Structures of Some Mononuclear Aromatic Hydrocarbons from a Heavy Gas Oil and Light Lubricating Distillate

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The mononuclear aromatic portion of the heavy gas oil and light lubricating distillate from the reference petroleum of the API Research Project 6 was separated by a combination of processes including distillation at very low pressures, fractionation with Molecular Sieve adsorbents, liquid-liquid chromatography, and crystallization. An examination of the final fractions by NMR and mass spectrometry showed that about 75% of the C_{24} to C_{26} alkylbenzenes contained one long straight chain and from 0 to 3 or 4 methyl and some ethyl substituents. The greater part of the monocyclanobenzenes also contain a single long chain substituent as well as methyl and possibly ethyl substituents. Fractions with a specific optical rotation, $[\alpha]_D^{25}$ = 6°, were obtained. The optically active components are tetra- or pentacyclanobenzenes with 25 to 26 carbon atoms per molecule.

THIS report describes the results of an investigation of the composition of the mononuclear aromatic portion of the heavy gas oil and light lubricating oil distillate, 305° to 405° C., from the reference petroleum of the API Research Project 6. A preceding investigation has covered the trinuclear aromatic material in this range (*7*).

PROCEDURE

The method used to separate the aromatic material from petroleum and to resolve it into mono-, di-, and trinuclear aromatic concentrates is illustrated in Figure 1 of (*7*). The principal steps in the additional resolution of the mononuclear aromatic material were as follows:

Distillation of the material in a multistage apparatus for distillation a 10^{-5} mm. of Hg.

Separation of a part of the distillate by fractionation with Molecular Sieve adsorbents in a columnar process to give three portions: A portion adsorbed on the lower half of the column, a portion adsorbed on the upper half of the column, and a nonadsorbed portion.

Fractionation of each of the portions from operation 2, by liquid-liquid chromatography.

Crystallization of fractions from operation 3.

The course of these fractionations was followed by spectral methods, principally by low voltage mass and NMR spectrometry.

Results of Distillation at Very Low Pressures. Figure 1 gives the results of the distillation at very low pressures. The upper part of the figure gives a plot of refractive index with respect to the volume of distillate. The lower part of the figure gives the distribution according to compound type. This is based on a low voltage mass spectral examination of selected fractions throughout the range and assumes equal sensitivities for all compound types. Carbon numbers increased from C_{16} at the front end of the distillate to about C_{27} near the tail end. Fractions in the last quarter of the distillate contained optically active components. The specific rotation increased from $[\alpha]_D^{25}$ = 0.15° (neat) at a distillate volume of 4.3 liters to a maximum, $[\alpha]_D^{25}$ = 0.49° (neat) at 5.6 liters, then decreased to $[\alpha]_D^{25}$ = 0.45° (neat) at 5.7 liters. The part of the distillate selected for further investigation encompasses the region of maximum optical activity and is designated *A* in the upper part of Figure 1.

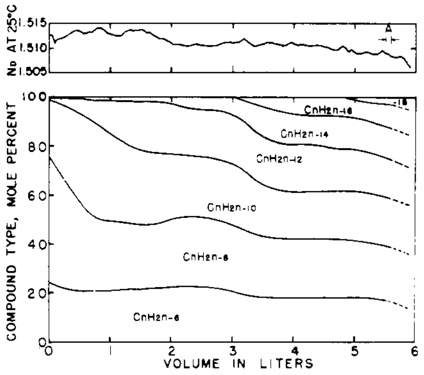

Figure 1. Results of the distillation of the mononuclear aromatic portion

The upper part of the figures gives the refractive index plot and the lower part the distribution with respect to compound type throughout the distillate

