for each final fraction, the mole percent of each type, (alkylbenzenes, monocyclanobenzenes, dicyclanobenzenes) and the distribution according to carbon number within each type.

Table II gives the results of the NMR analyses of typical final fractions obtained from the adsorbed and unadsorbed parts of Portions 1, 2, 3, and 4.

Figure 8 gives the average number of substituent groups on the benzene nucleus as determined by NMR analysis for the final fractions obtained from the adsorbed and unadsorbed parts of Portion 3. The vertical height of each block represents the uncertainty in the determination. The fractions from the unadsorbed portion have, on the average, more substituent groups on the benzene ring than do those from the adsorbed portion. This is to be expected since with a greater number of substituent groups on the benzene ring, it becomes more difficult for the molecules to enter the pores of the molecular sieve adsorbent.

Figure 9 gives the 7.2-7.3 micron region of the infrared spectrum for typical fractions from Portions 1, 2, and 3. As mentioned previously, this region shows a doublet when gem dimethyl or terminal isopropyl groups are present.

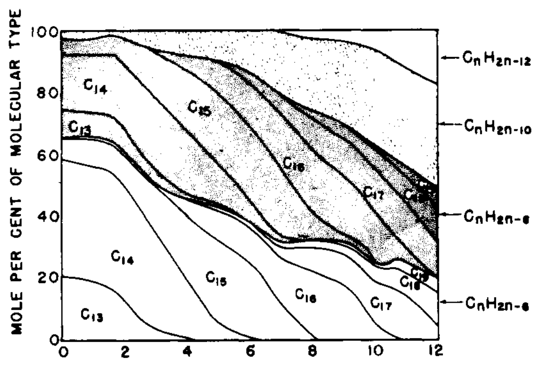


Figure 7. Distribution with respect to compound type and with respect to the carbon numbers of each type in the distillate. (From low voltage mass spectrometric analysis of the 12 distillate fractions numbered in Figure 2.)

Table I. Mass Spectral and Other Data on Typical Final Fractions[a]

Fraction	Amount of Hydrocarbon Type, Mole Percent															Refractive Index n_D at 25° C.	Percent of Portion
	C_nH_{2n-6}					C_nH_{2n-8}					C_nH_{2n-10}						
	Total	C_{13}	C_{14}	C_{15}	C_{16}	Total	C_{13}	C_{14}	C_{15}	C_{16}	Total	C_{13}	C_{14}	C_{15}	C_{16}		
Portion 1 (Adsorbed Part)																	
B	99	63	34	2	...	1	1	...	...	...	...	...	...	...	...	1.4879	11
C	97	65	28	4	...	3	1	2	...	...	...	...	...	...	...	1.4885	10
D	98	77	18	3	...	2	1	1	...	...	...	...	...	...	...	1.4890	20
E	90	65	23	2	...	10	4	6	...	...	...	...	...	...	...	1.4899	16
H	11	5	6	...	...	87	48	38	1	...	2	1	1	...	...	1.5106	14
Portion 1 (Unadsorbed Part)																	
B	98	22	62	14	...	2	1	1	...	...	...	...	...	...	...	1.4881	8
C	97	33	50	14	...	3	1	2	...	...	...	...	...	...	...	1.4893	25
G	22	6	16	...	...	75	22	44	9	...	3	...	2	1	...	1.5064	17
Portion 2 (Adsorbed Part)																	
C	97	52	38	6	1	3	1	2	...	...	...	...	...	...	...	1.4883	5
D	98	62	28	8	...	2	1	1	...	...	...	...	...	...	...	1.4885	10
J	13	1	6	3	3	81	24	55	2	...	6	1	3	2	...	1.5045	11
Portion 2 (Unadsorbed Part)																	
B	98	25	49	19	5	2	1	1	...	...	...	...	...	...	...	1.4887	12
C	96	29	37	25	5	4	1	2	1	...	...	...	...	...	...	1.4896	11
G	25	2	17	6	...	70	11	42	17	...	5	1	2	2	...	1.5072	32
Portion 3 (Adsorbed Part)																	
C	91	13	52	25	1	8	2	4	2	...	1	...	1	...	...	1.4890	12
D	84	5	58	20	1	15	3	9	3	...	1	...	1	...	...	1.4905	16
H	16	...	13	2	1	74	10	55	9	...	10	...	5	5	...	1.5153	15
Portion 3 (Unadsorbed Part)																	
A	96	7	42	35	12	2	...	1	1	...	2	...	1	1	...	1.4877	3
C	87	6	30	37	14	12	1	5	5	1	1	...	1	...	...	1.4914	18
H	6	1	3	2	...	74	8	58	8	...	20	...	6	13	1	1.5180	9
Portion 4 (Adsorbed Part)																	
A-b	91	3	80	7	1	9	...	6	3	...	...	...	...	...	...	1.4901	1.38
C-b	92	...	79	13	...	8	1	7	...	...	...	...	...	...	...	1.4880	6.06
D-b	91	...	50	39	2	9	...	5	2	2	...	...	...	...	...	1.4865	9.08
E-a	91	2	5	78	6	9	1	2	2	4	...	...	...	...	...	1.4879	4.64
E-c	12	...	11	1	...	82	13	63	6	...	6	...	4	2	...	1.5148	2.22
F-a	100	...	5	87	8	...	...	...	...	...	...	...	...	...	...	1.4889	3.38
F-c	11	...	9	2	...	87	3	64	20	...	2	...	1	1	...	1.5130	5.19
G-b	6	...	4	1	...	86	...	71	15	...	8	...	2	6	...	1.5135	8.45
Portion 4 (Unadsorbed Part)																	
B-b	88	6	62	20	...	12	...	2	9	1	...	...	...	...	...	1.4903	2.02
C-a	80	...	10	60	10	19	10	4	4	1	1	...	1	...	...	1.4875	1.93
D-c	23	4	17	2	...	76	10	58	8	...	1	...	...	1	...	1.5094	1.72
E-c	5	3	2	...	...	88	53	34	1	...	7	...	6	1	...	1.5165	2.75
F-c	...	...	...	...	...	85	61	23	1	...	15	3	11	1	...	1.5191	3.04
G-a	12	2	6	4	...	85	6	18	61	...	3	...	...	3	...	1.5125	5.58

