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IDENTIFICATION OF DISTILLABLE TAR ACIDS AND TAR BASES FROM A LOW-TEMPERATURE BITUMINOUS COAL TAR

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IDENTIFICATION OF DISTILLABLE TAR ACIDS AND TAR BASES FROM A LOW-TEMPERATURE BITUMINOUS COAL TAR[1]

By

Clarence Karr, Jr.,[2] Patricia A. Estep,[3] Ta-Chuang Lo Chang,[4] and Joseph R. Comberiati[4]

Summary and Introduction

An extensive characterization was conducted on the tar acids and tar bases in a low-temperature bituminous coal tar. Approximately 130 individual compounds were identified, mostly with respect to individual isomers, and the amounts were determined or estimated in nearly all instances.

On the basis of the nature of the tar acids and bases and the thermodynamic and kinetic distributions of isomers, consideration was given to the possibility of correlating tar composition with coal structure.

Detailed descriptions are presented for the separatory and qualitative and quantitative procedures for the characterization of the tar acids and bases. These include microvacuum fractional distillation, infrared and ultraviolet spectrophotometry, gas-liquid chromatography, and countercurrent distribution.

Descriptions are presented for the synthesis of authentic specimens of tar acids and tar bases. An appendix contains the ultraviolet and infrared spectra of 189 individual tar acids and tar bases.

Origin of Low-Temperature Tar Laboratory

In December 1954 Congress was requested to provide funds for a much-expanded program of research on low-temperature tars. The purpose of this program was "* * * to develop through analysis and research end uses and realization values for low-temperature tars and products therefrom * * * ."

In July 1955 the Federal Bureau of Mines established a Low-Temperature Tar Laboratory at its Appalachian Experiment Station, Morgantown, W. Va. Many inquiries from private industry for information on the composition and value of tars from low-temperature carbonization of coal pointed to the need for such a laboratory. Its objective is to investigate the yields and chemical and physical properties of tars from low-temperature carbonization processes, to investigate means of upgrading economically these tars, and to make available to industry and to the public data essential for increasing coal utilization by establishing a new coal-chemical industry based on utilization of low-temperature tars.

It appeared that initial experimental data of importance could be obtained relatively quickly by emphasizing the elucidation of the tar acids and tar bases in the low-temperature tar. The tar acids and tar bases are the most readily isolated classes of components and also the most economically important constituents at the present time.

Purpose of Identifying Individual Tar Acids and Tar Bases

The main reason for identifying and determining the amounts of individual compounds in a low-temperature coal tar is to obtain a true picture of the chemical nature of the tar so that refining and utilization can then be approached from a logical standpoint.

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The refining of low-temperature tars will require the development and application of a partly different set of chemical processes to suit the special chemical nature of these tars. It is impossible to say what these chemical processes should be without a correct idea of the chemical makeup of the tar.

A Productive Research Program Based on New Semi-Micro Techniques

Early in the development of the project a decision was made in favor of utilizing exclusively the separatory and analytical techniques developed in the last few years for composition studies of natural products in the pharmaceutical and petroleum field. All these techniques emphasize simplicity, accuracy, and especially micro or semi-micro quantities. The various chromatographic methods—gas-liquid chromatography and related partitioning processes such as countercurrent distribution—are preeminent and require only milligram quantities. Micro-infrared analysis and semi-micro physical-property determinations are also included. This new approach is strictly opposed to the classic approach to composition research in which large quantities of material are handled by cumbersome, time-consuming methods, which frequently alter the nature of the material being examined. Classically, components are invariably characterized by isolation of large quantities of each component and the formation of innumerable derivatives and degradative products to establish identity.

The problems involved in characterization are numerous; the characterization of low-temperature tars constitutes an essentially virgin field of investigation. Few standard procedures can be applied without modification, and even these fail to meet more than a small fraction of the required methods.

Essential Need for Infrared and Ultraviolet Spectra of Pure Compounds

The inescapable requirement for a very wide selection of reliable infrared and ultraviolet spectra of different tar acids and tar bases has forced its attention repeatedly upon the individuals responsible for characterization research. A typical situation was to have obtained a good separation of components but to be frustrated by lack of the required spectra for identification and accurate determination of quantity.

This situation has not been limited to original research in characterization. Even in the so-called "routine" analysis of the low-boiling tar acids there has been a lack of both spectra and accurate physical properties, such as boiling point. This is because in distillation, or any other separation, phenol, the 3 cresols, and the 6 xylenols are not neatly received as simple mixtures of these components but are intimately associated with various amounts of the 3 ethylphenols and more than 12 different ethylmethyl-trimethyl- and propylphenols. Reliable spectra of all of these have been difficult to obtain; indeed, it is not certain exactly which components must be considered, since accurate boiling points are not available for all of these compounds. As the spectroscopist knows, even if it is desired to have only the quantities of phenol, the cresols, and the xylenols, these other compounds must also enter into the equations and calculations of the analysis.

It was believed, therefore, that by far the most practical and desirable contribution, from the standpoint of persons doing research in the characterization and analysis of low-temperature tar and its refining products, would be a compilation of infrared and ultraviolet spectra used by the Low-Temperature

Tar Laboratory. This collection of spectra (in appendix) represents a great many man-hours devoted to the following fields of investigation:

1. Thorough search of the literature for infrared spectra, ultraviolet spectra, and boiling points—mainly in Chemical Abstracts.
2. Synthesis of some representative tar acids and tar bases, which could not be obtained by gift or purchase and for which no literature spectra were available. This necessitated a search of the literature and often modification of published methods of synthesis.
3. Accurate recording of purified compounds obtained by synthesis and purchase in both the infrared and ultraviolet regions. This invariably required determination at several concentrations to ascertain that the proper concentration was used for bringing out all absorption bands of analytical significance.
4. Preparation of lists of precise wavelength and intensity values for all analytical bands in the infrared and ultraviolet spectra of about 190 compounds. This is of special importance to other investigators, since it is not possible to look at spectra that have been reduced severalfold for publication and interpret the positions of absorption bands with the required degree of precision.

PREVIOUS INVESTIGATIONS OF ACIDS AND BASES FROM VARIOUS LOW-TEMPERATURE TARS REPORTED IN MODERN LITERATURE

Although a fairly large number of publications list tar acids and bases identified in various low-temperature tars, most of this information could not be utilized in this investigation because of the following limitations:

1. Most investigators list only a few compounds found in a particular tar, and since low-temperature tars vary so widely, depending on the nature of the coal used and the carbonization temperature, combining the results reported by different investigators can be misleading and illogical.
2. Many identifications, especially in the older work, are based on inconclusive evidence, such as melting points of picrates.
3. Amounts of the compounds usually are not given, and even if they are they are sometimes based on the quantity of compound that could be crystallized from a mixture or a technique that does not constitute a comprehensive analysis.

Table 1 shows the amounts of individual low-boiling phenols in various low-temperature tars as determined by Karr and others, of the Bureau of Mines Staff (*110*)[5], Brewer and Smith (*17*), Fowkes and others, of the Bureau of Mines Staff (*110*), and Jäger and Kattwinkel (*50*).

Table 2 gives the amounts of individual high-boiling phenols in a low-temperature tar as determined by Jäger and Kattwinkel (*50*). Irvine and Mitchell (*49*) and Parant (*89*) have identified individual high-boiling phenols but have not reported the amounts. Terres, Gebert, Hülsemann, Petereit, Toepsch, and Ruppert (*108*) have identified 2-isopropylphenol.

Table 3 gives the amounts of individual dihydric phenols as determined by Fowkes and others, of the Bureau of Mines Staff (*110*), and Barker and Hollingworth (*7*). The dihydric phenols produced from the aqueous liquor by Coalite and Chemical Products, Ltd., have been listed by Pound (*93*); and Leibnitz, Behrens, and Ringpfeil (*70*) have reported the identification of a number of dihydric phenols in a commercial carbonization water.

The amounts of individual pyridines have not been previously reported. Table 4 shows individual pyridines identified in some low-temperature tars by Jäger and Kattwinkel (*51*), Matsumoto and Ihara (*75*), and Yeh and Kalechits (*120*). Parant (*89*) identified aniline, 2-methylaniline, and 4-methylaniline, but did not report any amounts. Jäger and Kattwinkel (*51*) identified isoquinoline and quinoline but likewise did not report any amounts.

[5] Italicized numbers in parentheses refer to items in the bibliography at the end of this report.

TABLE 1.—*Amounts of individual low-boiling phenols from various low-temperature tars*

Type of tar	Wyoming subbituminous				Lignite		"Bituminous"
	Stansbury	Hanna	Big Horn	Wyodak	Texas (Sandow)	North Dakota	German
Reference	(*110*)	(*110*)	(*110*)	(*110*)	(*17*)	(*110*)	(*50*)
Dry tar, weight-percent:							
Phenol	0.27	0.63	0.75	0.81	0.80	1.5	[1] 1.4
o-Cresol	.19	.37	.57	.36	.39	.7	[1] 1.6
m-Cresol	.31	.43	.81	.72	.50	1.2	1.55
p-Cresol	.36	.60	1.1	.74	.42	1.2	1.55
o-Ethylphenol	.01	.01	.04	.11	.06	.1	Present.
m-Ethylphenol	.12	.13	.26	.34	.09	.1	Do.
p-Ethylphenol	.16	.27	.53	.43	.15	.4	.15
2, 3-Xylenol	.04	.03	.02	.02	.09	.2	.2
2, 4-Xylenol	.47	.57	.55	.14	.18	.4	.9
2, 5-Xylenol	.07	.14	.18	.43	.09	.3	1.1
2, 6-Xylenol	.01	.07	.07	.04	.03	.05	Present.
3, 4-Xylenol	.06	.16	.25	.20	.06	.4	.5
3, 5-Xylenol	.13	.21	.01	.30	.09	.2	1.3
2, 3, 5-Trimethylphenol	----	----	----	.06	----	----	.28
2, 4, 6-Trimethylphenol	----	----	----	.01	----	----	.4
3-Ethyl-5-methylphenol	----	----	----	.04	----	----	.30
4-Ethyl-2-methylphenol	----	.11	.26	.10	----	----	.6

[1] Including amount in aqueous liquor.

TABLE 2.—*Amounts of individual high-boiling phenols from various low-temperature tars*

Type of tar	German "bituminous"	English (low-rank)	French (Bruay) [1]
Reference	(50)	(49)	(89)
Dry tar, weight-percent:			
2, 3, 4-Trimethylphenol (?)	0.25		
2, 4, 5-Trimethylphenol	.75		Present.
3, 4, 5-Trimethylphenol	.13	Present	Do.
2-Ethyl-4-methylphenol (?).	Present		
2-Ethyl-5-methylphenol (?).	do		
3-Ethyl-2-methylphenol		Present	
3-Ethyl-4-methylphenol		do	
5-Ethyl-2-methylphenol	Present	do	
2-Isopropylphenol [2]			
3-Ispropylphenol		Present	
4-Isopropylphenol	Present (?)	do	Present.
3-n-Propylphenol	.09	do	
4-n-Propylphenol	.04	do	
2, 3, 4, 5-Tetramethylphenol (?).	.18		
2, 3, 5, 6-Tetramethylphenol.	.1		
2, 3-Dimethyl-6-ethylphenol (or 3, 4-Dimethy-6-ethylphenol).	.02		
3, 5-Dimethyl-4-ethylphenol.	<.01		
2, 4-Diethylphenol	.025		
2, 6-Diethylphenol (?)	Present		
3, 5-Diethylphenol	.015	Present	Present.
2-Isopropyl-4-methylphenol (?).	.035		
4-Isopropyl-3-methylphenol (?).	<.01		
5-Isopropyl-2-methylphenol.		Present	
2-Methyl-4-n-propylphenol.			Present.
4-Methyl-2-n-propylphenol (?).	.08		
2-n-Butylphenol (?)	.09		
4-n-Butylphenol	<.01	Present	
4-Indanol	.5	do	Present.
5-Indanol	.4		Do.
6-Methyl-4-indanol	.25		Do.
6-Methyl-5-indanol	.3		Do.
X-Methyl-X-indanol (?)	.16		
4-Phenylphenol	<.01		
1-Naphthol	.13		Present.
2-Naphthol [3]	.45		Do.
5-Methyl-2-naphthol [4]			
7-Methyl-2-naphthol (?)			Present (?).

[1] In mixed tar; 30 percent produced at 475° C., 70 percent produced at 675° C.
[2] Identified in a German bituminous tar by Terres and others (*108*).
[3] Quantity in North Dakota lignite tar, 0.4 percent of the crude tar, Fowkes and others (*110*).
[4] Identified in North Dakota lignite tar by Fowkes and others (*110*).

There is only one instance among previous investigations in which a significantly large number of tar acids and tar bases have been identified in a single low-temperature tar and the amounts of many of these determined. Jäger and Kattwinkel have identified about 60 individual tar acids and bases in a German tar produced at 600°–650° C. in a Krupp-Lurgi plant. There is some question that this is a true low-temperature tar since aromatization reactions start to make a significant contribution at about 600° C.

TABLE 3.—*Amounts of individual dihydric phenols from low-temperature tars, weight-percent*

Type of tar	North Dakota lignite [1]	English (Derbyshire) [2]	English bituminous [3]	German (brown coal) [4]
Reference	(110)	(7)	(93)	(70)
Catechol	0.7	1.03	Percent	Present.
3-Methylcatechol	.2	.58	do	Do.
4-Methylcatechol	.3	.65	do	Do.
Guaiacol (2-Methoxyphenol).	.4			
4-Methylguaiacol	.8			
4-Ethylguaiacol	.4			
3,5-Dimethylcatechol	.03	[5] 34		Present.
3,6-Dimethylcatechol				Do.
4,5-Dimethylcatechol				Do.
3-Ethylcatechol	.05			
4-n-Propylcatechol	Present			
Resorcinol		.51	Present	Present.
2-Methylresorcinol		.36	do	
5-Methylresorcinol			do	Present.
4-Methylresorcinol		.29	do	Do.
2,4-Dimethylresorcinol		[6] 27	do	
4,5-Dimethylresorcinol				Present.
4,6-Dimethylresorcinol				Do.
Hydroquinone		.06		
2-Methylhydroquinone		.03	Present	Present.
2,3-Dimethylhydroquinone.				Do.
2,5-Dimethylhydroquinone.				Do.
2,6-Dimethylhydroquinone.				Do.
Pyrogallol				Do.

[1] Weight-percent on basis of crude tar.
[2] Concentration (g./l.) in ammoniacal liquor.
[3] In aqueous liquor from "Coalite" process (carbonization temperature 600–620° C.).
[4] In aqueous liquor.
[5] Concentration of "higher catechols."
[6] Concentration of "higher resorcinols."

TABLE 4.—*Identification of individual pyridines in low-temperature tars*

Type of tar	German "bituminous" [1]	Japanese "coal"	Chinese "coal"
Reference	(51)	(75)	(120)
Compound:			
Pyridine	Present	Present	Present.
2-Methylpyridine	do	do	Do.
3-Methylpyridine	do	do	Do.
4-Methylpyridine	do	do	Do.
2,3-Dimethylpyridine	do	do	Do.
2,4-Dimethylpyridine		do	Do.
2,5-Dimethylpyridine		do	Do.
2,6-Dimethylpyridine	Present	do	Do.
3,4-Dimethylpyridine	do	do	Do.
3,5-Dimethylpyridine	do		Do.
3-Ethylpyridine			Do.
4-Ethylpyridine	Present		Do.
2,3,4-Trimethylpyridine		Present	
2,3,5-Trimethylpyridine	Present		Present.
2,3,6-Trimethylpyridine		Present	Do.
2,4,5-Trimethylpyridine	Present	do	Do.
2,4,6-Trimethylpyridine	do	do	Do.
2-Ethyl-4-methylpyridine			Do.
2-Ethyl-6-methylpyridine			Do.
4-Ethyl-2-methylpyridine		Present	Do.
2,6-Dimethyl-4-ethylpyridine			Do.

[1] Total tar bases distilling to 300° C. comprised 2.5 weight-percent of tar.

PRIMARY SEPARATION PROCEDURES

DISTILLATION OF TAR

The tar used in this work was made from Arkwright (W. Va.) Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at about 480° to 510° C. The raw tar was deashed, dehydrated, and topped to about 175° C. at the plant.

The tar was distilled under very mild temperature conditions so as to reduce structural alterations of tar components to a minimum. For this purpose, a rotary vacuum stripper was constructed.

The stripper consisted of a 12-liter-capacity stainless-steel spherical flask, which was rotated about 6 r.p.m. in a 20-gallon-capacity oil bath. A mechanical vacuum pump with a free air-flow rate of 375 liters per minute was used to reduce the pressure, and oxygen-free nitrogen was employed to maintain an inert atmosphere in the system. An ionization vacuum gage with a range of 1,000 mm. to 1 micron was used for continuous pressure indication. The main distillate was recovered with a cold-water Friedrichs condenser. A small portion of distillate representing components distillable at room temperature and about 133 microns pressure (equivalent to approximately 215° C. at 1 atmosphere) was recovered in a trap cooled by a mixture of trichloroethylene and solidified carbon dioxide. A similar trap was used to protect the sensing head of the ionization gage. In operation, the bulk of distillation took place from the fresh film of hot tar, which was continually drawn up the wall at one side of the flask, owing to the slow rotary motion. Near 125° C. and 133 microns, about 21 weight-percent of the tar was distillable. The equivalent temperature at atmospheric pressure was calculated to be about 350°–360° C., with 20.8 weight-percent of the tar in the main distillate and less than 1 percent collected in the dry-ice trap.