Fractionation with Molecular Sieve Adsorbents. In previous work in this laboratory Molecular Sieve adsorbents have been used for the separation of aromatic hydrocarbons according to the size and shape of the molecules (*5, 6, 9*). Over the years a number of improvements have been made in the application of this technique to enhance its effectiveness. The apparatus now in use is shown in Figure 4 of reference (*5*). The procedure is as follows: A 15- to 20-gram portion of the oil which is to be separated is introduced at the bottom of a column which has been packed with 135 grams of 42 to 60 mesh Molecular Sieve (Linde 10X). This oil is forced upward through the column by introducing carbon tetrachloride at the bottom. The oil floats on the carbon tetrachloride and the portion which does not enter the pores eventually passes out at the top. The boundary between the oil and carbon tetrachloride is plainly visible and remains sharp throughout the course of the experiment. With this procedure, competition of oil and solvent for the pores of the adsorbent is eliminated because only oil comes in contact with fresh adsorbent. The rate of flow of carbon tetrachloride is adjusted so that the oil front moves up the column at a rate of approximately 1 cm. per hour, that is, the experiment takes approximately 100 hours. This slow rate is desirable to permit molecules with dimensions close to those of the pores sufficient time to become adsorbed.

That part of the oil which has entered the pores is recovered by removing the adsorbent from the column and extracting it with boiling toluene in a Soxhlet apparatus. The adsorbed material is strongly held so that continuous extraction for 120 to 150 hours is necessary. Under these conditions from 94 to 98% of the charge is recovered. In practice, the material which has been adsorbed in the upper and lower halves of the column is recovered separately, so that three portions are obtained: unadsorbed portion, adsorbed portion from upper half, and adsorbed portion from lower half of the column.

The amounts, in weight per cent of these three portions separated from part *A* (Figure 1) were as follows: unadsorbed, 45; adsorbed in upper half, 16; adsorbed in lower half, 39. The alkylbenzenes and monocyclanobenzenes are concentrated in the adsorbed portion from the lower half and the di-, tri-, tetra-, and higher cyclanobenzenes principally in the unadsorbed portion. All of the optically active components were found in the unadsorbed portion.

Fractionation by Liquid-Liquid Chromatography. For the fractionation by liquid-liquid chromatography the column packing consisted of *m*-chloroaniline immobilized on a large pore silica gel—Davison, Code 62, 60 to 200 mesh. This gel can retain up to 1 ml. of liquid per gram of adsorbent and remain free flowing. The moving phase consisted of a 75 to 25% (v.o/v.1) mixture of 2,2,4-trimethylpentane and a perfluorocyclic ether, $C_8F_{16}O$, (No. 0-75, Minnesota Mining and Manufacturing Co.) saturated with *m*-chloroaniline.

The selection of the solvent phases was based on solubility considerations. If 2,2,4-trimethylpentane is used by itself, the oil remains almost entirely in the moving phase and is swept rapidly out of the column without significant separation. The addition of the perfluorocyclic ether reduces the solubility of the oil so that it is more evenly distributed between the stationary and moving phases. The perfluorocyclic ether also influences the selectivity of the process, with the solubility of the components decreasing with increasing cycloparaffin ring content. A discussion of the special properties of perfluorochemicals which makes them effective as partitioning liquids for the separation of lower molecular weight paraffins from cycloparaffins has been given previously (*8*). With *m*-chloroaniline the solubilities of the components increase with increasing cycloparaffin ring content. Thus, the two solvents enhance each other.

The experiments were performed using glass columns, 150 cm. in length and 3 cm. in diameter, filled to contain 780 grams of the silica gel plus *m*-chloroaniline packing. Approximately 10 grams of oil was used in each experiment. Each fraction of eluate was extracted twice with dilute hydrochloric acid and once with water to remove traces of *m*-chloroaniline.

The results obtained with a 5.4-gram mixture containing 45.9% of 7-phenyltridecane and 54.1% of dodecahydrochrysene are given in Figure 2. The left part of the figure gives the concentration of hydrocarbon as a function of the volume of eluate; the right part gives the refractive index with respect to the weight of oil recovered. The separation is substantially quantitative.