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[a] Data on all final fractions are filed with the ADI.

Table II. Number of Different Types of Hydrogen Atoms in Typical Final Fractions[a]

Fraction	Type of Hydrogen 1[b]	2[c]	3[d]	4[e]	5
	Portion 1 (Adsorbed Part)				
B	3.7	2.6	2.1	6.2	6.0
C	3.8	2.6	2.1	6.0	6.1
D	3.7	2.1	3.3	6.4	5.0
E	4.1	2.6	2.6	7.2	4.0
H	3.0	2.4	2.8	7.2	3.5
	Portion 1 (Unadsorbed Part)				
B	3.4	2.3	2.9	7.4	5.9
C	3.4	2.0	3.0	6.2	5.8
G	3.2	2.0	3.8	7.6	3.2
	Portion 2 (Adsorbed Part)				
C	3.8	2.5	2.0	6.5	6.4
D	3.6	2.0	3.3	6.6	5.6
J	3.2	3.1	3.0	7.6	3.0
	Portion 2 (Unadsorbed Part)				
B	3.6	2.9	2.1	8.0	5.3
C	3.4	2.5	3.1	7.4	5.4
G	3.1	3.0	3.9	6.9	3.7
	Portion 3 (Adsorbed Part)				
C	3.8	2.4	2.7	8.0	5.2
D	3.8	2.3	3.0	8.4	4.5
H	3.0	2.0	3.2	7.3	4.8
	Portion 3 (Unadsorbed Part)				
A	3.0	2.0	2.5	8.5	6.9
C	3.3	2.4	3.4	8.0	6.1
H	3.0	2.2	3.8	6.9	4.2
	Portion 4 (Adsorbed Part)				
A-b	3.2	2.7	3.4	7.4	5.2
C-b	3.7	2.7	3.1	9.4	3.5
D-b	4.0	2.4	2.0	10.1	4.3
E-a	3.5	3.0	2.4	9.0	5.9
E-c	2.9	3.6	3.0	6.7	3.8
F-a	3.8	2.5	2.4	8.8	6.3
F-c	3.2	3.0	3.2	7.3	4.0
G-b	3.3	3.4	2.7	7.0	3.9
	Portion 4 (Unadsorbed Part)				
B-b	3.4	2.4	3.0	9.2	6.2
C-a	3.1	2.2	2.6	9.9	7.2
D-c	2.8	3.1	3.2	8.1	5.2
E-c	2.7	3.1	3.8	7.2	4.0
F-c	3.2	4.2	3.5	8.4	3.5
G-a	3.6	0.9	3.2	7.6	7.9