EXTRACTION OF TAR ACIDS AND BASES; BATCH PROCEDURES

A Claisen alkali extraction was performed on both portions of distillate following the procedure of Woolfolk and others (*118*). The phenols extracted from the low-boiling portion represented about 0.08 weight-percent of the tar, and the phenols extracted from the main distillate represented 3.54 weight-percent of the tar. About 3 liters (2,660 g.) of the main distillate was extracted by the method of Fisher and Eisner (*36*) to remove tar bases. These bases represented about 0.31 weight-percent of the total tar. Essentially no bases were present in the low-boiling portion from the dry-ice trap.

A special purification technique was devised for the tar bases. The pH of the acid extract containing the tar bases was adjusted to 12 by adding solid potassium hydroxide, and the resulting mixture was extracted with one 1-liter portion and three 500-ml. portions of ether. About 300 ml. of 15-percent sulfuric acid was added to the combined ether extracts, and most of the ether was removed by bubbling oxygen-free nitrogen through the mixture at room temperature. The acid solution was washed with one 200-ml. and two 100-ml. portions of pentane, the combined pentane washings were extracted twice with 50 ml. of 15-percent sulfuric acid, and these acid extracts were combined with the main acid solution. Enough potassium hydroxide pellets were added to the acid solution to adjust the pH to 12, and the liquid was decanted from the resulting precipitate of potassium sulfate. The precipitate was washed with three 70-ml. portions of benzene, and these washings were added to the base solution. The mixture of base and benzene was dried in a Dean-Stark apparatus for 3 days, utilizing an atmosphere of dry, oxygen-free nitrogen. The small amount of residual benzene was removed by fractional distillation and yielded about 40 g. dry tar bases, representing about 0.31 weight-percent of the total tar.

MULTISTAGE COUNTERCURRENT EXTRACTION

A series of five extraction runs was made on the main tar distillate, using 70 weight-percent methanol in water as the extractant and n-hexane as the raffinate solvent in the 1-inch by 4-foot, 11-stage Scheibel column (operation shown in fig. 1). Use of the Scheibel-type column for recovering high-purity tar acids from low-temperature coal tars has been described in detail, including the technique for determining tar acid purity (*81*). The results with these five runs are given in table 5. The

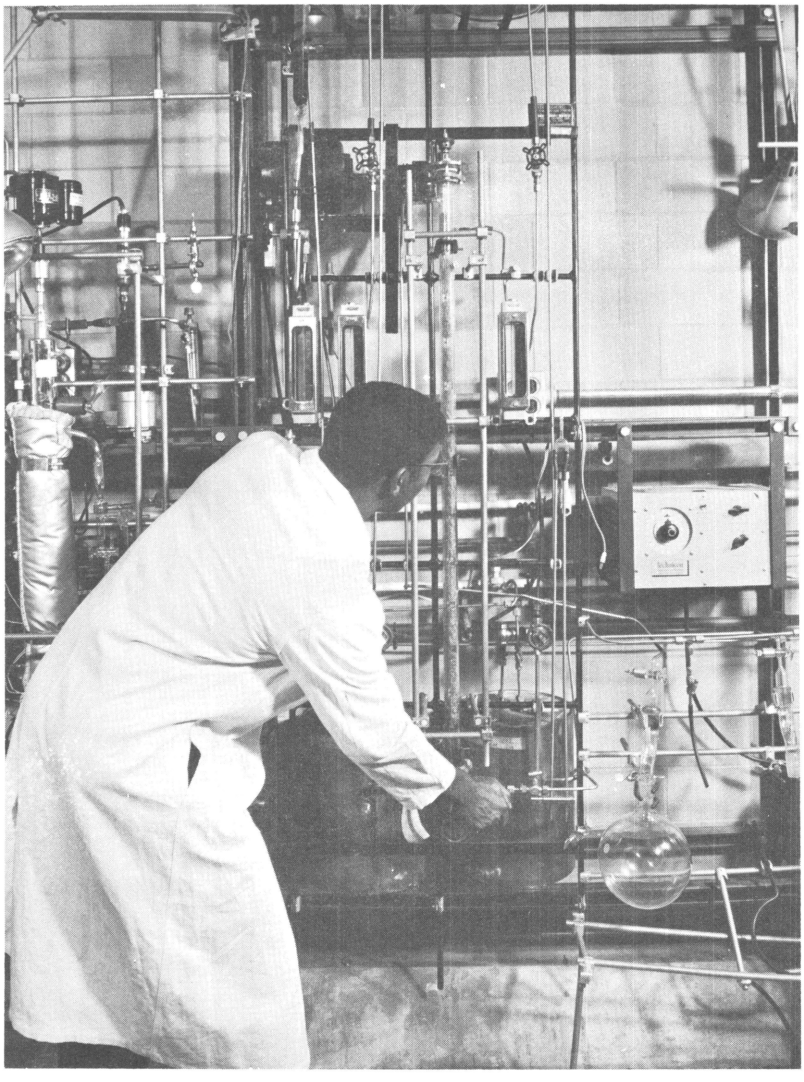

FIGURE 1.—Countercurrent Liquid-Liquid Extraction Apparatus Used to Recover Tar Acids From Tar Distillates.

TABLE 5.—*Extraction results from 1-inch by 4-foot, 11-stage Scheibel extraction column*

	Run No.				
	1	2	3	4	5
Length of run, hr.	4.75	4.75	3.5	4	1.75
Equilibrium time, hr.	----------	--------	2.75	2	2
Shaft speed, r.p.m.	1,200	920	920	927	1,195
Feed rates, ml./min.:					
Tar distillate	8.6	2.95	2.5	3	6
Methanol-water	5	5	2.5	4	6
n-Hexane	18	15	7.5	9	10.5
n-Hexane raffinate composition, vol.-pct.:					
Carboxylic acids	2.48	1.25	2.98	1.5	2.5
Tar bases	2.23	2.75	1.98	1.5	2.5
Tar acids	0	0	0.49	0	0
Neutral oil	95.29	96	94.55	97	95
Tar acid purity[1] vol.-pct.	----------	--------	95	97	90

[1] Aqueous methanol extract.

n-hexane raffinate was analyzed according to the method of Fisher and Eisner (*36*). From these runs it appeared that the tar acid content of the main distillate was about 26 volume-percent.

The column was converted from a 4-foot, 11-stage column to an 8-foot, 23-stage column, with three inlet choices: Below the 6th stage from the top, the 11th, and the 17th. The feed and both solvents were delivered to the column from stainless-steel reservoirs by a few pounds nitrogen pressure.

One run was made on this 8-foot column using bituminous coal-tar distillate as feed, aqueous methanol as the extractant, and n-hexane as the raffinate solvent; the flow rates were 5, 4.5, and 6 ml. per minute, respectively. Analysis

of the n-hexane raffinate gave the following volume-percents: Tar bases, 1.4; carboxylic acids, 1.0; phenols, 0.0; and neutral oil, 97.6. The aqueous methanol extract was subsequently fractionated in a cation-exchange column.

The purity of the tar acids obtained by countercurrent extraction with aqueous methanol was not as satisfactory as the purity of the tar acids obtained by Claisen alkali extraction. Therefore, only tar acids obtained by the latter procedure were used for detailed characterization.

ION-EXCHANGE CHROMATOGRAPHY

The aqueous methanol extract solution obtained by countercurrent liquid-liquid extraction of tar distillate in the 8-foot Scheibel column was percolated through a cation-exchange column in order to recover the tar bases. The column consisted of a 100-ml. burette containing 85 g. of wet amberlite IR 120 (H); moisture content was 45 percent and the bed length about 29 in. After backwashing with water, the bed volume was about 95 ml. Following a 500-ml. wash with 70 weight-percent aqueous methanol, about 1,500 ml. of methanol extract, representing about 1,200 ml. tar distillate was percolated through the column at a flow rate of about 19 ml. per minute, followed by about 25 ml. aqueous methanol. Total pyridines and total quinolines were determined by the ultraviolet spectrophotometric procedure developed in this laboratory on the distillate, the methanol extract solution, and the n-hexane raffinate solution. These results are shown in table 6.

The tar bases adsorbed by the resin were regenerated and recovered by percolating about 6 liters of 4-percent hydrochloric acid in 70 percent methanol through the column.

TABLE 6.—*Removal of tar bases from methanol extract by ion-exchange chromatography*

	Tar distillate	Methanol solution		n-Hexane solution
		Before ion exchange	After ion exchange	
Sample volume, ml.	1,200	1,487	1,510	1,507
Total pyridines, g.	12.7	0.181	.014	12.3
Total quinolines, g.	6.0	.019	trace	6.3
Total base, g.	18.7	.20	.014	18.6
Total base distribution, pct.	100	1.1	.0	98.9
Pyridine in total base, pct.	68	90	----------	65
Quinoline in total base, pct.	32	10	----------	35

SECONDARY SEPARATION PROCEDURES

FRACTIONATION OF TAR ACIDS AND BASES IN A MICRO-SPINNING-BAND VACUUM STILL

A Piros-Glover micro-spinning-band vacuum still, shown in operation in figure 2, constituted one of the most useful devices for obtaining a good fractionation at low pressures of 30- to 40-g. quantities of either tar acids or tar bases. The unique feature of this still is that the column contains a close-fitting, rapidly rotating metal band instead of the conventional packing. The pressure drop through this column is almost negligible, making it possible to conduct vacuum distillations with very low pressures in the pot.

Because of the large proportion of high-boiling components in the tar acids and bases, a test distillation was conducted at virtually the

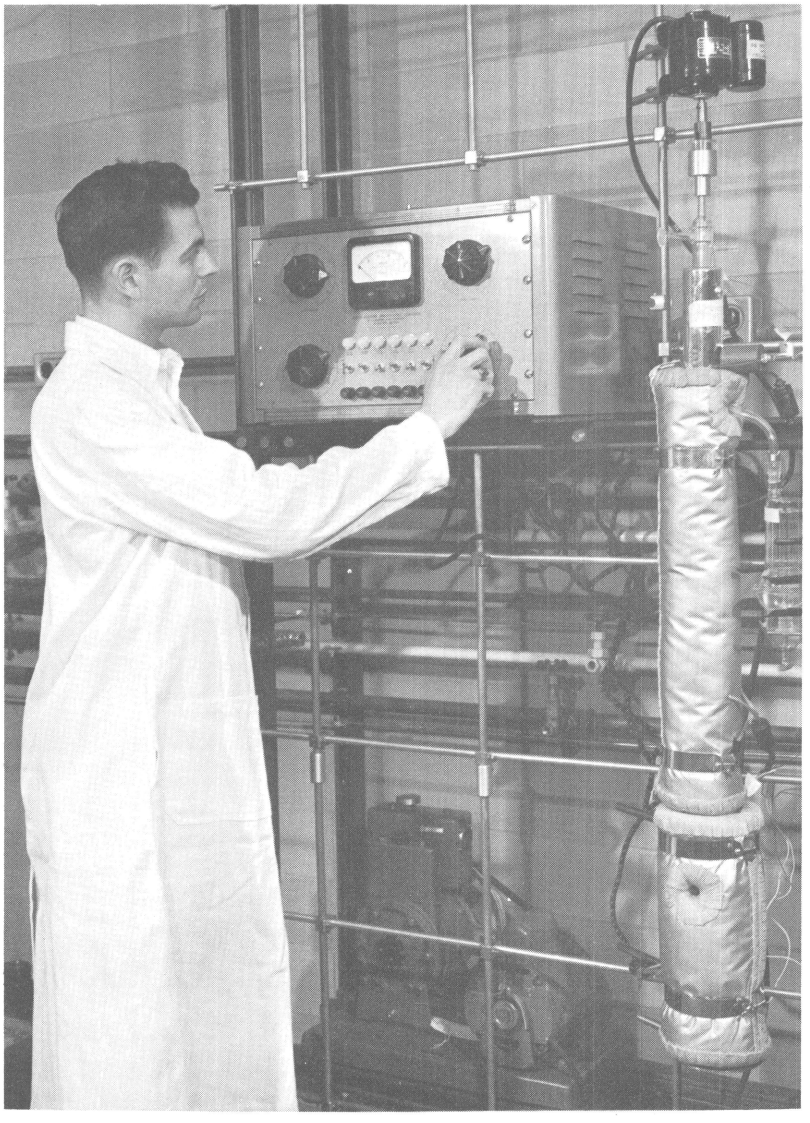

FIGURE 2.—Fractional Distillation of Tar Acids or Bases Using a Micro-Spinning-Band Vacuum Still.

lower pressure limit of the still; that is, 0.5 mm. head pressure. Since the pressure drop is about 0.5 mm. at normal boilup rates, lowering the head pressure below 0.5 mm. will have essentially no effect on the pot pressure. A suggested test mixture for operation at these pressures is n-hexadecanol and n-octadecanol (*80*). A 15.83-g. charge was distilled at 0.5 mm. Hg. Only 0.19 g. remained in the pot, probably all of which represented column hold-up. The results of this test distillation are shown in table 7. A good fractionation was indicated; the charge components were obtained in as pure a state as before blending to make the test mixture.

TABLE 7.—*Results of low-pressure fractionation of test mixture in spinning-band still*

	Refractive index, n_D^{70}	Melting point, ° C.
n-Hexadecanol[1]	1.4318	46.4
n-Octadecanol[1]	1.4345	56.8
Fraction 1	1.4316	46.0
Fraction 2	1.4342	56.4
Fraction 3	1.4346	57.3
Fraction 4	1.4347	57.1

[1] Test mixture.

DISTILLATION OF LOW-BOILING TAR ACIDS RECOVERED FROM DRY-ICE TRAP

A 37.25-g. portion of the low-boiling mixture of phenols isolated from the distillate in the dry-ice trap was fractionated in the Piros-Glover micro-spinning-band vacuum still. All air was flushed out of the still with oxygen-free dry nitrogen before the distillation was started. The still was operated at a head pressure of 20 mm. Hg, which very nearly represents the pot pressure since the pressure drop in the spinning-band column is almost negligible. The boilup rate was approximately 30 to 40 ml. per hour and the reflux ratio 10:1. The speed of the band was fixed at 1,800 r.p.m. Under these conditions the efficiency of the still was estimated to be about 30 theoretical plates. Seven fractions were isolated, with a recovery of 96.2 weight-percent. All fractions were initially colorless, but fraction 7 developed a slight color on standing 2 days. The results of this distillation are shown in figure 3. The temperature readings in figure 3 are for an iron-constantan thermocouple in the still head as recorded on a 10-mv., 5-inch span recorder; the cold junction is at room temperature, which was essentially constant.

DISTILLATION OF LOW-BOILING TAR ACIDS RECOVERED FROM MAIN TAR DISTILLATE

The phenols recovered from the main tar distillate were fractionated in the Piros-Glover micro-spinning-band still. The charge was 35.66 g., and the distillation was conducted at a pressure of 19.80 to 22.20 mm. with a reflux ratio of 20:1 and a boilup rate of 33 to 54 ml. per hour. The reflux temperature was measured with a model 8667 Leeds and Northrup potentiometer using a water-ice mixture for the reference junction. The total amount distilled after 26.2 hours was 77.79 weight-percent. The results are shown in figure 4.

DISTILLATION OF HIGH-BOILING TAR ACIDS RECOVERED FROM MAIN TAR DISTILLATE

A 200-g. portion of tar acids from the main distillate, representing 3.54 weight-percent of the low-temperature bituminous coal tar, was distilled at 20 mm. through a column filled with glass helices. All the material boiling up to 118° head temperature, equivalent to 232° at 760 mm., was removed as a single fraction, leaving a residue of 50 g. high-boiling phenols or 25 weight-percent of the original tar acid mixture. A charge of 41.68 g. high-boiling tar acids was distilled at 2.9 mm. and a reflux

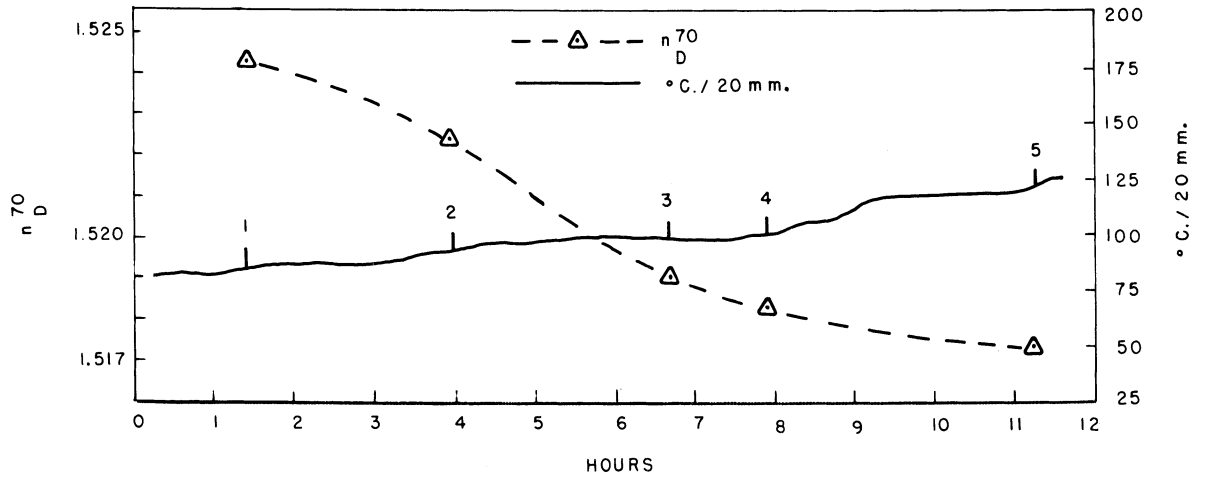

FIGURE 3.—Fractionation of Low-Boiling Phenol Distillate in Spinning-Band Still.