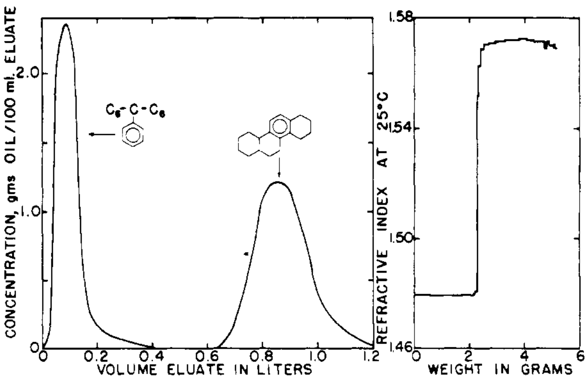

Figure 2. Results of the fractionation of a synthetic mixture of 7-phenyltridecane and dodecahydrochrysene by liquid-liquid chromatography

The left part gives the concentration of hydrocarbon in the eluate with respect to the volume of eluate, and the right part gives the refractive index of the recovered hydrocarbon with respect to its weight in grams

For the separation of the petroleum fractions, two series of experiments were performed with each of the portions from the fractionation with Molecular Sieve adsorbents. In the first series, 10-gram quantities of the original portion were used. For the second series, the charges were prepared by blending fractions with similar refractive indices from the first series.

Crystallization. Most of the fractions resulting from the chromatographic experiments gave crystals from solutions with 2,2,4-trimethylpentane or methyl ethyl ketone at −20° to −80° C. For the separation of these waxy crystals, filter sticks and similar devices were not effective. A simple, yet effective, procedure was devised. The oil fraction, 0.3 to 0.5 ml., mixed with 3 to 4 times its volume of solvent, was placed in a small test tube with the bottom blown paper thin. This tube was surrounded with a larger protecting tube and allowed to cool to −80° C. When the crystals had formed the small tube was rapidly withdrawn from its protecting tube, inserted in, and broken on the fritted plate at the bottom of a filter tube which was refrigerated with dry ice. The crystals were sucked dry, 0.5 ml. of refrigerated solvent was added, the crystals were scraped from the filter plate, mixed with the solvent, and again sucked dry.

Composition of the Portion Adsorbed in the Lower Part of the Column. Results of the liquid-liquid chromatographic experiments with the lower adsorbed portion are given in

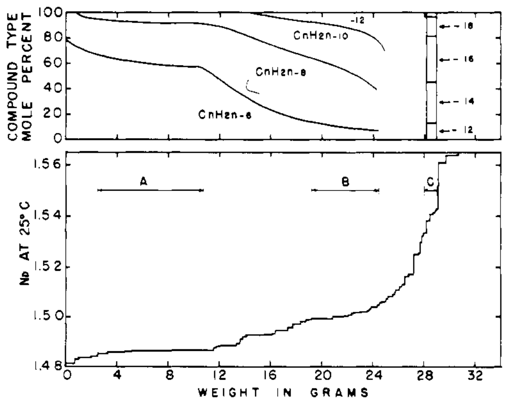

Figure 3. Results of the fractionation of the lower adsorbed portion of the oil by liquid-liquid chromatography

Figure 3. An ultraviolet spectrometric examination showed that the tail end fractions—the last 10%—contained dinuclear aromatics. The bar graph in the upper part of the figure gives the distribution with respect to compound type after removal of the dinuclear aromatics from lot *C* by liquid-solid chromatography using alumina.