[a] Data on all final fractions are filed with the ADI. [b] Aromatic (Benzenoid). [c] Methylene and methine alpha to benzene ring. [d] Methyl alpha to benzene ring. [e] Methylene and methine beta and farther removed from benzene ring plus methyl beta to benzene ring. [f] Methyl gamma and farther removed from benzene ring.

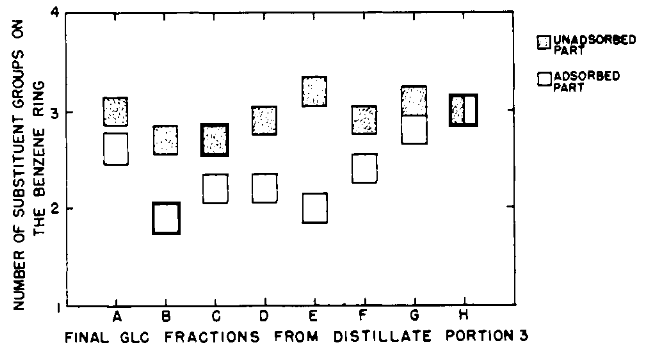


Figure 8. Average number of substituent groups on the benzene ring for final fractions from distillate Portion 3. The vertical height of each block represents the uncertainty in the determination

Since a significant amount of gem dimethyl branching seems very improbable, the presence of this doublet may be taken as an indication of isopropyl terminals. Infrared and NMR spectra of additional final fractions are deposited with the ADI.

Tables III, IV, V, VI, and VII give certain interpretations resulting from the analytical data on typical final fractions which are relatively homogeneous with respect to molecular type from Portions 1, 2, 3, and 4, respectively. These interpretations concern the number of substituent groups and the positions they occupy on the benzene nucleus, and also the nature of the side chains in terms of their length and extent of branching.

The data given in the foregoing tables lead to the following conclusions:

The "average" alkylbenzenes from the adsorbed portions are principally disubstituted. One of the substituents is a methyl group, the other consists of a longer chain of 6, 7, or 8 carbon atoms. In approximately two-thirds of this material the side chain contains a methyl branch; in many cases, but not always, this appears to be part of an isopropyl terminal. The remainder of the material contains an unbranched long chain. The disubstituted alkylbenzenes appear to be substituted principally in the 1, 3 and 1, 2 positions.

The alkylbenzenes from the unadsorbed portion consist principally of di- and trisubstituted molecules. These also have approximately one methyl group substituent per molecule indicating that in most of the trisubstituted molecules two of the alkyl groups consist of intermediate length chains.

There is some indication of branching on carbon atoms alpha to the ring for some fractions. For example, Fraction C (Portion 1, unadsorbed part) has one methyl and 1.6 longer groups. If these longer groups were attached to the ring entirely through methylene groups a value of 3.2 would be expected for non methyl hydrogens on carbons alpha to the ring instead of 2.0 actually found. This indicates that some of these are methine type hydrogens.

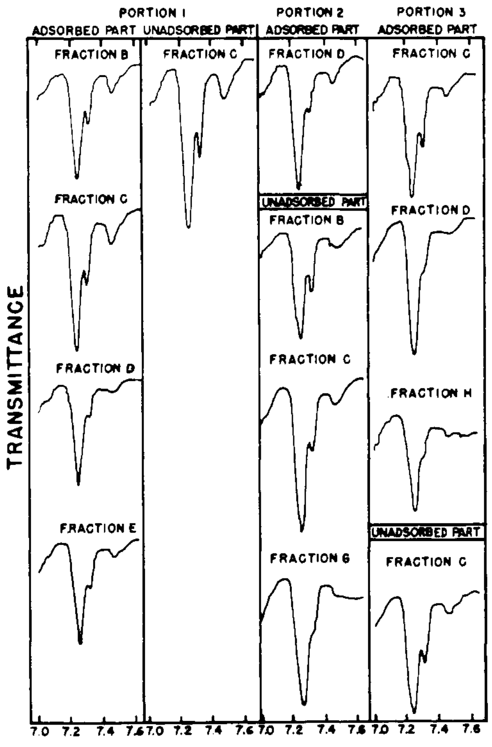


Figure 9. Infrared spectra in the 7.0 to 7.6 micron region for final fractions from Portions 1, 2, and 3