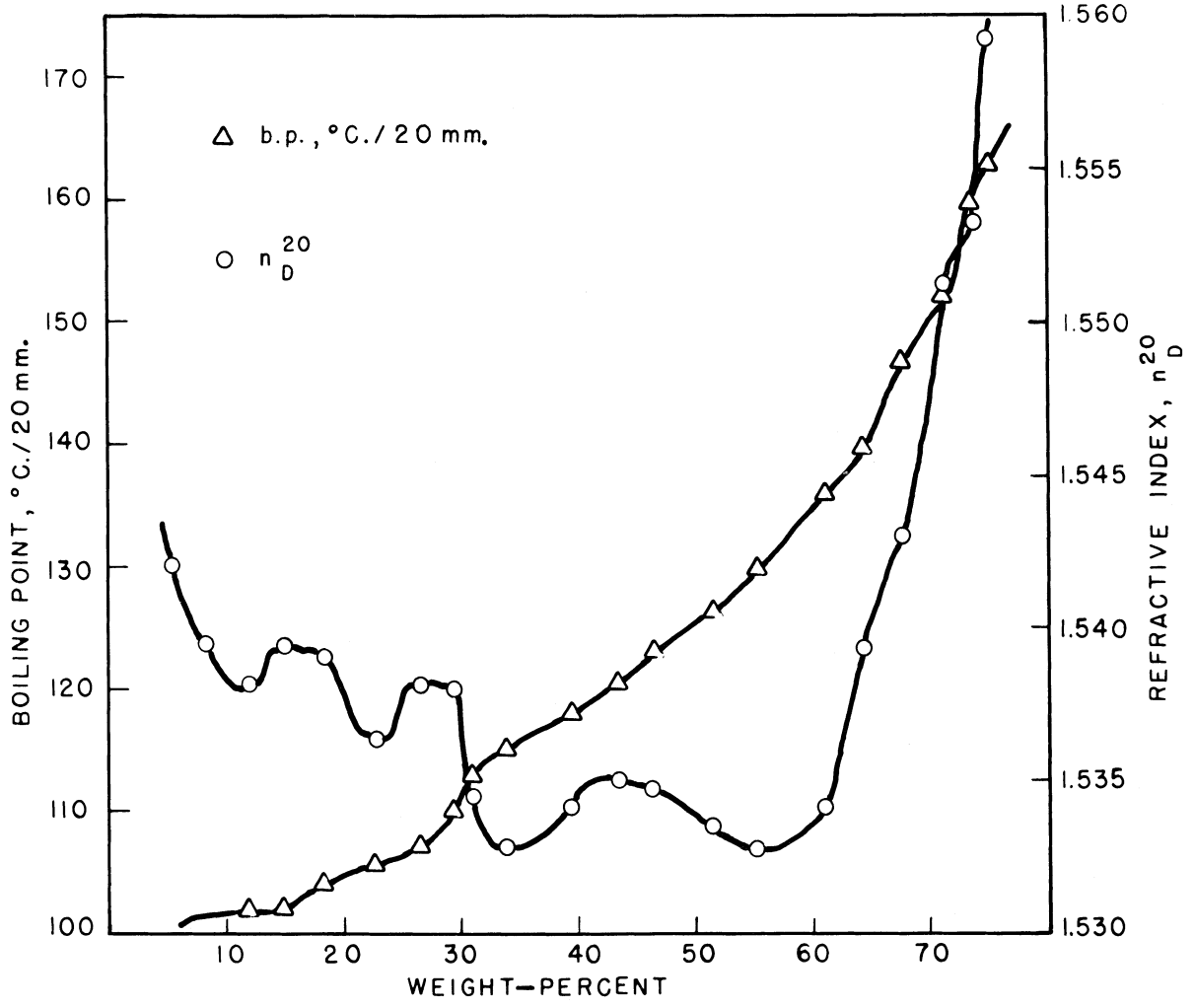

FIGURE 4.—Fractionation of Phenols From Main Tar Distillate in Spinning-Band Still.

ratio of 20:1 in the spinning-band still, with the results shown in table 8.

TABLE 8.—*Fractionation of high-boiling tar acids in spinning-band still*

Fraction No.	Boiling range		Weight, g.
	2.9 mm.	760 mm.	
1	77.5–78.0	231	0.71
2	78.0–79.0	231–232	1.31
3	79.0–84.0	232–238	1.10
4	84.0–88.0	238–244	1.35
5	88.0–91.0	244–247	1.14
6	91.0–94.0	247–251	1.00
7	94.0–96.0	251–253	1.40
8	96.0–98.0	253–255	.86
9	98.0–102.0	255–258	.86
10	102.0–103.0	258–260	.85
11	103.0–106.0	260–264	.51
12	106.0–110.0	264–270	.96
13	110.0–116.0	270–278	.87
14	116.0–117.0	278–280	1.15
15	117.0–124.0	280–290	1.15
16	124.0–129.0	290–297	1.17
17	129.0–132.0	297–300	1.08
18	132.0–139.0	300–308	.96
19	139.0–152.0	308–325	.85
20	152.0–157.0	325–331	.88
21	157.0	331	.24

DISTILLATION OF TOTAL TAR BASES RECOVERED FROM MAIN TAR DISTILLATE

A 37.50-g. portion of the dry tar bases was fractionated in the Piros-Glover micro-spinning-band still, using a reflux ratio of 15:1, a kettle temperature of about 25° to 186° C., and a head pressure of 80 to 3 mm. from the beginning to the end of the run, respectively. The boilup rate ranged from 32 to 95 drops per minute but was usually around 50 drops. The results of this distillation are presented in table 9; all head temperatures have been converted to those at 760 mm. Hg pressure by means of a standard nomograph.

TABLE 9.—*Fractionation of bases from low-temperature bituminous coal tar distillate in spinning-band still*

Fraction No. 1 [1]	Boiling-point range, ° C./760 mm.	Weight of sample, g.	Weight, percent
0	75–152	0.1	0.27
1	152–173	.41	1.09
2	173–183	.42	1.12
3	183–200	1.16	3.09
4	200–201	.64	1.71
5	201–208	.59	1.57
6	208–210	.39	1.04
7	210–224	1.24	3.31
8	224–228	.96	2.56
9	228–231	1.10	2.93
10	231–238	1.10	2.93
11	238–240	1.14	3.04
12	240–245	1.03	2.75
13	245–252	1.22	3.25
15	252–263	.98	2.61
16	263–265	.93	2.48
17	265	1.00	2.67
18	265	1.03	2.75
19	265	1.02	2.72
20	265–270	1.42	3.79
21	270	.91	2.43
22	270	1.02	2.72
23	270	.83	2.21
24	270–277	.93	2.48
25	277–280	.88	2.35
26	280	1.20	3.2
27	280–286	1.21	3.23
28	286–290	1.45	3.87
29	290–298	1.48	3.95
30	298–301	.83	2.21
31	301–305	.84	2.24
32	305–310	.95	2.53
34	310–335	.96	2.56
35	335–345	.75	2.0
	Total distilled over	32.12	85.66
36	Receiver holdup	.26	.69
37	Column holdup	.47	1.25
38	Residue in kettle	4.10	10.93
	Total recovery	36.95	98.53
	Loss	.55	1.47

[1] No fractions 14 and 33.

QUALITATIVE AND QUANTITATIVE ANALYTICAL PROCEDURES

ANALYSIS OF TAR ACIDS AND BASES BY INFRARED SPECTROPHOTOMETRY

A Model 21 Perkin-Elmer infrared recording spectrophotometer, shown in operation in figure 5, was the analytical instrument with the greatest utility; it was indispensable for characterization of the tar acids and bases. The essential need for spectra of pure compounds is discussed in the introduction to this report. The compilation of spectra used by the Low-Temperature Tar Laboratory is given in the appendix of this report.

INFRARED SPECTROPHOTOMETRIC ANALYSIS OF TAR-ACID DISTILLATE FRACTIONS

The seven distillate fractions of low-boiling tar acids recovered from the dry-ice trap were analyzed by infrared spectrophotometry, using the analytical wavelengths, in microns, listed in table 10. The same analytical wavelength was not always used for a compound that appeared in more than one fraction, but the most suitable wavelength was chosen, depending on the particular mixture that had to be analyzed. The weights of each component in each fraction,

FIGURE 5.—Identification and Analysis of Tar Acids and Bases With an Infrared Recording Spectrophotometer.

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TABLE 10.—*Wavelengths for infrared spectrophotometry of low-boiling tar acids recovered from dry-ice trap*

Compound	Fraction microns,						
	1	2	3	4	5	6	7
Phenol	14.57	14.57					
o-Cresol	11.86	11.86	13.35				
2,6-Xylenol			11.02				
p-Cresol			12.25	12.25			
m-Cresol			14.58	14.58			
o-Ethylphenol				13.37	13.37	13.37	
2,4-Xylenol				12.50	12.30	12.30	
2,5-Xylenol					10.04	10.04	
2,3-Xylenol					11.12	14.17	
p-Ethylphenol						12.08	
m-Ethylphenol						11.04	
3,5-Xylenol						9.73	14.64, 10.56
3,4-Xylenol							12.35, 12.56

as determined by this analysis, are shown in table 11. This table also gives the weight, in grams, and the refractive index, at 70° C., for each fraction.

The distillate fractions through number 17 of low-boiling tar acids recovered from the main tar distillate were analyzed by infrared spectrophotometry. Care was taken to select the most suitable analytical wavelength for each component in each fraction. For example, in the case of 2,4-xylenol it was necessary to use 13.97 microns in fractions 5, 6, and 7, 12.30 microns in fractions 8, 9, and 10, and 13.03 microns in fractions 11 and 12. Fair and Friedrich (*34*), however, show that for their synthetic mixtures one analytical wavelength suffices for a phenol. The various analytical wavelengths used and the quantitative results are given in table 12. Due to the unusually low proportion of phenol and o-cresol in these particular tar acids, these compounds could not be separated from the other phenols and the first four fractions are much more complex than in a typical tar acid distillation. This is reflected in the accuracy of the infrared analysis, in particular for the cresols.

ANALYSIS OF TAR ACIDS AND BASES BY ULTRAVIOLET SPECTROPHOTOMETRY

A Beckman DK–2 ultraviolet recording spectrophotometer, shown in operation in figure 6, was a highly useful analytical instrument in the characterization of tar acids and bases. Ultraviolet analysis offered the special advantages of simplicity, speed, and ability to work with very dilute solutions. Infrared analysis is, however, generally superior for positive identification of components that are isomers. These two spectrophotometric methods are largely complementary rather than duplicative.

ULTRAVIOLET ANALYSIS OF SMALL QUANTITIES OF INDIVIDUAL TAR BASES OBTAINED BY SUCCESSIVE EXTRACTIONS

In studying the sorption of individual pyridine bases by cation-exchange resins, an accurate and relatively quick method was developed to determine small quantities of these tar bases in aqueous methanol solutions (*22*).

The analytical method that was developed was based on extracting the pyridine bases from an aqueous solution with iso-octane wherein the bases were subsequently determined spectrophotometrically. Owing to an unfavorable distribution of some of the bases in iso-octane, several extractions would usually have been required for quantitative recovery, therefore the operation would have become cumbersome. However, with the data from two successive extractions, the distribution coefficients could be estimated. From this coefficient the amount of pyridine bases in the original solution was readily calculated.

Before developing this procedure, a literature search revealed that the Kjeldahl method for

TABLE 11.—*Infrared analysis of low-boiling tar acids recovered from dry-ice trap*

Fraction No.	Weight, g.	Refractive index, n_D^{70}	Components by infrared analysis, g.		
			Major	Minor	Trace
1	8.00	1.5243	Phenol, 5.2	o-Cresol, 2.8	
2	7.84	1.5224	o-Cresol, 4.8	Phenol, 3.0	
3	7.88	1.5190	m-Cresol, 3.4	p-Cresol, 2.3 o-Cresol, 1.4	2,6-Xylenol, 0.8.[1]
4	3.39	1.5180	m-Cresol, 1.35 2,4-Xylenol, 1.3	p-Cresol, 0.6	o-Ethylphenol, 0.15.
5	3.07	1.5173	2,4-Xylenol, 2.1	2,5-Xylenol, 0.74	2,3-Xylenol, 0.12. o-Ethylphenol, 0.1.[1]
6	4.76	1.5150	2,4-Xylenol, 1.5	3,5-Xylenol, 0.9 p-Ethylphenol, 0.8 m-Ethylphenol, 0.6 2,5-Xylenol, 0.6	2,3-Xylenol, 0.3. o-Ethylphenol, 0.1.
7	.90	1.5152	3,4-Xylenol, 0.3 [1] 3,5-Xylenol, 0.3 [1]	m-Ethylphenol 2,3-Xylenol 2,3,5-Trimethylphenol	

[1] Estimated quantities.

TABLE 12.—*Infrared analysis of distillate fractions of low-boiling tar acids from main tar distillate* [1]

Fraction No.	Weight, g.	Phenols, weight-percent					
		Phenol	o-Cresol	m-Cresol	p-Cresol	2,6-Xylenol	
1	1.96	13.8 (9.37 μ)	41.8 (14.12 μ)	20.9 (10.77 μ)	13.8 (12.25 μ)	10.2 (11.02 μ)	
2	.99	10.1	12.1	44.5	29.3	6.1	
3	1.27	3.2	3.2	54.3	37.0	4.7	
4	1.12	7.1	5.4	51.8	33.9	1.8	
		2,4-Xylenol	2,5-Xylenol				
5	1.25	12.8 (13.97 μ)	12.8 (10.04 μ)	42.4 (10.77 μ)	32.0 (13.54 μ)		
6	1.47	34.0	23.1	25.8	17.0		
7	1.38	58.0	33.4	5.8	2.9		
				2,3-Xylenol	m-Ethyl-phenol	p-Ethyl-phenol	3,5-Xylenol
8	1.04	67.3 (12.30 μ)	15.4 (10.04 μ)	8.7 (14.17 μ)	2.9 (11.04 μ)	6.7 (12.08 μ)	0 (9.73 μ)
9	1.53	37.3	15.0	15.0	11.1	11.1	11.1
10	1.09	24.8	4.6	4.6	22.0	23.8	19.3
			3,4-Xylenol	4-Ethyl-2-methylphenol			
11	1.94	20.1 (13.03 μ)	4.6 (9.98 μ)	8.3 (11.35 μ)	18.0 (11.04 μ)	17.0 (12.08 μ)	32.0 (9.73 μ)
12	1.40	5.0	15.7	25.0	7.9	5.0	40.7
		2,3,5-Trimethyl-phenol			3-Ethyl-5-methyl-phenol		
13	1.04	8.7 (9.27 μ)	28.8 (9.98 μ)	25.0 (13.10 μ)	0 (10.40 μ)	----------	36.6 (9.73 μ)
14	1.80	32.2	27.8	27.2	5.0	----------	8.9
						4-Indanol	5-Indanol
15	1.34	34.3 (9.27 μ)	5.2 (9.98 μ)	11.9 (11.35 μ)	34.3 (10.40 μ)	6.0 (10.18 μ)	9.0 (10.69 μ)
16	1.06	34.9	2.8	5.7	28.3	25.5	3.8
17	1.31	19.1	8.4	9.9	16.0	29.0	16.8

[1] Values in parentheses are analytical wavelengths.

total nitrogen and several methods based on acid-base titration, or on color formations of the bases with reagents, were available. However, the Kjeldahl method and the titration methods can only determine the total amount of the bases and cannot differentiate among individual compounds in the case of simple mixtures. The colorimetric methods either suffer from fading of the color with time or are not rapid enough.

Two ultraviolet methods have been described, one by LeRosen and Wiley (*71*) and the other by Herington (*44*). In the former procedure the absorbance of total pyridines was measured in phosphoric acid solution. In the latter, the estimation of individual water soluble pyridines was based on the difference in extinction coefficients in 0.1*N* acid and 0.1*N* alkaline solutions. The difficulty in applying either method to the present base samples was that these fractions were recovered from a cation-exchange column by eluting with hydrochloric acid in 70-percent methanol solution. The concentrations of both acid and methanol naturally varied from fraction to fraction. In removing the methanol by distillation, the acidities of the samples were altered by different amounts. Since the concentration of acid affects the absorbance of pyridines, accurate results could not be obtained under these conditions. In addition, the fractions from the exchange column were often found to be either cloudy or yellow in color, indicating that some impurities were present. These impurities interfered in the ultraviolet determination by absorbing strongly in this region. To overcome these difficulties, extracting the base in alkaline solution with iso-octane was found to be satisfactory.

The present method gave about 98- to 102-percent recovery and was suitable for samples that could be purified by extracting with iso-octane or similar solvents.