All of the material comprising lots *A* and *B* was crystallized. Starting with material with a refractive index, n_D at 25° C., of 1.4865 (lot *A*), two crystallizations produced a crystal portion with a refractive index of 1.4783 and a melting point of 15° C. Additional crystallization changed the refractive index by only a few units in the fourth decimal place. For the material with refractive indices from 1.4990 to 1.5040 (lot *B*), two crystallizations gave a crystal portion with a refractive index of 1.4882 and a melting point of −1° C. The low voltage mass spectrometric analysis of the crystal portion from lot *A* gave the following values for the amounts of the components in mole per cent: C_{24} alkylbenzenes, 16; C_{25} alkylbenzenes, 74; C_{26} alkylbenzenes, 6; monocyclanobenzenes, 4. The NMR spectrum of this material obtained on a Varian 100 megacycle instrument is given in Figure 4. The very sharp peak at 8.75 τ is characteristic of an unbroken chain of methylene groups at least 10 carbon atoms in length. Broader peaks are obtained with shorter chains; see Figure 6 in (*2*). Also, the peak at 9.14 τ is characteristic of a methyl group at the end of a long chain. Values for the different types of protons computed from peak areas in conjunction with the average molecular formula are given in Table I. These show that the average molecule contains approximately 2.5 substituent groups, that every molecule contains a single long unbranched alkyl chain—the difference between 1.00 and 1.12 is not believed to be significant. Also, that the average molecule contains approximately one methyl group attached directly to the ring. Since the long alkyl chain is unbranched no methine hydrogens are present and the peak near 7.5 τ is attributable only to methylene protons. The difference between the number of methylene groups alpha to the ring and methyl groups at the end of the long chain (1.67 − 1.12 = 0.55) indicate the presence of ethyl substituents on some molecules. The β-methyl of these groups could easily escape detection since they would be hidden by the γ and γ plus methylenes in the peak at 8.75 τ.

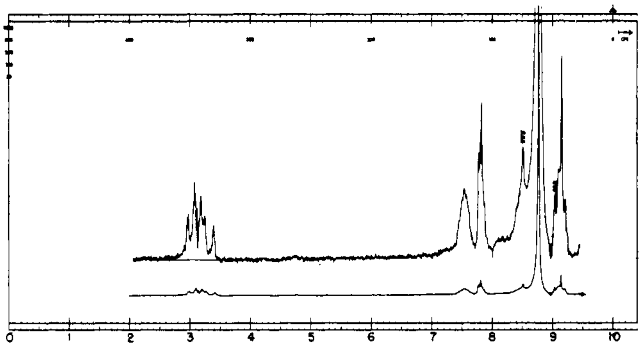

Figure 4. Nuclear magnetic resonance spectrum of the crystal portion from lot A

The high voltage mass spectrum of the crystal portion from lot *A* is given in Figure 5. Data for synthetic C_{26} and C_{27} alkylbenzenes with a single long chain and one or more methyl group substituents show intense peaks corresponding to the splitting of the long chain at the bond β to the ring while the methyl groups remain intact (*1*, *4*). Thus an alkylbenzene containing only a single long chain shows intense peaks at *m/e* values of 91 and 92. These containing, in addition, 1, 2, or 3 methyl substituents

Table I. Values for Different Types of Protons and Groups in Final Fractions[a]

Final Fraction	Type of Proton	Numbers Protons	 Groups	 Substituents on ring
	Aromatic	3.50		2.50
Crystal portion from lot *A*, Figure 3	Methylene (and methine) α to ring	3.34	1.67	
	Methyl α to ring	2.89	0.96	2.63
	Methylene β or further from ring plus methyl β from ring	30.90	15.45[b]	
	Methyl γ or further form ring	3.35	1.12	
	Aromatic	3.02		2.98
Crystal portion from lot *B*, Figure 3	Methylene (and methine) α to ring	3.33	1.66	
	Methyl α to ring	4.02	1.34	3.00
	Methylene β or further from ring plus methyl β to ring	28.16	14.08[b]	
	Methyl γ or further from ring	2.99	1.00	
	Aromatic	2.73		3.27
Crystal portion from lot *D*, Figure 6	Methylene (and methine) α to ring	4.15	2.08	
	Methyl α to ring	4.15	1.38	3.46
	Methylene β or further from ring plus methyl β to ring	28.96	14.48[b]	
	Methyl γ or further from ring	4.94	1.65	
	Aromatic	2.79		3.21
Crystal portion from lot *E*, Figure 6	Methylene (and methine) α to ring	3.90	1.95	
	Methyl α to ring	4.03	1.34	3.29
	Methylene β or further from ring plus methyl β to ring	26.85	13.43[b]	
	Methyl γ or further from ring	6.12	2.04	

[a] Computed from NMR spectra obtained with a 100 megacycle instrument. The spectra are recorded in the Preprints of the ACS Division of Petroleum Chemistry, Vol. 11, No. 3, August 1966. [b] Computed assuming only methylene groups. See text.