Table III. Structures of "Average" Molecules in Typical Final Fractions (Portion 1)

Fraction	Number of Substituent Groups[a]	Position of Substituents on Ring[b]	Nature of Substituent Groups on "Average" Molecule
			Adsorbed Part
B	2.3	1,3	A methyl group and a group of 6 carbon atoms with a methyl branch at the carbon beta or farther removed from the ring. NMR shows 2 methyl groups attached to a carbon beta or farther from the ring. Infrared indicates some isopropyl terminals on the chain (Figure 9).
C	2.2	1,3 with some 1,2	A methyl group and a group of 6 carbon atoms with a methyl branch at the carbon beta or farther from the ring. NMR shows 2 methyl groups attached to a carbon atom beta or farther from the ring. Infrared indicates some isopropyl terminals on the chain (Figure 9).
D	2.3	1,3 with some 1,2	A methyl group and a group of 6 carbon atoms. Some chains branched at the carbon beta or farther removed from the ring. Infrared indicates a very small amount of isopropyl terminals on the chain (Figure 9).
E	1.9	1,3 with some 1,2	A methyl group and a group of 6 carbon atoms. Very little branching of side chains. NMR shows approximately one methyl group attached to a carbon atom beta or farther from the ring. Infrared indicates a small amount of isopropyl terminals on the chain.
H	3.0	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring.
			Unadsorbed Part
B	2.6	Uncertain	A mixture of di- and trisubstituted alkylbenzenes with an average of one methyl group and between one and two longer groups attached to the ring. Infrared indicates some isopropyl terminals on long chain.
C	2.6	Uncertain	Similar to Fraction B (See above). Infrared spectra indicates some isopropyl terminals on the chain (Figure 9).
G	2.8	1,2,4	Principally monocyclanobenzenes with a methyl group on the aromatic ring and methyl or longer groups on the cycloparaffin ring.

[a] Computed as described from Mass and NMR data. [b] From infrared spectra. The assignment of positions is uncertain. These appear to be the most probable positions of the substituent groups of the main components.

Table IV. Structures of "Average" Molecules in Typical Final Fractions (Portion 2)

Fraction	Number of Substituent Groups[a]	Position of Substituents on Ring[b]	Nature of Substituent Groups on "Average" Molecule
			Adsorbed Part
C	2.2	1,3 with some 1,2	A methyl group and a group of 6 or 7 carbon atoms with a methyl branch at the carbon beta or farther removed from the ring. NMR shows 2 methyl groups attached to a carbon beta or farther from the ring. Infrared indicates some isopropyl terminals on the chain.
D	2.4	1,3 with some 1,2	A mixture of di- and trisubstituted alkylbenzenes with approximately one methyl group and between one or two longer groups. Infrared indicates a small amount of isopropyl terminals on the chain (Figure 9).
J	2.8	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring.
			Unadsorbed Part
B	2.4	Uncertain	A mixture of di- and trisubstituted alkylbenzenes with an average of slightly less than one methyl group and between one and two longer groups. Infrared indicates some isopropyl terminals on the chain (Figure 9).
C	2.6	Uncertain	A mixture of di- and trisubstituted alkylbenzenes with an average of one methyl group per molecule and between one and two longer groups. Infrared indicates some isopropyl terminals on longer chains (Figure 9).
G	2.9	1,2,4	Principally monocyclanobenzenes with somewhat more than one methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring.

[a] Computed as described from Mass and NMR data. [b] From infrared spectra. The assignment of positions is uncertain. These appear to be the most probable positions of the substituent groups of the main components.