Specific extinction coefficients (K) for four

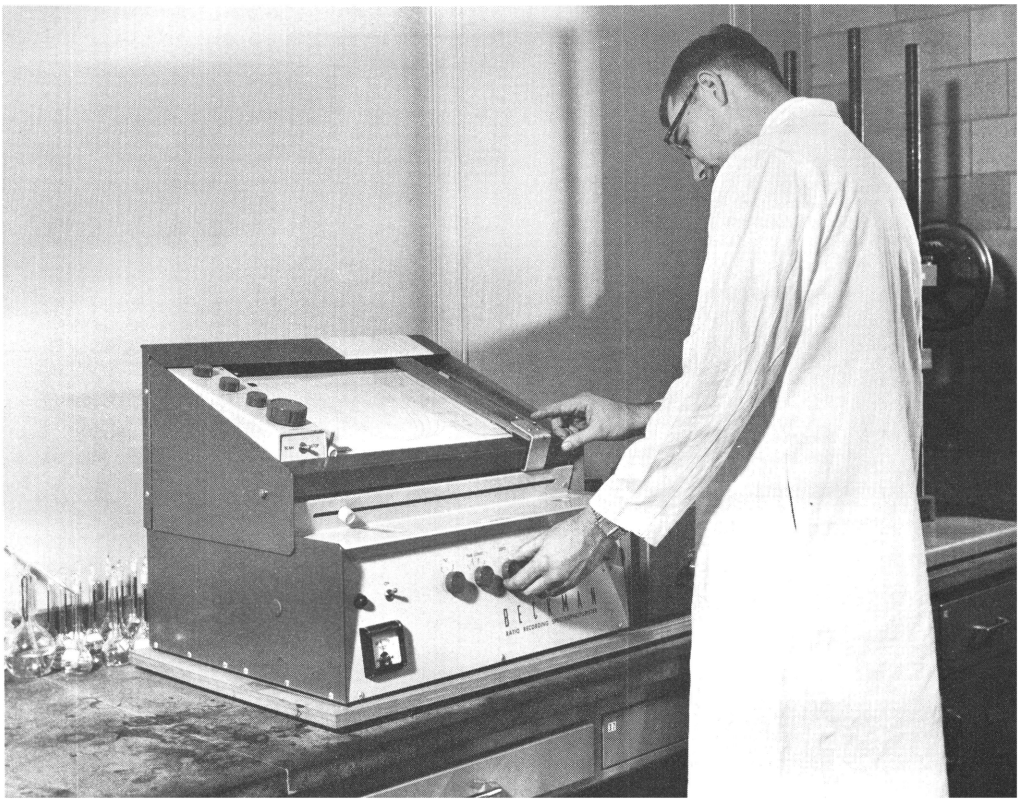


FIGURE 6.—Characterization of Tar Acids and Bases With an Ultraviolet Recording Spectrophotometer.

bases were first determined, using iso-octane as the solvent and reference. These results are shown in table 13.

Known solutions of bases were prepared by dissolving a definite amount of base in 70-percent methanol solution. For analyzing a known solution, 25 ml. was pipetted into a 50-ml. distilling flask, followed by the addition of 12.5 ml. of 10-percent HCl and 1–2 boiling chips. The pH of the solution was about 2. The flask was then connected to the fractional distilling apparatus, and the temperature of the column heating jacket was adjusted to 45° C. About 25 ml. of distillate was collected at a distilling head temperature below 73° C. The purpose of the distillation was to remove the methanol. After distillation the heating mantle of the flask was removed immediately,

TABLE 13.—*Extinction coefficient (K) of individual tar bases in iso-octane at given wavelengths* [1]

	251 mμ	256 mμ	265 mμ	313 mμ
Pyridine	23.75	22.71	13.33	0
α-Picoline	21.91	26.57	20.57	0
2,3-Lutidine	18.17	23.37	27.81	0
Quinoline	18.36	20.92	26.07	20.07

[1] Cell thickness=1 cm.

and a stream of cooling air was introduced through the bottom of the jacketed column. After the column was cooled, it was washed from the top several times with a fine stream of distilled water. The flask was then removed and placed in an ice-cold water bath. The pH of the residue solution was adjusted to about 10, as indicated by multirange pH paper, by adding enough potassium hydroxide pellets with constant stirring. Solid potassium hydroxide was required to avoid dilution of the sample. The final solution was transferred quantitatively to a 25-ml. volumetric flask and diluted to the mark with distilled water. After shaking well, 10 ml. of the solution was pipetted to a separatory funnel and extracted with 10 ml. of iso-octane. The lower layer (aqueous layer) was then transferred to another separatory funnel and extracted again with 10 ml. of iso-octane. The concentrations of base in the iso-octane layers were then determined spectroscopically, and the total amount of base present in the original sample was calculated.

In calculating the distribution coefficient from the successive extractions, it was assumed that, for such low concentrations as were encountered in this work, the distribution curve would be linear. Following this assumption,

the following three equations were used for calculating the total amount of base in the original sample:

Since

$$Y_1=\frac{X_1}{k}$$

and

$$Y_1-X_2=Y_2,$$

$$k=\frac{X_2}{Y_2}=\frac{X_2}{\frac{X_1}{k}-X_2}$$

or

$$X_2=X_1-X_2k.$$

Therefore,

$$k=\frac{X_1}{X_2}-1,$$

$$Y_1=\frac{X_1}{k},$$

$$T=X_1+Y_1,$$

where

X_1 and X_2 = concentrations of base, grams per liter present in the first and second iso-octane extracts,

Y_1 and Y_2 = concentrations of base, grams per liter present in first and second aqueous layer,

k = distribution coefficient of base between iso-octane and aqueous layers, and

T = total concentration of base, grams per liter present in original sample.

For bases less soluble in water, the total concentration could be obtained directly by adding the concentration of the bases in the iso-octane layer, that is, X_1 and X_2. In other words, the distribution coefficient of the slightly water-soluble base is so great that two successive extractions with iso-octane result in substantially quantitative recovery. For example, quinoline has an average distribution coefficient around 20 (the k values of all of the bases depend on the actual pH of the aqueous solution). Its Y_1, 0.00107, calculated from k, almost equals X_2, 0.00104. Therefore, calculation of its distribution coefficient can be omitted, and its total concentration equals (X_1+X_2). This is also true for 2,3-lutidine. Table 14 compares the results. The variation in distribution coefficient for the same compound is due to the fact that the pH was seldom adjusted to exactly the same value. This was of no significance as long as the correct k value was used for the particular pH involved.

For a mixture of several bases, X_1 and X_2 of each component were calculated from the spectra of the two iso-octane extracts of the mixture at proper wavelengths. The wavelengths used for calculating α-picoline, 2,3-lutidine, and quinoline mixtures were 256 mμ, 265 mμ, and 313 mμ, respectively.

A direct extraction of the base with iso-octane from the original sample at pH 10 without distillation was tried, and the results were unsatisfactory because the base was preferentially soluble in 70 percent methanol and passed to iso-octane only in a small amount. As a result, the concentrations of the first and the second extracts were so close that only a slight error in readings of the absorbances would have resulted in a great error in the distribution coefficient. The distillation part

TABLE 14.—*Determination of tar bases obtained by two different calculations*

Compound	Present, g./l.	In iso-octane layers, g./l.		Distribution coefficient, k	Found, g./l. calculated from k	Recovery, pct.	Found, g./l. calculated from X_1+X_2	Recovery, pct.
		X_1	X_2					
Single base sample:								
Pyridine	0.0240	0.01052	0.00593	0.773	0.02412	101.0	0.02088	89.0
	.0240	.01132	.00593	.909	.02367	98.6	.01725	71.9
	.03504	.0158	.00868	.825	.03499	99.9	.02448	69.9
α-Picoline	.0276	.01981	.00596	2.34	.0282	102.2	.02577	93.3
	.0276	.01900	.00526	2.38	.02698	97.8	.02426	87.9
2,3-Lutidine	.0340	.03045	.0030	9.15	.033	99.3	.03345	98.4
	.0340	.03066	.0032	8.58	.03416	100.5	.03386	99.6
Quinoline	.0262	.0252	.00104	23.0	.02629	100.3	.02624	100.2
	.0262	.0252	.00145	16.38	.0267	101.9	.02665	101.8
No. 1 mixture of bases:								
α-Picoline	.0138	.00866	.00317	1.73	.0137	99.3	.01183	85.8
2,3-Lutidine	.01136	.01042	.00091	10.45	.01141	101.0	.01133	99.9
Quinoline	.01308	.0126	.00059		(.0132)	100.8	.0132	100.8
Total	.03824				.03831	100.2	.03636	95.0
No. 2 mixture of bases:								
α-Picoline	.0069	.00458	.00167	1.74	.00721	104.5	.00625	90.6
2,3-Lutidine	.02272	.02079	.00172	11.087	.02266	99.7	.0225	99.0
Quinoline	.01308	.01285	.00059		(.01344)	102.8	.01344	102.8
Total	.0427				.04331	101.4	.04219	98.8

of this procedure was mainly to remove the methanol from the solution so that the extraction could be improved. Table 15 compares the results obtained with and without distillation. If the distribution coefficient calculated from X_1 and X_2 should be greater than 0.5, it would be quite possible to extract the sample directly with iso-octane and eliminate the distillation. If the sample is an aqueous solution containing no methanol, the distillation can be eliminated. According to the distribution law, the fraction of solute left in the aqueous layer after a number of successive extractions with equal volumes of solvent equals $[1/(1+k)]^n$, where n is the number of extractions. When $n=3$ and $k=4$, the fraction of original base left in the aqueous layer should be $[1/(1+4)]^3=1/125$, which is so small that it will not cause appreciable error in recovery of the base. Therefore, when the distribution coefficient is greater than 4, three successive extractions can be used and the concentration of the base can be determined directly from the combined extracts by ultraviolet spectrophotometry. When the original solution contained less than 0.01 g./l. of total base, the concentration of the second extract, X_2, was usually so low that the absorbance was close to zero. This concentration, therefore, was considered as the lower limit for this method at the desired accuracy of about ± 2 percent.

TABLE 15.—*Effect of distillation on results with pyridine*

Concentration present, g./l.	X_1, g./l.	X_2, g./l.	k	T, g./l.
Without distillation				
0.024	0.00291	0.00211	0.31	0.0106
.03504	.00421	.00333	.272	.01971
With distillation				
.024	.01052	.01036	.773	.02412
.03504	.0158	.00868	.825	.03499

DETERMINATION OF TOTAL PYRIDINES AND TOTAL QUINOLINES BY ULTRAVIOLET SPECTROPHOTOMETRY

For the analysis of pyridine and quinoline and their homologs according to chemical type (that is, as pyridines and quinolines), it was desired to develop a method that would apply to low-temperature coal-tar distillates and crude-tar bases (*23*). Previously LeRosen and Wiley (*71*) had attempted to determine pyridines in petroleum products by extracting the sample with phosphoric acid wherein the pyridines were determined by ultraviolet spectrophotometry and expressed as pyridine by referring to a standard graph of pyridine itself.

TABLE 16.—*Absorptivities of individual tar bases*

	Absorptivity, at wavelength	
	260 mμ	316.5 mμ
Pyridine bases:		
Pyridine	17.44	0
2-Methylpyridine	25.43	0
3-Methylpyridine	23.47	0
4-Methylpyridine	14.22	0
2,3-Dimethylpyridine	26.86	0
2,4-Dimethylpyridine	22.41	0
2,6-Dimethylpyridine	26.74	0
3,5-Dimethylpyridine	22.87	0
2-Ethylpyridine	24.47	0
4-Ethylpyridine	13.07	0
5-Ethyl-2-methylpyridine	20.99	0
3-Ethyl-4-methylpyridine	18.87	0
2,4,6-Trimethylpyridine	20.33	0
Average	21.25	0
Quinoline bases:		
Quinoline	24.23	9.84
2-Methylquinoline	23.90	24.71
4-Methylquinoline	27.69	8.97
6-Methylquinoline	17.79	12.39
7-Methylquinoline	19.16	18.95
8-Methylquinoline	12.56	12.87
2,4-Dimethylquinoline	24.24	17.25
2,6-Dimethylquinoline	21.25	13.56
Isoquinoline	28.67	27.27
3-Methyl-isoquinoline	27.08	13.69
Average	23.24	15.95

The ultraviolet spectra of 23 individual tar bases were determined in iso-octane. The absorptivities of the bases and their averages at 260mμ and 316.5 mμ were then calculated and are presented in table 16.

Stocks of 12 synthetic mixtures containing bases listed in table 16 were prepared in 10-percent sulfuric acid. The concentration of each compound was about 0.001 to 0.002 g./l. Neutral oil (0.03 g./l.) from low-temperature coal tar was added to four of these, and they were washed three times with an equal volume of iso-octane, which was discarded. For all mixtures, 10 ml. of the acid layer was adjusted to pH 12 by slowly adding potassium hydroxide pellets. The alkaline solution was extracted three times with 10 ml. of iso-octane, the extracts were combined, and the ultraviolet spectrum was determined. The concentrations of total quinolines and pyridines were determined by the absorbances and average absorptivities at 316.5 and 260 mμ. The recovery of bases was excellent for all mixtures, as shown in table 17.

The procedure used for tar distillates was as follows: For samples containing 1 to 2 percent base by weight, 10 ml. of distillate was weighed in a separatory funnel and extracted three times with 10-percent sulfuric acid, 20 ml. the first time and 10 ml. each the second and the third times. The acid layers were col-

TABLE 17.—*Recovery of total pyridines and quinolines from synthetic mixtures by using average absorptivities*

Mixture No.	Total pyridines present, g./l.	Total pyridines found, g./l.	Recovery, pct.	Total quinolines present, g./l.	Total quinolines found, g./l.	Recovery, pct.
1	0.0202	0.0201	99.3	0.0155	0.0155	100.0
2	.0282	.0281	99.7	.0093	.0091	97.8
3	.0081	.0080	99.8	.0248	.0245	98.7
4	.0181	.0181	100.0	.0171	.0166	97.3
5	.0179	.0173	96.2	.0184	.0201	109.0
6[1]	.0179	.0192	107.0	.0184	.0206	112.0
7	.01875	.0193	103.0	.01238	.0116	93.7
8[1]	.01875	.0206	109.8	.01238	.0117	94.5
9	.01875	.0208	111.0	.01238	.0117	94.5
10[1]	.01875	.0199	106.0	.01238	.0119	96.1
11	.02203	.01905	87.0	.01354	.0135	99.0
12[1]	.02203	.01868	85.0	.01354	.0135	99.0

[1] These mixtures contained 0.03 g./l. neutral oil obtained from low-temperature tar.

lected in a 100-ml. volumetric flask. The oil residue remaining in the funnel was extracted three times with 10 ml. of 10-percent sodium hydroxide to remove tar acids that make complete extraction of tar bases difficult. The alkaline layer was discarded, and the oil layer was extracted three times with 10-percent sulfuric acid as before. These extracts were added to the flask, and the volume was diluted to 100 ml. with 10-percent sulfuric acid.

The procedure used for crude-tar base was as follows: About 0.1 g. of crude-tar base was weighed and dissolved in 10-percent sulfuric acid in a 50-ml. volumetric flask. The solution was diluted to the mark with 10-percent sulfuric acid.

Twenty-five milliliters of either of the above acid solutions was washed three times with an equal volume of iso-octane to remove any residual neutral oil, and the acid solution was adjusted to 25 ml. with water if necessary. Two milliliters of the acid solution was pipetted into a small beaker containing a few milliliters of water, and the beaker was placed in an ice-water bath. Potassium hydroxide pellets were added to the acid solution with constant stirring until the pH of the solution reached 12. The solution was transferred quantitatively to a 25-ml. volumetric flask and diluted to the mark with distilled water. Five milliliters of the alkaline solution was extracted three times with 10 ml. of iso-octane, the extracts were combined, and an ultraviolet spectrum was determined. Total quinolines and total pyridines were obtained from equations (1) and (2), respectively.

$$Q=\frac{A_{316.5}}{15.95}\times F_1\times F_2. \qquad (1)$$

$$P=\frac{A_{260}-\left(\frac{A_{316.5}}{15.95}\times 23.24\right)}{21.25}\times F_1\times F_2, \qquad (2)$$

where Q = total quinolines, grams,
P = total pyridines, grams,
$A_{316.5}$ = absorbance at 316.5 mμ,
A_{260} = absorbance at 260 mμ,
F_1 = dilution factor for final iso-octane extract, if any ($F_1=1$ in aforementioned procedure),
F_2 = dilution factor for sample ($F_2=7.5$ for distillate and 3.75 for crude-tar base).

The pyridine bases of tar distillate contain a great many pyridine and quinoline derivatives, and the exact composition varies with the type of tar and manner of distillation. To represent all possible compositions an unlimited number of synthetic mixtures would be required. To develop this procedure the best approach was to make representative synthetic mixtures containing the main bases found in tar distillates. The spectra of the synthetic mixtures followed the general pattern that also applied to the spectra of bases extracted from the tar distillates.

In extracting the bases from the distillate, a small amount of acid-soluble phenols and hydrocarbons that also possess an absorption for ultraviolet energy at 250 to 260 mμ is carried over to the acid solution and eventually will interfere with the determination of the bases. This interference can be overcome by washing the acid extract with iso-octane and by holding all phenols in the alkaline solution during the final extraction of the bases with iso-octane. The four synthetic mixtures, which were contaminated purposely with hydrocarbons from tar distillate, demonstrated the removal of the hydrocarbons by washing the acid extract with iso-octane.