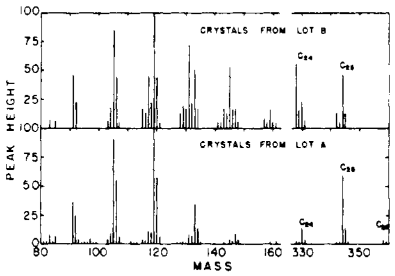

Figure 5. High voltage mass spectra of the crystal portions from lots *A* and *B*

give intense peaks at 105 and 106, 119 and 120, and 133 and 134 mass units, respectively. Assuming for the moment, that the fractions from petroleum contain only methyl groups and a single long chain substituent, the peaks in Figure 6 at 91 and 92, 105 and 106, 119 and 120, 133 and 134, and 147 and 148 mass units indicate the presence of mono-, di-, tri-, tetra-, and penta-substituted benzenes, and the relative intensities indicate very approximately the amounts present.

With alkylbenzenes containing two long alkyl chains peaks of moderate intensity are found in the spectra corresponding to the loss of one chain (*1, 4*). In the spectrum of the alkylbenzenes derived from lot *A* no peak with an intensity greater than 0.5% of the base peak appears between an *m/e* value of 175 and the parent peak region. This indicates that the molecules contain a single long chain and confirms the conclusion derived from the NMR data. Mass spectral data for ethyl hexadecylbenzene (*12*) show that with alkylbenzenes which contain both a long chain and an ethyl group only the long chain is split at the β-bond. Thus, the mass spectral data is not inconsistent with the presence of ethyl substituents, and the peaks at 119 and 120, 133 and 134, and 147 and 148 mass units may be attributed to the presence of ethyl as well as methyl substituents on the ring.

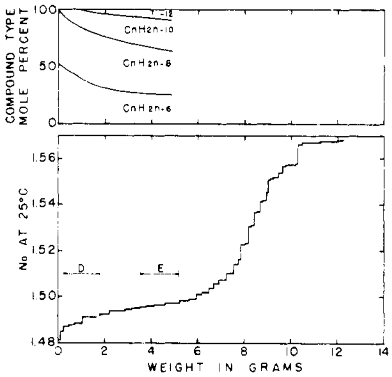

Figure 6. Results of the fractionation of the upper adsorbed portion of the oil by liquid-liquid chromatography

Values for the different types of protons and the results of the low voltage mass spectrometric analysis of the crystal portion from lot *B* are given in Tables I and II, respectively. The NMR data show that these molecules, both alkylbenzenes and cyclanobenzenes contain a single long chain substituent, and that the average molecule contains about 1.3 methyl groups attached directly to the ring. Because of the presence of monocyclanobenzenes no meaningful conclusion can be drawn from the difference between the α-methylene groups and the methyl groups at the end of the long chain.

The peaks in the high voltage mass spectrum attributable to the alkylbenzenes in the crystal portion from lot *B* (Figure 5) resemble those for the alkylbenzenes from lot *A* and indicate a similar structure. The peaks at 117 and 118, 131 and 132, 145 and 146, and 159 and 160 mass units are attributable principally to the monocyclanobenzenes. Monocyclanobenzenes with a single long chain substituent can lose this group in several ways. For alkyltetrahydronaphthalenes and alkylindans with a long chain substituent on the aromatic ring, the chain is broken principally at the bond β to the ring; these alkyltetrahydronaphthalenes and alkylindans give their most intense peaks at *m/e* values of 145 and 146 and 131 and 132, respectively. With alkyltetrahydronaphthalenes substituted on the cycloparaffin ring the cleavage occurs principally at the α-bond so that the peaks at 131 and 132 mass units are the most intense. With indans substituted on the cycloparaffin ring the cleavage also occurs principally at the α-bond to give the most intense peaks at 117 and 118 mass units. β-bonds are ruptured also and peaks of moderate intensity at 131 and 132 mass units are observed (*1*).