Table V. Structures of "Average" Molecules in Typical Final Fractions (Portion 3)

Fraction	Number of Substituent Groups[a]	Position of Substituents on Ring[b]	Nature of Substituent Groups on "Average" Molecule
			Adsorbed Part
C	2.2	1,2 and 1,3	A methyl group and a group of 7 carbon atoms with a methyl branch at the carbon beta or farther removed from the ring. NMR shows nearly two methyl groups attached to carbons beta or farther from the ring. Infrared indicates some terminal isopropyl groups on the chain (Figure 9).
D	2.2	1,2 and 1,3	A methyl group and a group of 7 carbon atoms. A small amount of branching is indicated by NMR as 1.5 methyls are attached to carbons beta or farther removed from the ring. Infrared shows no significant terminal isopropyl branching (Figure 9).
H	3.0	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring. The infrared spectrum is shown in Figure 9.
			Unadsorbed Part
A	3.0	1,3,5	A methyl group and two larger groups attached to the ring. Infrared indicates substantial terminal isopropyl branching.
C	2.7	Uncertain	A methyl group and two larger groups attached to the ring. Infrared indicates some terminal isopropyl branching (Figure 9).
H	3.0	1,2,4	Principally monocyclanobenzenes with a methyl group attached to the benzene ring and methyl or longer groups on the cycloparaffin ring. Infrared spectrum shown in Figure 9.

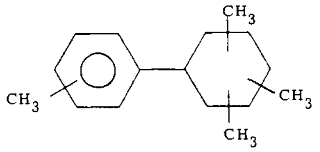
[a] Computed as described from Mass and NMR data. [b] From infrared spectra. The assignment of positions is uncertain. These appear to be the most probable positions of the substituent groups of the main components.

Table VI. Structures of "Average" Molecules in Typical Final Fractions (Portion 4)

Fraction	Number of Substituent Groups[a]	Position of Substituents on Ring[b]	Nature of Substituent Groups on "Average" Molecule
			Adsorbed Part
A-b	2.8	Uncertain	Slightly more than one methyl group and between one and two longer groups. NMR shows 1.7 methyl groups attached to a carbon beta or farther from the ring. NMR also shows the alpha methylene splitting due to an adjacent methylene group.
C-b	2.3	1,3 with some 1,2	A methyl group and an unbranched group of 7 carbon atoms. For discussion, see text.
D-b	2.0	1,2 with some 1,3	Nearly one methyl group and a long chain of seven or eight carbon atoms. NMR shows principally one methyl group attached to a carbon beta or farther from the ring. Infrared shows only a trace of isopropyl terminals. NMR shows the alpha methylene splitting due to an adjacent methylene group. Thus, the principal components have a C_7 or C_8 straight chain.
E-a	2.5	Uncertain	A mixture of di- and trisubstituted alkylbenzenes with nearly one methyl group and one or two longer chains. NMR shows two methyl groups attached to a carbon beta or farther from the ring. Infrared shows slight terminal isopropyl branching.
E-c	3.1	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring.
F-a	2.2	Uncertain	A methyl group and a larger group of 8 carbon atoms. NMR shows an alpha methylene split by an adjacent methylene group and two methyl groups attached to a carbon beta or farther from the ring. Infrared shows only a trace of isopropyl terminals. This implies a methyl group on the 3rd to 5th carbon atom from the ring.
F-c	2.8	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring.
G-b	2.7	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and methyl or longer groups on the cycloparaffin ring.

[a] Computed as described from Mass and NMR data. [b] From infrared spectra. The assignment of positions is uncertain. These appear to be the most probable positions of the substituent groups of the main components.

Table VII. Structures of "Average" Molecules in Typical Final Fractions (Portion 4)

Fraction	Number of Substituent Groups[a]	Position of Substituents on Ring[b]	Nature of Substituent Groups on "Average" Molecule Unadsorbed Part
B-b	2.6	Uncertain	Principally a mixture of di- and tri-alkylbenzenes with one methyl group and between one and two larger groups. NMR shows two methyl groups attached to carbons beta or farther from the ring.
C-a	2.9	Uncertain	Nearly one methyl group and two larger groups. Infrared indicates some terminal isopropyl branching. NMR shows 2.4 methyls attached to carbons beta or farther from the ring.
D-c	3.2	1,2,4	Principally monocyclanobenzenes with a methyl group on the aromatic ring and methyl or longer groups attached to the cycloparaffin ring.
E-c	3.3	1,2,4	Principally monocyclanobenzenes with a methyl group on the benzene ring and a methyl or longer groups on the cycloparaffin ring.
F-c	2.8	1,2,4	Principally monocyclanobenzenes with a methyl group on the aromatic ring and methyl or longer groups on the cycloparaffin ring.
G-a	2.4	Mostly 1,3	Principally a monocyclanobenzene with a methyl group on the benzene ring. Infrared shows an unusual pattern in the 7.2–7.4 micron region. Unlike the other cyclanobenzene fractions, this one appears to be principally disubstituted. Since one of the substituents is a methyl group the cycloparaffin ring must be joined through a single bond. This is in accord with the findings of one methine type hydrogen alpha to the benzene ring (Table II). The NMR spectrum also shows 3 methyl groups beta or farther from the aromatic ring. The spectrum also shows the splitting characteristic of methyl groups on carbon atoms with a single proton. All of these strongly indicate a structure such as: 