The distillate from the bituminous low-temperature tar contained a significant amount of anilines. Therefore, this procedure was expanded to include total anilines by using average absorptivities of 19.7 and 14.2 at 290 and 260 mμ, respectively, based on measure-

TABLE 18.—*Spectrophotometric identification of individual compounds in tar-base distillate fractions*

Compound identified	Fractions	Observed analytical wavelengths [1] (infrared in μ, ultraviolet in mμ)
2,4-Dimethylpyridine	0 to 2	13.80, 12.75, *12.30*, 10.95, 9.70
2,3-Dimethylpyridine	1	13.70, *12.76*, 10.30, 9.80, 8.92
3,5-Dimethylpyridine	1	*14.12*, 11.70, 9.68, 8.78, 8.57
2,4,6-Trimethylpyridine	0 to 3	13.85, *11.90*, 10.80, 9.70, 8.20
4-Isopropylpyridine	2	*12.25*, 13.30, 9.47, 8.19, 7.62
5-Ethyl-2-methylpyridine	2, 3	15.50, 13.65, *12.10*, 9.72, 8.82, 8.05
4-Ethyl-2-methylpyridine	1, 2	13.33, *11.93*, 11.20, 9.41, 8.91, 8.55
2,3,5-Trimethylpyridine	1 to 3	14.00, 13.82, *11.41*, 8.77, 8.03
Aniline	2 to 4	14.53, *13.42*, 11.47, 9.72, 8.52, 7.83
2,6-Dimethyl-4-ethylpyridine	2 to 4	*11.67*, 11.24, 10.03, 9.69, 9.39, 8.17, 7.47
N,N-Dimethylaniline	3	14.52, *13.35*, 10.57, 8.58, 8.40, 8.14
3-Ethyl-4-methylpyridine	2 to 6	13.42, *12.12*, 12.00, 10.84, 10.36, 9.43
2,3,5,6-Tetramethylpyridine	4 to 5	*13.70*, 11.10, 10.00, 9.79, 8.25
2,3-Cyclopentenopyridine	4 to 5	13.85, *12.76*, 9.25, 8.70, 8.23
3-Methylaniline	4 to 8	14.55, *13.00*, 10.78, 8.54, 7.73
2,3,4,6-Tetramethylpyridine	3 to 7	13.57, *11.67*, 10.47, 9.85, 8.13
N-Methyl-2-methylaniline	5, 6	14.02, *13.42*, 11.47, 9.72, 8.52, 7.83, 7.69
3,4-Diethylpyridine (?) [2]	7 to 9	15.32, *12.19*, 11.69, 10.85, 10.36, 9.43, 8.37
2,5-Dimethylaniline	8, 9	*12.59*, 11.76, 10.05, 7.80, 7.72, 7.65
2-Ethylaniline	5 to 7	*13.45*, 10.82, 9.45, 8.75, 8.66, 7.85, 7.22
2,6-Dimethylaniline	7 to 12	13.72, *13.22*, 9.17, 8.13, 7.86
3,5-Dimethylaniline	7 to 11	14.60, *12.11*, 9.70, 8.51, 7.52
Quinoline	7 to 12	13.65, 12.76, *12.46*, 10.55, 9.69, 8.95, 7.61
2-Methylquinoline	10 to 16	13.46, 12.80, *12.25*, 10.55, 10.32, 8.96, 8.77, 8.19
8-Methylquinoline	11 to 13	14.46, 13.31, *12.69*, 12.23, 10.26, 9.34, 8.86, 7.61
2,8-Dimethylquinoline	11 to 17	*13.21*, 12.66, *12.08*, 8.83, 8.17, 7.64
7-Methylquinoline	15 to 18	13.09, 12.78, 12.50, *12.07*, 11.31, 10.25, 9.66, 8.73
6-Methylquinoline	15 to 17	13.16, 12.60, *12.06*, 10.26, 9.67, 8.94, 7.55
4-Methylquinoline	15 to 23	14.22, *13.25*, 11.95, 11.75, 10.52, 9.81, 8.80, 8.05
2,7-Dimethylquinoline	15 to 21	12.88, *11.97*, 11.47, 9.74, 8.77, 8.20, 7.68
2,4-Dimethylquinoline	15 to 25	15.47, 13.45, *13.22*, 11.67, 10.52, 9.76, 8.39, 7.47
2,6-Dimethylquinoline	16 to 24	15.41, 12.39, *12.08*, 11.41, 8.95, 8.19, 7.61
2-Phenylpyridine	18 to 22	14.35, *13.35*, 12.50, 10.80, 10.07, 9.80, 9.30, 8.72
2,4,8-Trimethylquinoline	24 to 30	13.96, *13.16*, 11.62, 9.70, 8.60, 8.31
2,6,8-Trimethylquinoline	19 to 26	*12.68*, *11.67*, 9.66, 8.30, 7.47
4,6-Dimethylquinoline (?)	24 to 27	12.24, *11.92*, 11.48, 8.79, 8.04
4-Phenylpyridine	22 to 25	14.50, *13.30*, 12.07, 10.90, 9.30, 8.17, 7.64
2-Methyl-6-phenylpyridine (?)	26, 27	14.45, 13.95, *13.15*, 10.35, 9.67, 9.25
2,4,7-Trimethylquinoline	25 to 30	15.45, 15.06, 12.90, *12.59*, 11.65, 11.31, 10.87, 9.71, 8.79, 8.36
2,4,6-Trimethylquinoline	26 to 32	15.40, 12.92, *12.15*, 11.70, 11.45, 9.70, 8.85
3,4-Dimethylquinoline (?)	29 to 32	14.20, 13.25, 11.22 (or 11.35)
2-Naphthylamine	30 to 34	*13.55*, 12.42, *11.97*, 9.82, 8.90, 8.75, 8.47, 8.18, 7.78
N-Benzyl-2-methylaniline	30 to 32	14.40, 14.05, 13.85, *13.45*, 9.52, 8.87
N-Benzyl-4-methylaniline	34, 35	*14.40*, 13.55, 12.44, 9.74, 8.91, 8.03, 7.95, 7.72
Benzo[h]quinoline (7,8-Benzoquinoline)	38	13.92, 13.46, 12.44, *12.05*, 8.54 (330, 315, 295, 264.5)
Acridine (2,3-Benzoquinoline)	34, 35	*13.61*, 12.72, 11.75, 11.05, 10.47, 8.78 (360, 339, 331, 323, 310)
Phenanthridine (3,4-Benzoquinoline)	34 to 37	13.94, *13.41*, 13.06, 11.28, 10.46, 9.65, 8.08 (356, 343.5, 336, 328, 313)
Benzo[f]quinoline (5,6-Benzoquinoline)	34 to 38	14.17, *13.37*, 12.25, 11.92, 11.49, 9.13, 8.80, 8.09, 7.69 (345, 331, 315, 293.5)
2,4-Dimethylbenzo[h]quinoline (?)	37, 38	(347, 330, 316, 297, 287)
2,4-Dimethylbenzo[g]quinoline (?)	34 to 38	(381, 357, 347, 338, 331)
2,4-Dimethylbenzo[f]quinoline (?)	35	(347, 330, 295, 268)

[1] Major absorption band in italics; ultraviolet bands in parentheses.
[2] (?) indicates uncertainty as to which isomer is present.

ments of 22 individual anilines. Also these bituminous-tar bases contained a large proportion of polymethylquinolines. For this reason eight polymethylquinolines, synthesized in this laboratory, were included in the determination of the average absorptivity. The average absorptivities that may be employed for a tar distillate or a total tar-base mixture are as follows: Total quinolines (based on 18 compounds), 14.4 at 316.5 mμ, 17.5 at 290 mμ, and 23.3 at 260 mμ; total anilines (based on 22 compounds), 0 at 316.5 mμ, 19.7 at 290 mμ, and 14.2 at 260 mμ; total pyridines (based on 13 compounds), 0 at 316.5 mμ, 0 at 290 mμ, and 21.3 at 260 mμ. When applied to the tar-base mixture isolated from the bituminous low-temperature tar, this gave 49 weight-percent total quinolines, 16 weight-percent total anilines, and 35 weight-percent total pyridines.

SPECTROPHOTOMETRIC ANALYSIS OF TAR-BASE DISTILLATE FRACTIONS

Infrared spectra of the tar-base distillate fractions shown in table 9 were obtained with the Model 21 Perkin-Elmer infrared spectrophotometer and ultraviolet spectra with the Beckman DK–2 spectrophotometer. For the infrared spectra 1.0 to 3.5 weight-percent sample in carbon disulfide was used in a 0.5-mm. sodium chloride cell, and for the ultraviolet spectra 0.015 to 0.035 g./l. in iso-octane was used in a 10-mm. quartz cell.

These spectra were compared with those of individual compounds that conceivably could be present in the various fractions on the basis of boiling point. For this purpose the tar-base

boiling-point index, given in the appendix of this report, was found to be very useful. The compounds found in the distillate fractions are listed in table 18, which also gives the wavelengths of absorption bands, by means of which the compounds were identified. The distillate fraction or fractions involving the wavelengths for each compound are listed in table 18. By referring to table 9, it is apparent which identifying wavelengths are involved in the analysis of any specific fraction.

It was possible in almost all instances to make at least an approximation of the quantity of each compound in each fraction, and in many instances it was possible to employ conventional infrared and/or ultraviolet quantitative analyses (*59*). In the latter situation, when both methods could be employed, the quantitative results compared satisfactorily with each other.

For the higher boiling fractions containing quinolines, the ultraviolet spectrophotometric method for total pyridines and total quinolines was used; modification for including total anilines was employed. The weight-percentages of total quinolines, total anilines, and total pyridines for each tar-base distillate fraction were determined and are presented in figure 7. The wavelengths used for quinolines were 313 mμ for fractions 7 to 10, 316.5 mμ for fractions 11 to 26, 319 mμ for fractions 27 to 28, 321 mμ for fractions 29 to 32, and 329.5 mμ for fractions 34 to 38. The wavelengths used for anilines and pyridines were 290 mμ and 260 mμ, respectively, for all fractions. The average absorptivities, however, varied slightly from one fraction to the other, reflecting the information on individual compounds identified mainly through infrared analysis.

Possible methods of correlating the infrared spectra of quinolines with their structures, such as those discussed in this report, were also employed to obtain some preliminary ideas as to which quinolines might be present.

It is not feasible to discuss the analytical details of each of the approximately 75 infrared and ultraviolet spectra of tar-base fractions involved in this work; however, two such spectra were chosen and are presented in figures 8 and 9. Figure 8 shows the infrared spectrum of fraction 13, which contained three different alkyl quinolines as significant components. Some of the smaller absorption bands are not too evident after the size of the spectrum is reduced for reproduction, but the more prominent bands are indicated. Each of the 51 compounds identified usually had a single fraction that was best for definite spectral identification. For example, 2-methylquinoline was readily identified in the spectrum shown in figure 8. Once the characteristic absorption bands were clearly identified for a given compound, they could usually be followed in the spectra of the adjacent fractions, even when they were too small to have been noticed in the original inspection. The three high-intensity absorption bands marked A (B,C), B (A,C), and C (A,B) in figure 8 were those used for quantitative analysis of the three different alkyl quinolines in fraction 13. The absorption bands marked A,X could not be used for this quantitative analysis, because a small amount of a fourth component was present, which also absorbed at these two wavelengths. This is cited as an example of the fact that sometimes there were high-intensity absorption bands that could not be used for quantitative analysis.

Figure 9 shows the ultraviolet spectrum of fraction 35. It can be seen that identification of the components in a fairly complex mixture, such as fraction 35, would have been rather difficult if restricted solely to the ultraviolet spectum. Although at least seven well-defined absorption peaks or shoulders can be picked out, this is not a large enough number for really positive identification of all of the four or five components present in significant amounts. However, components A, B, and C were all readily identified by means of the infrared spectrum of this same fraction, as well as adjacent fractions. Having this information on the composition of the fraction, the ultraviolet absorption due to components A, B, and C was easily determined. This left about three distinct features of the ultraviolet spectrum that appeared to be due to alkylated benzoquinolines, on the basis of the ultraviolet spectra of the 2,4-dimethyl derivatives of benzo[f], [g], and [h] quinoline,[6] all of which were available from the literature. Also the last distillate fraction or two contained material boiling at about 355° C. or a little higher. This could have included alkylated benzoquinolines such as 2,4-dimethylbenzo[h]quinoline, boiling point 355° C. Although the spectra of other methyl derivatives of benzoquinolines were not available, it was assumed that, in general, it would be impossible to distinguish between isomers of the same parent benzoquinoline from the ultraviolet spectra alone. Therefore there may be some doubt as to the location of the methyl groups in these three compounds.

[6] The *Chemical Abstracts* system of structural formulas assigns the name 1,3-dimethylbenzo[f]quinoline to the structure that is named 2,4-dimethylbenzo[f]quinoline by many investigators.

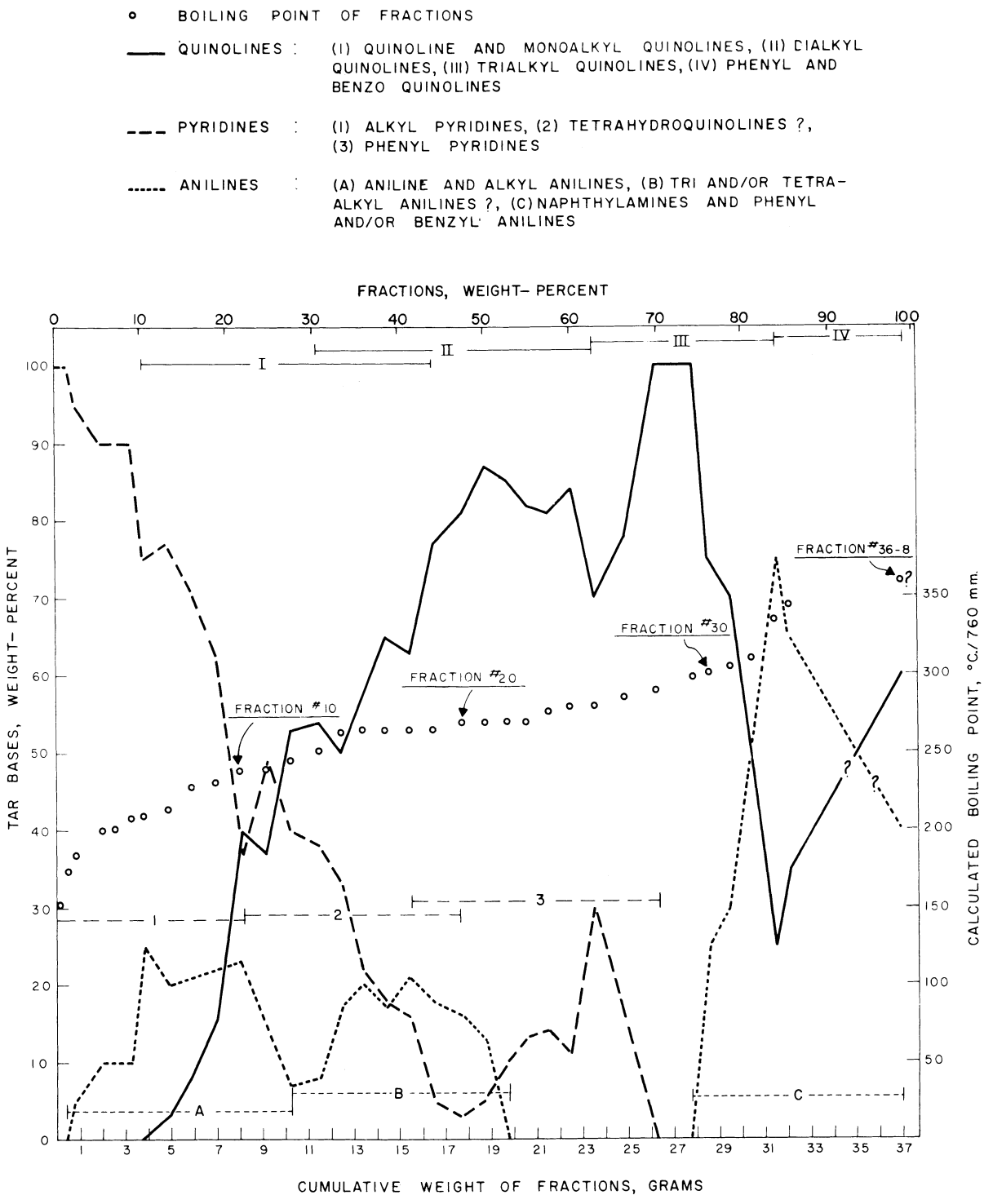


FIGURE 7.—Distribution of Pyridines, Quinolines, and Anilines in Distillable Tar Bases.