Apparently from the foregoing, the mass spectral data cannot be used to determine the extent of substitution of the monocyclanobenzenes. However, the presence in lot *B* of intense peaks at 117 and 118 mass units strongly suggests the presence of some mono-substituted indans with a single long alkyl group on the cycloparaffin ring since the data available indicate that only this type will give these peaks.

Table II. Low Voltage Mass Spectrometric Analyses of Final Fractions

		Mole Per Cent									
Final Fraction	Compound Type	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	Total
Crystal portion from lot *B*, Figure 3	Alkylbenzenes	12	30	2							44
	Monocyclanobenzenes	38	14	1							53
	Dicyclanobenzenes	1	1								2
Crystal portion from lot *D*, Figure 6	Alkylbenzenes	3.8	30.7	29.5	10.3	3.1					77.4
	Monocyclanobenzenes	2.0	8.5	8.2	3.9						22.6
Crystal portion from lot *E*, Figure 6	Alkylbenzenes	2.7	18.2	16.1	5.6	1.9					44.5
	Monocyclanobenzenes	6.8	14.3	10.7	4.6	1.5					37.9
	Dicyclanobenzenes	1.7	5.1	4.7	2.4						13.9
	Tricyclanobenzenes		1.2	1.6	1.0						3.8
Lot *G*, polycycloparaffin free	Alkylbenzenes			3.7	13.6	12.2	5.9	2.2	0.5		37.5
	Monocyclanobenzenes			1.8	7.7	13.8	11.3	4.4	1.2	0.4	40.6
	Dicyclanobenzenes			0.3	1.1	3.6	5.2	4.0	1.7	0.6	16.5
	Tricyclanobenzenes				0.3	0.4	1.0	1.4	1.1	0.5	4.7
	Tetracyclanobenzenes							0.3	0.4		0.7

Composition of the Portion Adsorbed in the Upper Part of the Column. Results of the liquid-liquid chromatographic experiments with the upper adsorbed portion are given in Figure 6. All of the material comprising lots *D* and *E* were crystallized. From lot *D* with a refractive index, n_D at 25° C., of 1.4878 to 1.4913, 10 stages of crystallization gave a crystal portion with a refractive index of 1.4830. The carbon numbers of the components of this crystal portion (Table II) are slightly higher than those from the lower adsorbed portion.

The NMR data (Table I) lead to the conclusion that the molecules in this material are more highly substituted than the corresponding fractions from the lower adsorbed portion; also, the value for methyl groups γ or further from the ring, 1.65 compared with 1.12, indicates the presence of some molecules with more than one alkyl chain or to branching of the alkyl chains. Unlike the spectra for the fractions from the lower adsorbed portions, the high voltage mass spectrum shows a number of low intensity peaks between an m/e value of 175 and the parent peak region. Presumably, these are due to the loss of one of the substituent chains or to the splitting of an alkyl chain adjacent to a branch.

From lot *E* with a refractive index, n_D at 25° C., of 1.4960 to 1.4974, repeated crystallizations gave a portion with refractive index of 1.4898. Values for the different types of protons and the results of the low voltage mass spectrometric analysis of this portion are given in Tables I and II, respectively. As with the crystal portion from lot *D*, the high voltage mass spectrum of this material shows a number of low intensity peaks between an m/e value of 175 and the parent peak region.

Composition of the Unadsorbed Portion. Results of the liquid-liquid chromatographic experiments with the unadsorbed portion are given in Figure 7. In contrast to the material from the lower part of the column, this portion has a low content of alkylbenzenes and a high content of polycyclanobenzenes. Fractions near the front end of this material contained some polycycloparaffins, and those near the tail end, the last 12%, contained significant amounts of dinuclear aromatics. Although the first 75% of the material yielded crystals from methyl ethyl ketone, fractionation by crystallization was not effective in producing any significant separation of compound types.