[a] Computed as described from Mass and NMR data. [b] From infrared spectra. The assignment of positions is uncertain. These appear to be the most probable positions of the substituent groups of the main components.

Monosubstituted alkylbenzenes were not detected though they may be present in small amounts. This is in accord with the findings of Project 6 (*13*) for the lower molecular weight fraction of this petroleum for which the monosubstituted components constitute about 12% of the C_9 alkylbenzenes and about 6% of the C_{10} alkylbenzenes.

Tetra and higher substituted alkylbenzenes were not detected. However, some may be present in Lot *B* (Figure 1) which has not yet been investigated.

It may be noted that there is a similarity between these results for the C_{13} to C_{15} alkylbenzenes and those reported by Hood, Clerc, and O'Neal (*4*) for the alkylbenzenes in the lubricant fraction. By comparing the mass spectral data of pure alkylbenzenes and alkylbenzene concentrates from petroleum Hood, Clerc, and O'Neal concluded that petroleum alkylbenzenes contain a long alkyl group and from one to five methyl substituent groups per molecule.

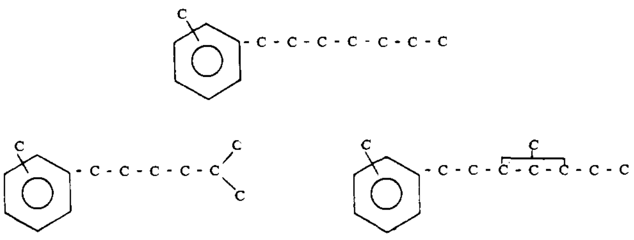
Most of the cyclanobenzenes contain an aromatic ring condensed with a cycloparaffin ring. These have, on the average, one methyl group on the aromatic ring and methyl or longer groups on the cycloparaffin ring. One cyclanobenzene concentrate was found which constituted an exception to the foregoing. For the major component of this fraction the rings appear to be joined through a single bond, that is, the compound is an alkylphenylcyclohexane with one methyl group on the benzene ring and three methyl groups on the cyclohexane ring.

SIGNIFICANCE OF RESULTS

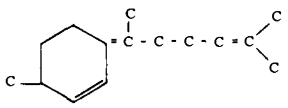
Spectroscopic methods for the analysis of petroleum fractions are frequently based on calibrations with hydrocarbon standards which are not necessarily representative of those in petroleum. For example, in the low voltage mass spectroscopic analysis of the aromatic portions of the kerosine fraction it is sometimes assumed that the principal alkylbenzenes are monosubstituted. Since the monosubstituted benzenes have markedly different sensitivities from the di- and trisubstituted alkylbenzenes, which, as this investigation has shown, are the major components, gross errors can result. Thus, this investigation has provided the information necessary for the selection of representative hydrocarbons for use as calibration standards.

Recently, a number of individual hydrocarbons have been isolated from petroleum which have the skeletal structures or very large fragments of the skeletal structures of the terpenoids or related steroids (*1, 9, 10*). The alkylbenzenes found in petroleum in this investigation have structures which strongly suggest that they are derived from certain terpenoids, which also have one long branched chain and one, two, or three methyl groups attached directly to the ring. These compounds are:

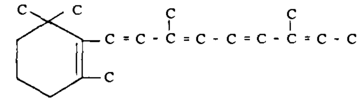
Typical alkylbenzenes from petroleum



Structures from the terpenoids



bisaboline



1/2 carotene molecule

By hydrogenation and dehydrogenation plus some degradation of the molecule it is possible to convert the terpenoids shown above into alkylbenzenes of the type found in petroleum.

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