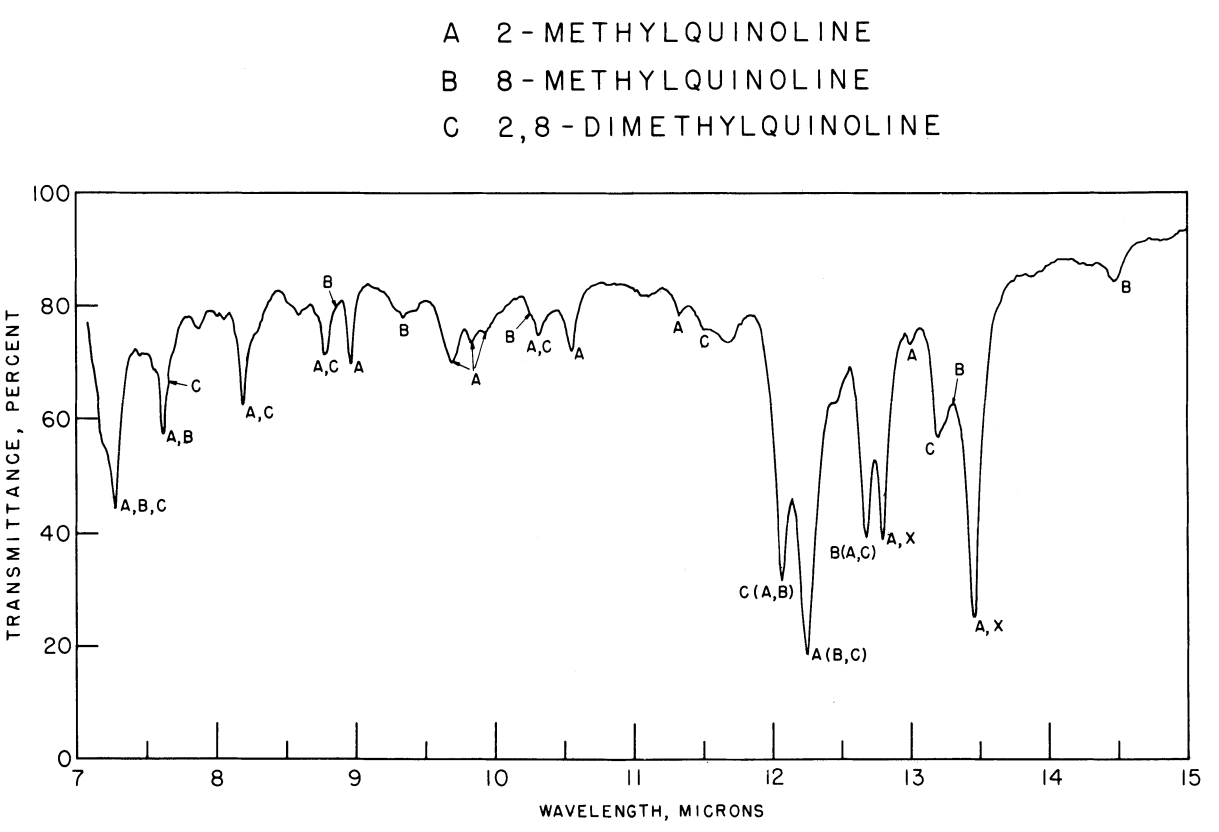


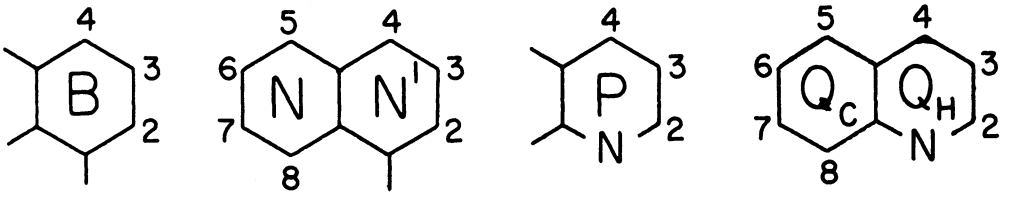
FIGURE 8.—Infrared Spectrum of Tar-Base Fraction 13.

INFRARED SPECTRAL-STRUCTURAL CORRELATIONS OF QUINOLINES

It was desired to obtain spectral-structural correlations of quinolines that might aid in the characterization of high-boiling tar-base distillate fractions consisting of polymethylquinolines (*61*). There are well over 100 isomeric possibilities, with very few published spectra and no practical possibility of synthesizing all of the compounds. Nine quinolines were synthesized to supplement the few spectra available from the literature.

The occurrence of strong absorption bands, originating in the out-of-plane deformation vibrations of hydrogens on aromatic rings, in the approximate region between 900 and 700 $cm.^{-1}$, is a well-established phenomenon that has been thoroughly reviewed by Bellamy (*9*). He points out (*9*, p. 236) that, although he could locate infrared spectra of only six quinolines in the literature, these appeared to fall in line very well with the expected absorption pattern for aromatics in general. Apparently no other reference to quinolines exists except a Japanese publication by Shindo and Tamura (*104*). For the correlations with the general aromatic pattern they considered the carbocyclic and heterocyclic rings separately, in the same manner as Bellamy; that is, the possibility of bands arising from vibrational interaction of adjacent hydrogens on the carbocyclic and heterocyclic rings was not discussed. They go farther than Bellamy in pointing out that, when bands originating from the heterocyclic ring are compared with the bands of a pyridine with the same hydrogen structure, the quinoline band is "always" at slightly higher frequency. This is, of course, due to the fact that a benzene ring has been fused to the pyridine ring in the 2,3-position, replacing two adjacent alkyl substituents. The same phenomenon can be observed in going from benzenes to naphthalenoid benzene rings with the same hydrogen structures; that is, replacing two adjacent alkyl substituents with a fused benzene ring shifts the frequency to a

greater value. When benzenes (B), naphthalenoid benzene rings (N′), pyridines (P), and quinoline heterocyclic rings (Q_H), all of the same hydrogen structures, are considered it is observed that the frequency increase in going from benzenes to naphthalenes is about the same as the frequency increase in going from pyridines to quinolines. In addition, when naphthalenoid benzene rings (N) and quinoline carbocyclic rings (Q_C) with the same hydrogen structures are considered, the frequencies are about the same. These relationships appear reasonable and are best evaluated by examination of the pertinent frequencies. It was therefore proposed that these relationships, as expressed in the following two equations, were worth studying as a possible means of better understanding the similarities that may exist among benzenes, naphthalenes, pyridines, and quinolines.



$$\tilde{\nu}_{Q_C} \cong \tilde{\nu}_N \,, \qquad (1)$$

with hydrogens in the same positions in Q_C and N.

$$\tilde{\nu}_{Q_H} \cong \tilde{\nu}_P + \left(\tilde{\nu}_{N'} - \tilde{\nu}_B\right), \qquad (2)$$

with hydrogens in the same positions in Q_H, P, N′ and B.

To examine these equations it was necessary to collect as many spectra of benzenes, naphthalenes, pyridines, and quinolines as possible. The American Petroleum Institute (API) series of hydrocarbon spectra (*2*) was the main source for spectra of benzenes and naphthalenes. Mosby (*79*) has published the spectra of nine different polymethylnaphthalenes. The infrared spectra of various alkylpyridines and alkylquinolines, and their sources, are presented in the appendix of this report.

Using the above-mentioned spectra, observed values for the frequencies of B, N, N′, P, Q_C, and Q_H were obtained, and these are all presented in table 19 so that they may be readily available for the study of possible relationships.[7]

In most instances assignment of the bands to a specific number of hydrogens was straightforward. In these, only a few major bands occur in the 900- to 700-cm.$^{-1}$ region, as can be seen in the infrared spectra of the quinolines presented in the appendix of this report. Bellamy's ranges for the different numbers of hydrogens in aromatic compounds were used as a guide in making these assignments. In a few instances there were bands of approximately equal probability for a certain assignment; and in these, whichever major band agreed better with the various pertinent correlations was chosen. A few errors may have been made in band assignment.

In some instances infrared spectra were available for the naphthalenes that correspond exactly in structure to the quinolines. In

[7] Two tables, (1) the frequencies and intensities of all bands in the 900 to 700 cm.$^{-1}$ region for all of these compounds, and (2) the compounds used to obtain each observed frequency listed in table 19, have been deposited as Document 5711, with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C.

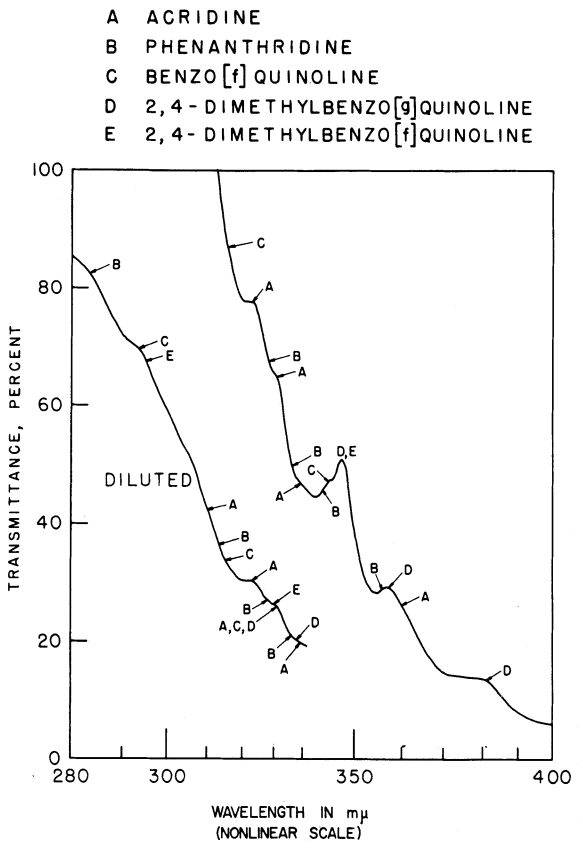


FIGURE 9.—Ultraviolet Spectrum of Tar-Base Fraction 35.

others, it was necessary to use one naphthalene for the N ring and another naphthalene for the N′ ring. In two instances for the N′ ring the required naphthalene spectra could not be located; namely, for 1,2,3- and 1,2,4-trimethylnaphthalene. In these, satisfactory estimates of the two missing single hydrogen frequencies were obtained as follows: A number of naphthalenes were chosen approximating one of the missing naphthalenes in structure and having single hydrogens. The benzenes having the same structures as the naphthalene rings with the single hydrogens were then located, and the frequency differences were obtained for each pair, as indicated by the term in parentheses in equation 2. The average difference was obtained and added to the single hydrogen frequency for the benzene, or benzenes, with the same hydrogen structure as the missing N′ ring.

Using equations 1 and 2, calculated values for the frequencies of Q_C and Q_H were obtained, and these are recorded in table 19 so that ready comparisons with observed values can be made. With very few exceptions, the following relationships can be seen to hold for the observed frequencies when the identical hydrogen structures are considered: $Q_H > P > B < N'$. Two of these relationships have been discussed previously; the fact that the pyridine frequencies are greater than the frequencies of benzenes with the same hydrogen structures has been mentioned, but not elaborated on, by Cannon and Sutherland (*21*).

When the observed Q_C frequencies are compared with the calculated Q_C frequencies and the observed Q_H frequencies compared with the calculated Q_H frequencies, for the identical hydrogen structures (for the same individual quinoline), they agree well in most instances. In 27 out of 50 instances the above-mentioned comparisons showed differences ranging from 0 to 5 $cm.^{-1}$, which is very good agreement. In 16 out of 50 instances the differences ranged from 6 to 10 $cm.^{-1}$, which should be considered fair agreement; in 3 instances the differences ranged from 11 to 15 $cm.^{-1}$, which is poor agreement; and in 4 instances the differences ranged from 16 to 22 $cm.^{-1}$, which is very poor agreement. Therefore, there is a significant number of instances in which the relationships proposed for study are not in agreement with the observed frequencies. This could be due in part to improper band assignments or inaccurate spectra, but probably in other instances these discrepancies indicate that a different relationship exists than is shown in the equations. This may imply that all these relationships are more complex than can be visualized at the present time.

When the carbocyclic and heterocyclic rings of a quinoline each have the same number of adjacent hydrogens, two separate absorption bands are calculated from the equations and apparently are also always observed. In general, the frequency of the heterocyclic band is greater than that of the carbocyclic band, for the same number of adjacent hydrogens. This is what would be expected from the fact that the pyridine frequencies are greater than the benzene frequencies for the identical hydrogen structures.

USE OF SPECTRAL-STRUCTURAL CORRELATIONS FOR TAR-BASE DISTILLATE FRACTIONS

In several spectra of tar-base distillate fractions there were some absorption bands that could not be accounted for with the available spectra of individual compounds. Spectral-structural correlations were employed to advantage in demonstrating the probable presence of several tar bases.

Fractions 7 and 8, boiling 210°–228° C., had absorption bands at 12.19 microns in the range for the out-of-plane deformation vibration of

TABLE 19.—*Infrared absorption bands for out-of-plane hydrogen deformation vibrations of methylquinolines*

Methylquinoline	Hydrogen		Frequencies, cm.$^{-1}$							
	No.	Position	B	N	N′	P	Q_C		Q_H	
							Observed	Calculated	Observed	Calculated
2-	2	3, 4	804		808	817			817	821
	4	5, 6, 7, 8		743			742	743		
3-	1	2 & 4	849		861	876			888	888
	4	5, 6, 7, 8		746			752	746		
4-	2	2, 3	804		824	815			836	835
	4	5, 6, 7, 8		754			754	754		
5-	3	2, 3, 4	766		784	784			799	802
	3	6, 7, 8		810			813	810		
6-	3	2, 3, 4	766		784	784			794	802
	1	5		870			874	870		
	2	7, 8		816			830	816		
7-	3	2, 3, 4	766		775	784			799	793
	1	8		870			885	870		
	2	5, 6		824			828	824		
8-	3	2, 3, 4	766		765	784			788	783
	3	5, 6, 7		815			818	815		
2,3-Di-	1	4	862		871	893			898	902
	4	5, 6, 7, 8		739			749	739		
2,4-Di-	1	3	862		871	857			856	866
	4	5, 6, 7, 8		739			743	739		
2,6-Di-	2	3, 4	804		808	817			828	821
	1	5		883			876	883		
	2	7, 8		810			807	810		
2,7-Di-	2	3, 4	804		808	817			835	821
	1	8		883			877	883		
	2	5, 6		792			770	792		
2,8-Di-	2	3, 4	804		808	817			829	821
	3	5, 6, 7		791			791	791		
2,3,8-Tri-	1	4	862		871	893			907	902
	3	5, 6, 7		769			764	769		
2,4,6-Tri-	1	3	862		882	857			875	877
	1	5		853			857	853		
	2	7, 8		810			826	810		
2,4,7-Tri-	1	3	862		882	857			885	877
	1	8		861			860	861		
	2	5, 6		810			808	810		
2,4,8-Tri-	1	3	862		871	857			862	866
	3	5, 6, 7		752			761	752		
2,5,7-Tri-	2	3, 4	804		808	817			819	821
	1	6 & 8		861			858	861		
2,5,8-Tri-	2	3, 4	804		808	817			818	821
	2	6, 7		824			830	824		
2,6,8-Tri-	2	3, 4	804		808	817			829	821
	1	5 & 7		861			859	861		
2,7,8-Tri-	2	3, 4	804		808	817			838	821
	2	5, 6		808			791	808		
2,4,5,8-Tetra-	1	3	862		871	857			857	866
	2	6, 7		824			818	824		
2,4,7,8-Tetra-	1	3	862		871	857			860	866
	2	5, 6		808			815	808		

two adjacent hydrogens on an aromatic ring and 11.69 microns for a single hydrogen. This suggested the presence of a 2,4-, 2,5-, or 3,4-dialkylpyridine. These two bands and bands at 15.32, 10.85, 10.36, 9.43, and 8.37 microns were similar to those of 3-ethyl-4-methylpyridine, boiling point 196° C., found in fractions 2 to 6. From this it appeared probable that these bands were due to the presence of 3,4-diethylpyridine, boiling point 212° C.

Fraction 26, boiling point 280° C., had a band at 13.95 microns for five adjacent hydrogens, that is, a phenyl group, and 13.15 microns for three adjacent hydrogens. This immediately suggested a pyridine with a phenyl group and an alkyl group in the 2,3- or 2,6-positions. The only such compound that boils low enough is the diortho-substituted isomer, 2-methyl-6-phenylpyridine, boiling point 281° C. The strong likelihood of its presence was substantiated by bands at 10.35, 9.67, and 9.25 microns for 1,2,3-substitution in a benzene ring (the pyridine N being one of the substituents, of course), and by a band at 14.45 microns for monosubstitution in a benzene ring (the phenyl group).

Fractions 29 to 31, boiling 290°–305° C., had a strong absorption band at 13.25 microns in the range for four adjacent hydrogens, which can be observed in the spectra of these specific lower boiling quinolines: 2-methyl-(13.42 microns), 3-methyl-(13.32 microns), 4-methyl-(13.25 microns), 2,3-dimethyl-(13.42 microns), and 2,4-dimethyl-(13.21 microns). These fractions likewise had a medium band at 11.1 to 11.3 microns in the range for a single hydrogen, which can be observed in the spectra of two specific lower boiling quinolines, 3-methyl-(11.25 microns) and 2,3-dimethyl-(11.14 microns). These two bands in fractions 29 to 31 thus strongly indicated the presence of 3,4-dimethylquinoline, boiling point 295° C.

GAS-LIQUID CHROMATOGRAPHY OF TAR ACIDS RECOVERED FROM DRY-ICE TRAP

To complement as well as check the results obtained by distillation and infrared analysis, a completely independent method of separation and analysis was chosen for the tar acids recovered from the dry-ice trap. This was a gas-liquid chromatographic technique for phenols (*56*), which had been developed early in 1956. A Perkin-Elmer model 154 chromatographic apparatus, shown in operation in figure 10, was used for gas-liquid chromatography of tar acids.

For this investigation a 12-foot column of ¼-inch tubing packed with Johns-Manville C–22 firebrick, 30–60 mesh, containing 31 weight-percent di-n-octyl phthalate was used at 160° C., with a carrier gasflow rate of 150 cc. helium per minute (15 p.s.i.g. inlet, outlet at 1 atm.), and a 250-μl. sample (*57*). The efficiency of this column was determined using a charge of o-cresol and the equation given by Wiebe (*115*):

$$p \cong 2\left(\frac{V_m}{V_m - V_e}\right)^2,$$

where p = number of theoretical plates,
V_m = volume of effluent that has passed through the column when the zone maximum appears in the effluent,
V_e = volume of effluent that has passed through the column when a point on the elution curve has been reached where the solute concentration is $1/e^{th}$ of the maximum ($e = 2.71828$).

A value of 966 theoretical plates was obtained.