The polycycloparaffins were removed from lot *G* by chromatography with alumina. The low voltage mass spectrometric analysis of the polycycloparaffin free material from lot *G* (Table II) shows that the alkylbenzenes and monocyclanobenzenes from the unadsorbed portion have higher molecular weights, by 2 to 5 carbon atoms, than those from the lower adsorbed portion. This difference can be attributed to the presence of multiple relatively short chain substituents or to alkyl side chain branching. (For a given carbon number, hydrocarbons with branched chains have lower boiling points than those without branching.) The NMR spectrum obtained on a 60 megacycle instrument shows a very broad peak near 8.75 τ which also suggests the presence of multiple short chain substituents or side chain branching. Integration of the aromatic and nonaromatic portions of the spectrum leads to the conclusion that in the average molecule the benzene ring contains 3.71 substituents. Because of severe band overlap the other types of protons were not determined.

As noted previously, all of the optically active components were contained in the unadsorbed portion. These were concentrated additionally by the liquid-liquid chromatographic process and appeared in the tail end fractions. (See insert in Figure 7.) Three lots, *H*, *I*, and *J*, were processed by liquid-solid chromatography to separate the dinuclear aromatics from the mononuclear aromatics, to determine which of these types contained the optically active components and to make the subsequent mass spectral analysis meaningful in terms of the number of rings per molecule. For the separation by liquid-solid chromatography, the experiments were performed with 0.6-gram portions of oil in columns containing 1000 grams of alumina with 2,2,4-trimethylpentane as the eluant. The oil was recovered in three fractions. The first fractions from each portion contained from 45 to 50% of the charge. These first fractions contained nearly all of the optically active components and, as indicated by ultraviolet spectroscopy, were essentially free from dinuclear aromatics. The second and third fractions showed little or no optical activity and contained substantial amounts of dinuclear aromatics.

Optical activities and the distribution according to compound type for the first fractions produced from lots *H*, *I*, and *J* by the liquid-solid chromatographic process are given in Figure 8. Because these fractions are free from dinuclear aromatics the *X* values indicate the number of cycloparaffin rings per molecule, for example, those with $X = -12$ are tricyclanobenzenes, those with $X = -18$ are hexacyclanobenzenes. Because of the small amounts present, the tricyclanobenzenes do not appear to be responsible for the optical activity. Since the optical activity decreases while the amounts of hexacyclanobenzenes increase in going from *H* to *J*, it seems unlikely that the optical activity is associated with this type. Instead the optically active components are either tetra- or pentacyclanobenzenes. These tetra- and pentacyclanobenzenes were composed principally of molecules which contained 25 to 26 carbon atoms.

An optical rotatory dispersion experiment with material from lot *I* gave a plane curve with $[\alpha]^{25}_{590} = 6°$ and $[\alpha]^{25}_{340} = 24°$. An analysis of the NMR spectrum of the material

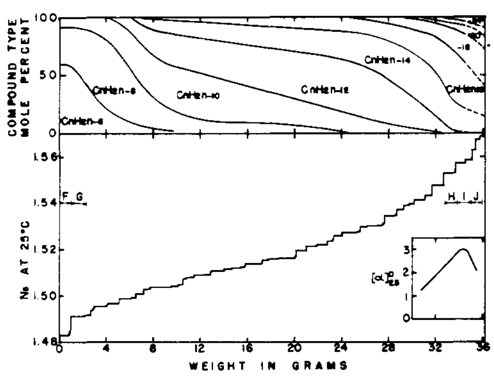

Figure 7. Results of the fractionation of the nonadsorbed portion of the oil by liquid-liquid chromatography

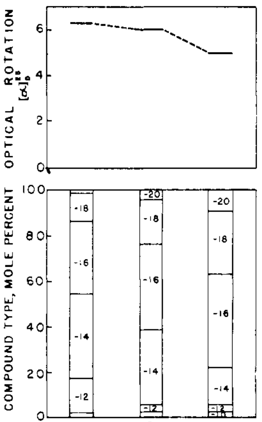

Figure 8. Optical activities and distribution according to compound type for the first fractions from the processing of lots *H*, *I*, and *J*

The figures in the bar graphs refer to the *X* values in the formula C_nH_{2n+X}

from lot *I* indicates that the average aromatic ring is tetrasubstituted. Because of band overlap no attempt was made to interpret the nonaromatic portion quantitatively.