The results of fractionating the tar phenols are shown in figure 11, where there are eight obvious concentration maxima. Traps, consisting of a short length of 12-mm.-i.d. glass tubing fitted with a rubber serum bottle cap and syringe needle, were filled with about 1 ml. of spectrograde cyclohexane and used in an attempt to isolate the components producing the major peaks in the elution curve. Infrared

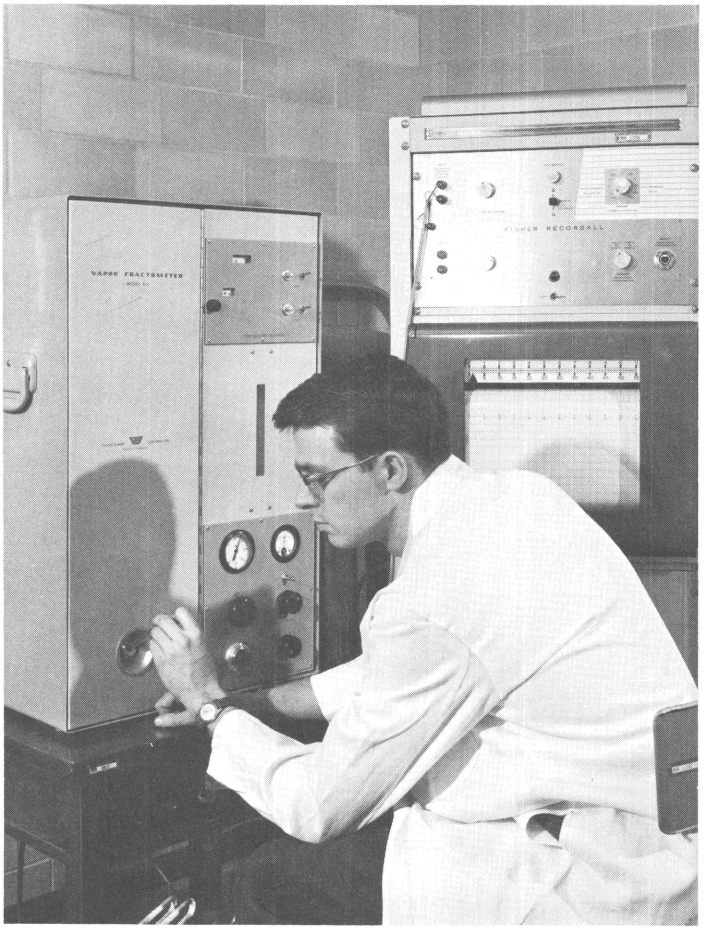


FIGURE 10.—Separation and Analysis of Low-Boiling Tar Acids Using Gas-Liquid Chromatography.

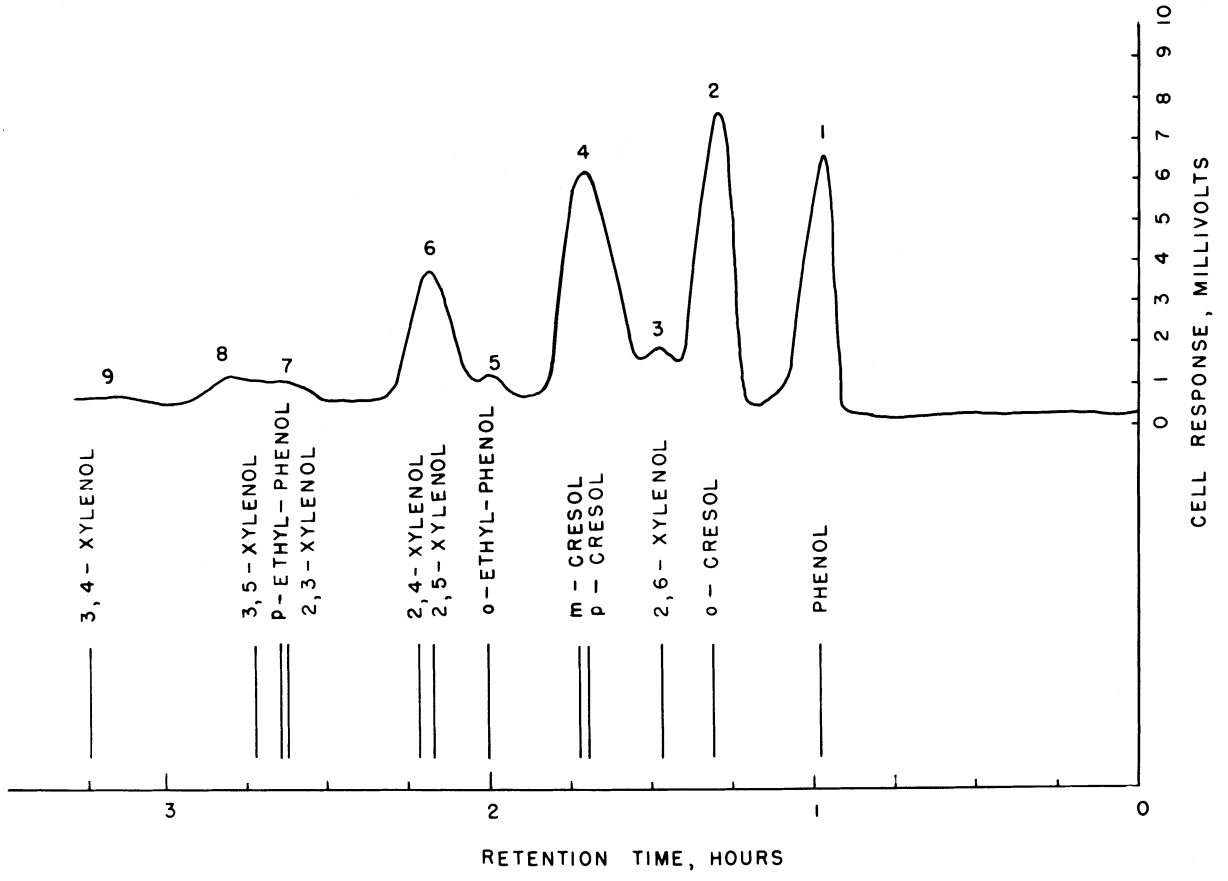


FIGURE 11.—Gas-Liquid Chromatography of Tar Acids Recovered From Dry-Ice Trap and Retention Times of Individual Pure Phenols.

analysis of the solutions corresponding to peaks 1 and 2 showed beyond any doubt that the compounds responsible for these peaks were phenol and o-cresol, respectively. However, contamination of subsequent solutions with residual phenol and o-cresol in the collection system made positive identification of the components responsible for other peaks impossible with this type of collecting device. Further identification was possible by comparing the relative retention times of the various peaks with the relative retention times of individual pure low-boiling phenols under identical operating conditions, as shown in table 20. The retention times of the individual pure phenols are indicated in the lower portion of figure 11.

The areas under each of the peaks in figure 11 were obtained by a planimeter and the weight-percentages of phenols were calculated from these areas and the total area. The thermal conductivities of the components are assumed equal, being homologs; therefore, areas under the recorded curves are directly proportional to the weight-percent of the components (*19*). Synthetic blends showed that, for the phenols involved, the areas were closely proportional to the grams of phenols but not to the moles of phenols. These values are given in table 21, which also includes the weight-percents calculated from the infrared data given in table 11.

TABLE 20.—*Comparison of relative retention times of tar acids recovered from dry-ice trap with those of pure compounds*

Peak No.	Retention time relative to peak 2	Compound	Retention time relative to o-cresol
1	0.75	Phenol	0.79
2	1.00	o-Cresol	1.00
3	1.13	2,6-Xylenol	1.12
4	1.31	m-Cresol	1.29
		p-Cresol	
5	1.53	o-Ethylphenol	1.53
6	1.67	2,5-Xylenol	1.66
		2,4-Xylenol	1.70
7	2.01	2,3-Xylenol	1.98
		p-Ethylphenol	2.02
8	2.16	3,5-Xylenol	2.08
9	2.42	3,4-Xylenol	2.47

Figure 11 demonstrates that by means of gas-liquid chromatography alone a low-boiling mixture of phenols with as many as a dozen components can be fairly well characterized,

both qualitatively and quantitatively. There can be no question about the identity of a component for those retention times for which calibrations have been made on all theoretically possible phenols and where the peaks for individual phenols are essentially isolated in time. Examples of this would be peaks 1, 2, 3, and 5. The quantitative analysis is always obtainable with acceptable accuracy from the areas under these peaks. In general the gas-liquid chromatographic analysis is more simple and direct. However, it is limited in scope by the difficulty of resolving certain phenols that have very similar partition coefficients.

In table 21 the agreement between weight-percentages of phenols by infrared analysis and gas-liquid chromatographic analysis is fairly good. In the case of two compounds, 2,6-xylenol and o-ethylphenol, only an estimate of the quantity could be made by infrared analysis. In the gas-liquid chromatographic analysis, these two compounds gave two distinct peaks whose areas could be obtained with fair accuracy

TABLE 21.—*Comparison of infrared and gas-liquid chromatographic analysis of tar acids recovered from dry-ice trap*

Compound	Weight-percent	
	IR	GLC
Phenol	22.5	21
o-Cresol	25	26
m-Cresol	13 } 21	} 26
p-Cresol	8 }	
2,4-Xylenol	13 } 16.5	} 13
2,5-Xylenol	3.5 }	
2,6-Xylenol	>2	5
3,5-Xylenol	3	3
o-Ethylphenol	~1	2
m-Ethylphenol	1.5 } 4.5	} 3
p-Ethylphenol	2 }	
2,3-Xylenol	1	
3,4-Xylenol	~.8	<1
	~96	~99

GAS-LIQUID CHROMATOGRAPHY OF LOW-BOILING TAR ACIDS RECOVERED FROM MAIN TAR DISTILLATE

The mixture of tar acids boiling up to 234° C., that is, including 3-ethyl-5-methylphenol and 2,3,5-trimethylphenol, was fractionated in the gas-liquid chromatographic apparatus (*58*). For this separation the total mixture of tar acids was subjected to a preliminary vacuum distillation to remove most of the material boiling above approximately 240° C., as these phenols, starting with the indanols, had excessively long retention times, which flattened their peaks sufficiently to make them useless. A 4-meter column of ¼-inch copper tubing packed with Johns-Manville C–22 firebrick, 30–60 mesh, containing 34.7 weight-percent di-n-octyl phthalate was used at 160° C., with a carrier gasflow rate of 127 cc. helium per minute, measured at approximately 26° C. and 1 atm., the column inlet pressure being 15 p.s.i.g. The sample size was approximately 250 μl. The results are shown in figure 12. Thirteen peaks, or shoulders on peaks, were obvious, indicating a minimum of 13 phenols. Retention times of the substances producing these peaks, relative to peak 1, were determined and compared with the relative retention times of individual pure phenols under identical operating conditions. This comparison is shown in table 22.

A collecting system, based on one previously described (*92*), was used to advantage in identifying the components in peaks that were incompletely resolved. This system consisted of a short length of electrically heated ⅛-inch stainless steel tubing leading from the thermal conductivity cell and connected to an electrically heated stainless steel sample block into which

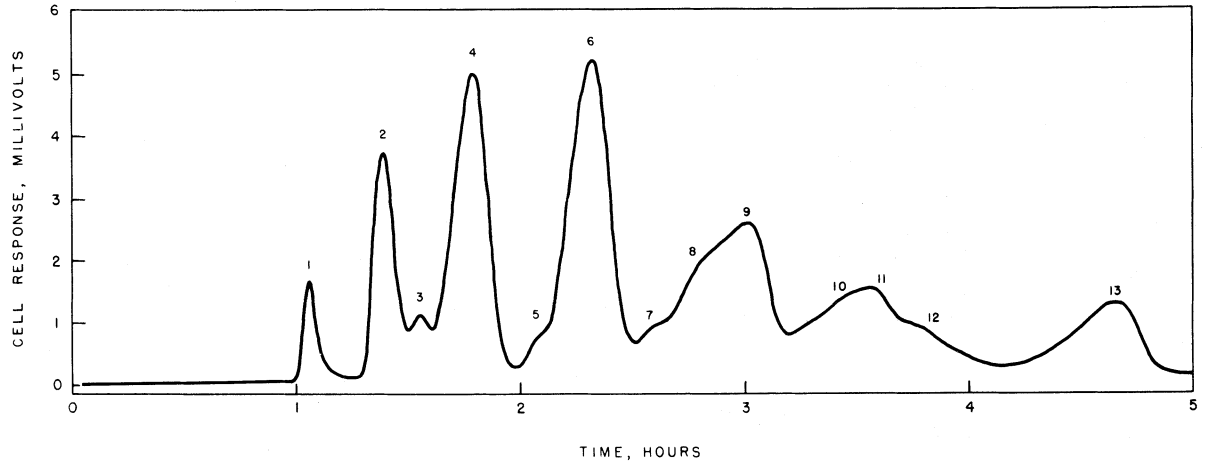


FIGURE 12.—Chromatogram of Tar Acids From Main Tar Distillate.

569705 O—61——3

TABLE 22.—*Comparison of relative retention times of tar acids from the main tar distillate with those of pure compounds*

Peak No.	Retention time relative to peak 1	Compound	Retention time relative to phenol
1	1.00	Phenol	1.00
2	1.37	o-Cresol	1.32
3	1.48	2,6-Xylenol	1.49
4	1.70	m-Cresol	1.72
		p-Cresol	1.72
5	2.00	o-Ethylphenol	2.04
6	2.20	2,5-Xylenol	2.21
		2,4-Xylenol	2.27
7	2.48	2,4,6-Trimethylphenol	2.45
8	2.70	2,3-Xylenol	2.64
		p-Ethylphenol	2.69
9	2.86	3,5-Xylenol	2.77
		2-n-Propylphenol	3.03
10	3.28	3,4-Xylenol	3.29
11	3.38	4-Ethyl-2-methylphenol	3.46
12	3.59	Unknown [1]	
13	4.42	2,3,5-Trimethylphenol	4.52
		3-Ethyl-5-methylphenol	4.60

[1] Possibly 5-ethyl-2-methlyphenol.

were screwed eight stainless steel capillaries. These capillaries were about 3 inches long and were threaded at one end to fit an infrared microcell. In operation the capillaries were surrounded by powdered dry ice, with cork insulation placed between the heated block and the dry ice container. The capillaries were plugged with round-type toothpicks. When collection of a portion of a peak was desired, the toothpick was removed from a capillary for the proper time interval. Figure 13 shows this collecting system. For analysis, the capillary was screwed into the microcell, and a drop or two of carbon disulfide was introduced at the top and forced down with nitrogen. Figure 14 shows a capillary in place in the microcell and solvent being introduced with a syringe and needle. As little as 0.5 mg. of sample per capillary was sufficient for infrared analysis. In addition to collecting samples for infrared analysis, it was found that, by collecting about 5 mg., good molecular-weight determinations or melting-point determinations could also be made, thus extending the usefulness of this device. For example, during the determination of the retention times of the individual pure phenols, samples of 2,4-xylenol and also 2,6-xylenol were collected. The sample of 2,4-xylenol was washed into the microboiler of an ebullioscopic molecular-weight apparatus by suspending the capillary in the refluxing benzene.

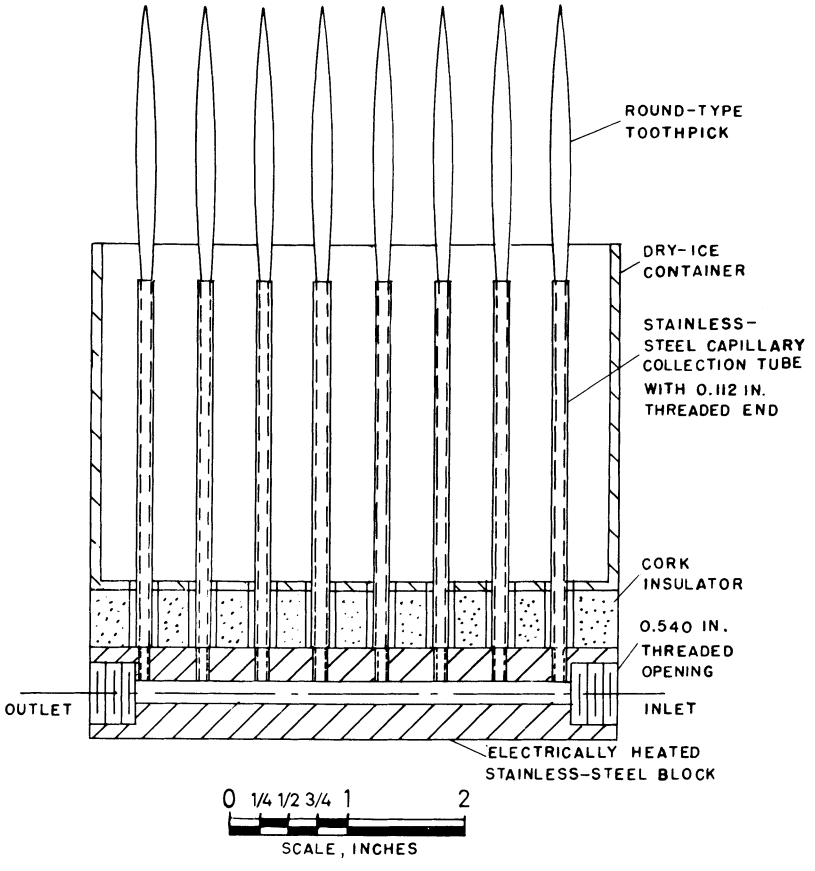


FIGURE 13.—Fraction Collector Used in Gas-Liquid Chromatography.