DISCUSSION

Hood, Clerc, and O'Neal (*4*), from a study of mass spectral patterns, came to the conclusion that the typical alkylbenzene from lubricating oil contains one long chain substituent and that the other substituents are methyl—and possibly ethyl—groups. The results of the present investigation, in which both mass and nuclear magnetic resonance spectrometry were used to examine an alkylbenzene concentrate which was substantially free from cyclanobenzenes, has shown that the greater part, about 75%, of the alkylbenzenes, that is, those from the lower adsorbed portion, contain one long straight chain substituent and that the other substituents are methyl and ethyl groups. This confirms the conclusions of Hood, Clerc, and O'Neal. A small part of the alkylbenzenes, principally those from the unadsorbed portion, about 10%, appear to be very different in structure and contain branched chains or multiple chains of intermediate length. The monocyclanobenzenes from the lower adsorbed portion contain a single long chain substituent as well as methyl and possibly ethyl substituents.

In a previous investigation, the API Research Project 6 (*10*) showed that the optical activity of the lubricant fraction of its reference petroleum could be concentrated in two sets of fractions, one set consisting of polycycloparaffins, the other of polycyclanobenzenes. Because of an overlap of distillation ranges, the optically active polycyclanobenzene fractions from the lubricant fraction and those obtained in the present investigation have approximately the same carbon number range, and the optical activity in both cases is due to the same component or components. The present investigation has shown that the optical activity is not attributable to the tricyclanobenzenes, as previously was thought probable, but is due instead to tetra- or pentacyclanobenzenes with 25 or 26 carbon atoms per molecule. Apparently, these optically active compounds are not derived from steroids which have four rings per molecule but are more probably derived from higher cyclic terpenoids; for example, the tetracyclano-benzenes could be generated from pentacyclic terpenoids of the β-amyrin group; these are widely distributed in plant materials.

Oakwood *et al.* (*11*) isolated crystalline materials with specific optical rotations in the range +32.7° to 36.8°. Hood (*3*) examined two of these materials by mass spectrometry and found that they were essentially mixtures of C_{29} and C_{30} pentacycloparaffins.

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Enthalpy, Heat Capacity, and Heat of Fusion of Magnesium from 404° to 1300° K.

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The enthalpy, $H_T - H_{298.15^\circ\,\mathrm{K.}}$, of magnesium has been redetermined, confirming a suspected error in earlier measurements. The heat of fusion was 2026 ± 50 cal. per mole. The heat capacity of the liquid appears to be essentially constant at 8.20 cal. per (mole deg.) from 922° to 1300° K. Smoothed values of enthalpy and heat capacity from 298° to 1300° K. are given.

AN EARLIER determination of the heat of fusion of magnesium (*10*) was questionable because of a possible container correction error related to the magnetic transformation in the stainless steel container. Ginnings has published an analysis of the effects of such a transformation (*3*). The present work, using a tantalum-lined platinum–10% rhodium container, was undertaken to check on the magnitude of this error and to obtain the enthalpy of liquid magnesium at higher temperatures.

EXPERIMENTAL

A cylindrical sample of doubly sublimed magnesium—commonly referred to as 99.95–99.98% magnesium—was provided by the Metallurgical Laboratory of the Dow Chemical Co. Surface oxidation was removed by washing with dilute nitric acid and rinsing with water and acetone. Spectrographic analysis indicated the presence of 0.002% Al, < 0.01% Ca, < 0.0005% Cu, < 0.0005% Fe, 0.0006%