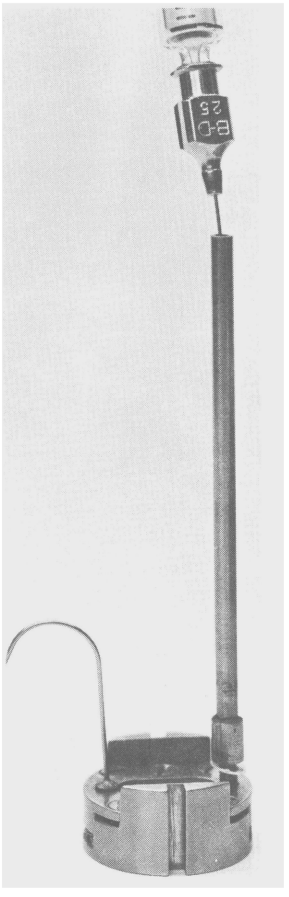


FIGURE 14.—Fraction Collection Tube and Micro-infrared Cell.

The weight of sample removed by washing was determined to be 5.637 mg., and the molecular weight was subsequently determined to be 119, compared with the theoretical value of 122. The capillary containing the sample of 2,6-xylenol was scraped with a fine wire to remove a small amount of white powder, which was examined in a melting-point apparatus having a low-power microscope. A sharp melting point of 45° C. was obtained, the same as the literature value (*54*).

By using the collecting system, followed by infrared analysis, identities of the phenols producing the various peaks were confirmed in nearly all instances. In particular, all phenols listed in table 22, except 2-n-propylphenol, were shown beyond any doubt to be present in the same peaks indicated by the retention times of the individual pure phenols. This indicates that retention times of pure compounds could be used as the sole means of identification of the materials producing peaks, without introducing widespread errors. The material producing peak 8 appeared to contain m-ethylphenol in addition to the other phenols shown in table 22. The presence of 2-n-propylphenol could not be definitely established, although the spectral evidence was fairly good. This consisted of its orthoband at 13.33 μ in conjunction with the required boiling point. The unknown phenol was believed to be 5-ethyl-2-methylphenol, but an authentic sample was not available for confirmation. The material producing the first portion of peak 13 contained 2,3,5-trimethylphenol, and the last portion contained 3-ethyl-5-methylphenol—the peak having a gradient composition of these two components. This phenomenon of a gradient composition was observed for other peaks containing two or more components. It appeared unlikely that any of the peaks were due to azeotropic mixtures.

The areas under the peaks in figure 12 were obtained by means of a planimeter and the weight-percents of phenols were calculated from these areas. Examination of synthetic blends showed that, for the phenols involved in this work, the areas were closely proportional to the grams of phenols but not to the moles of phenols. Synthetic blends of the available pure phenols were also examined to test quantitative recoveries using peak areas and to test the sample-collecting system. Determination of the areas under ill-defined peaks, such as 5, was aided by sketching in peak 6 as it would probably look if it were an isolated peak, thus establishing a reasonable baseline for peak 5. The weight-percents of the phenols, on the basis of the total tar acids obtained from the main tar distillate, are presented in the right-hand column of table 23. Table 23 also contains, for the purpose of comparison, the weight-percents of these phenols obtained from

TABLE 23.—*Comparison of infrared and gas-liquid chromatographic analysis of tar acids from main tar distillate*

Compound	Weight-percent in total tar acids	
	By IR	By GLC
Phenol	1.4	1.9
o-Cresol	3.2	5.1
m-Cresol	8.7	11.8
p-Cresol	5.9 (14.6)	
2,4-Xylenol	9.7	12.8
2,5-Xylenol	3.9 (13.6)	
2,6-Xylenol	1.0	1.3
o-Ethylphenol	(1)	1.5
m-Ethylphenol	2.5	
p-Ethylphenol	2.5	
2-n-Propylphenol	(1) (12.2)	10.9
2,3-Xylenol	1.3	
3,5-Xylenol	5.9	
3,4-Xylenol	3.7	
Unknown	(1) (8.2)	7.9
4-Ethyl-2-methylphenol	4.5	
3-Ethyl-5-methylphenol	3.0 (7.9)	5.4
2,3,5-Trimethylphenol	4.9	
2,4,6-Trimethylphenol	(1)	1.4

[1] Quantitative infrared analysis not possible.

the results of the infrared analysis given in table 12.

It can be seen in table 23 that fairly good agreement was obtained in the quantitative analysis of the bituminous coal-tar phenols by the completely independent techniques of infrared analysis and gas-liquid chromatographic analysis. It should be emphasized that, although there are several phenols that cannot be completely resolved by gas-liquid chromatography, the quantities of the resolved phenols and the total quantities of the various combinations of unresolved phenols can be obtained with a much larger measure of assurance that they are correct than is frequently the case in infrared analysis of distillate fractions. In the latter technique no matter how efficient a distillation column one has, the many possible azeotropic systems that exist amongst phenols (*88*) smear most of them together. As an example, 2,4-xylenol (b. p., 210° C.) has been shown to form an azeotrope with 2,4,6-trimethylphenol (b. p., 222° C.), and the occurrence of 2,4-xylenol with 4-ethyl-2-methylphenol (b. p., 222° C.) and 3,4-xylenol (b. p., 225° C.) in distillate fractions 11 and 12 may be due to azeotropism. In addition, the choice of an appropriate analytical wavelength for each component is not always as easy as it may appear; as a general rule, when dealing with a mixture of homologs, a component in the range of about 10 percent can be analyzed only semiquantitatively, and around 5 percent or lower components are frequently missed altogether. On the other hand, in gas-liquid chromatography certain phenols produce their own discrete peaks, which can be identified readily by retention time and of which the area is easily calculated for the quantitative analysis. As far as is known, no azeotropes have ever been reported as occurring in gas-liquid chromatography. Symmetrical-appearing peaks containing two components can be shown to have a gradient composition by collecting different portions of the peak and analyzing for the two compounds by conventional methods.

Two phenols, o-ethylphenol and 2,4,6-trimethylphenol, defied analysis by infrared spectrophotometry due to low concentrations in their respective distillate fractions but were readily identified and analyzed by gas-liquid chromatography. As previously explained, the infrared analysis of the cresols was not as accurate as it would have been had the typical distillation fractionation been possible. This is shown in table 23 in the comparison of the infrared results with the more reliable gas-liquid chromatography results. It can be seen that, by the combination of retention times, infrared analysis of peaks containing more than one phenol, and the peak areas, a reasonably good analysis of a total tar acid mixture boiling up to 234° C. can be obtained with gas-liquid chromatography without recourse to time-consuming procedures such as fractional distillation.

COUNTERCURRENT DISTRIBUTION OF HIGH-BOILING TAR-ACID DISTILLATE FRACTIONS

To complete the characterization of the tar acids it was necessary to fractionate and analyze the high-boiling phenols. The method chosen for this complex material was countercurrent distribution, supplemented by ultraviolet and infrared spectrophotometry (*60*).

Complex mixtures of phenols are frequently encountered in various fields of research, but the capabilities of countercurrent distribution for fractionation of these substances have never been fully demonstrated. The only previous use of countercurrent distribution for high-boiling phenols is that described by Golumbic and others (*41*) for material obtained from coal-hydrogenation oils. This work was done more than 10 years ago, prior to the availability of modern equipment with its distinct advantages of all-glass construction, higher number of transfers, greater sample capacity, fraction collector, and completely automatic operation. In addition, a considerably larger selection of authentic specimens and spectra have become available in recent years. The net result of these new factors is an analytical method especially well suited to extremely complex mixtures of high-boiling phenols.

Infrared spectra were obtained on all the high-boiling tar-acid distillate fractions shown in table 8; they were then combined on the basis of qualitative similarity to give 10 samples and subsequently fractionated by countercurrent distribution, except for the lowest boiling one.

The instrument used was a 60-tube all-glass model with 200 tubes in the fraction collector and an automatic robot mechanism. This apparatus is shown in operation in figure 15. Each tube held 40 ml. of each phase. The instrument was operated so as to obtain 100 to 105 transfers or plates. The average sample size was about 185 mg.; the upper phase consisted of spectrograde cyclohexane, and the lower phase was a phosphate buffer made from varying proportions of 0.5M Na_3PO_4 and 0.5M Na_2HPO_4 so as to give a pH from 9.94 to 11.86. The pH selection was made on the basis of the phenols that might be present in each boiling range and the known partition coefficients at various pH values of these phenols. After the completion of each fractionation, 8 ml. of 1:1 hydrochloric acid was added to each tube to

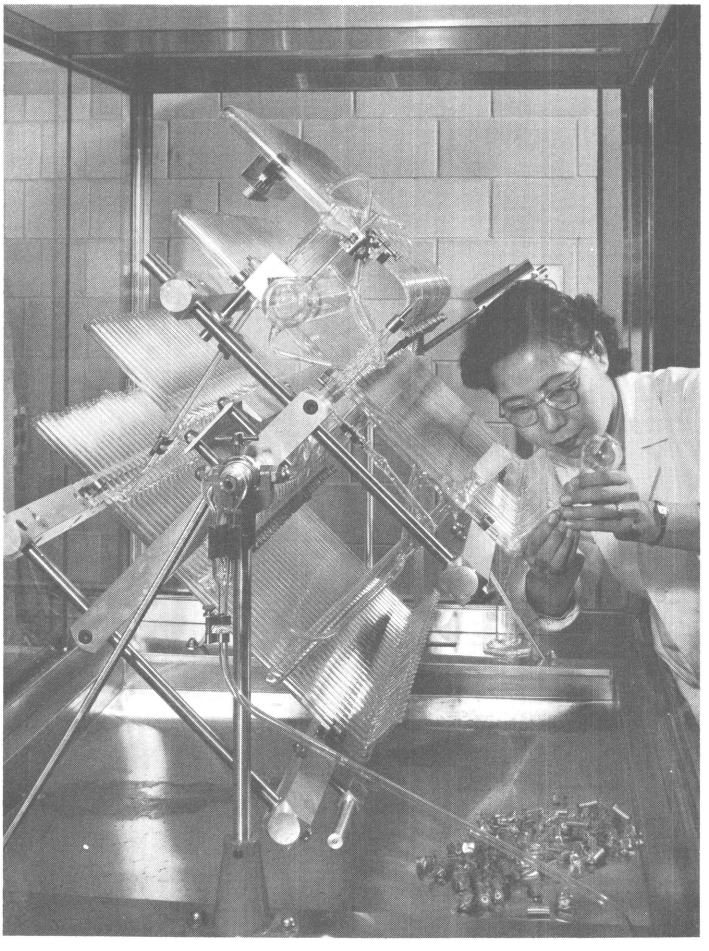


FIGURE 15.—Separation and Analysis of High-Boiling Tar Acids Using Countercurrent Distribution.

neutralize the buffer and mixed well so as to dissolve the phenols in the cyclohexane.

Ultraviolet spectra were obtained on each cyclohexane solution, and plots of total absorbance (most of them at two informative wavelengths) versus tube number were prepared. These are presented in the upper halves of figures 16 to 24, inclusive. On the basis of these plots and the qualitative similarity of the ultraviolet spectra, combinations of the cyclohexane solutions were made for infrared analysis. Almost all the cyclohexane had to be evaporated off to get good infrared spectra, and it was found that conventional methods resulted in the loss of the easily sublimed phenols. A satisfactory technique was as follows: About 150-ml. cyclohexane solution, containing on the average 6 mg. phenols, was placed in an ordinary distillation flask with sidearm; the cold finger was kept at 0°–5°. The cyclohexane was almost completely removed in about 45 minutes, with no detectable loss of phenols, by reducing the pressure to about 65 mm. and immersing the flask in a water bath maintained at 40°–50°. The volume of the solution was reduced to 0.25 ml., which was just enough to fill a 0.5-mm. sodium chloride cell. A matched cell containing cyclohexane was used in the reference beam to obtain the infrared spectrum.

On the basis of the combined qualitative results from the ultraviolet and infrared spectra the constituents from each countercurrent distribution fractionation were distinguished from one another and assigned numbers, as shown in tables 24 to 32, inclusive. The distribution curve of each constituent was readily visualized by following the appearance and disappearance of characteristic absorption bands in the spectra of consecutive countercurrent fractions. This was made easier by the fact that the distributions were essentially Gaussian as well as symmetrical. Distribution peaks observed in this manner always coincided with peaks in the plot of total absorbance versus tube number.

For example, the first appearance of constituent 6, 3-ethyl-5-methylphenol, was in tube 22 (upper half of fig. 16), as indicated by its characteristic bands. The last appearance was

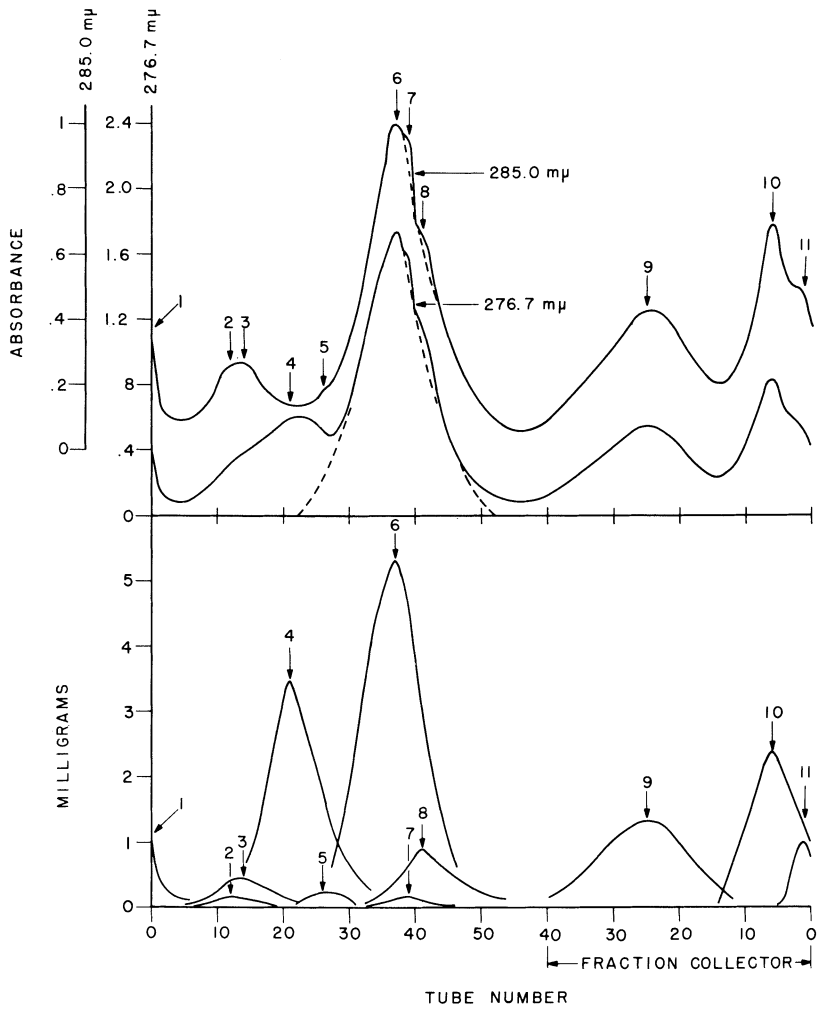


FIGURE 16.—Countercurrent Distribution of Tar Acids Boiling 238°–251°; 100 Transfers; pH 11.58.

TABLE 24.—*Countercurrent distribution of tar acids boiling 238°–251°; 100 transfers; pH 11.58*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
1	Unknown I	285.2, 275.2, 252.5, 245.5 mμ	0		0
2	3,5-Xylenol	281.2, 273.8 mμ	[1] 1.14	12	12
3	3,4-Xylenol	285.0, 278.7 mμ, 13.72, 12.52, 12.32, 11.85, 11.58, 10.57, 9.95, 9.80, 8.97, 8.66, 8.42, 7.90, 7.73 μ.	[1] 1.16	13	14
4	4-Indanol	276.4, 271.0, 268.7 mμ, 14.25, 13.07, 12.98, 10.18, 10.00, 9.52, 8.72, 8.32, 7.85, 7.62 μ.	[1] 1.31	23	21
5	5-Indanol	289.6, 283.3, 280.2, mμ, 14.45, 13.49, 12.52, 12.32, 11.91, 11.65, 10.68, 9.23, 8.82, 8.52, 7.92 μ.	[1] 1.35	26	26
6	3-Ethyl-5-methylphenol	280.9, 276.5, 273.3, 271.0, 267.0, 264.0 mμ, 14.47, 12.02, 11.86, 11.67, 11.07, 10.40, 8.68, 8.58 μ.	[1] 1.59	37	37
7	3-Ethyl-4-methylphenol	12.40, 11.49, 10.81, 8.61, 8.31, 7.95, 7.70 μ	.64		39
8	4-n-Propylphenol	285.4, 278.9, 276.0, 273.0, 270.0, 267.0, 264.0, 261.0 mμ, 14.20, 13.08, 12.62, 12.20, 9.02, 8.56, 6.19 μ.	[1] 1.87	46	41
9	2,3,5-Trimethylphenol	282.4, 277.9, 273.4 mμ, 12.06, 11.90, 10.30, 9.27, 8.77, 8.62, 8.17, 7.88, 7.62 μ.	[1] 2.6	[2] 23FC	25FC
10	2,6-Dialkylphenol (2-Ethyl-6-n-propylphenol)	285.0, 277.5 mμ, 13.83, 13.08 μ	9.8		6FC
11	2,3,5,6-Tetramethylphenol	13.08, 12.95, 12.06, 9.17, 8.46 μ	[1] 59	1FC	1FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube.
[2] Tube in fraction collector.

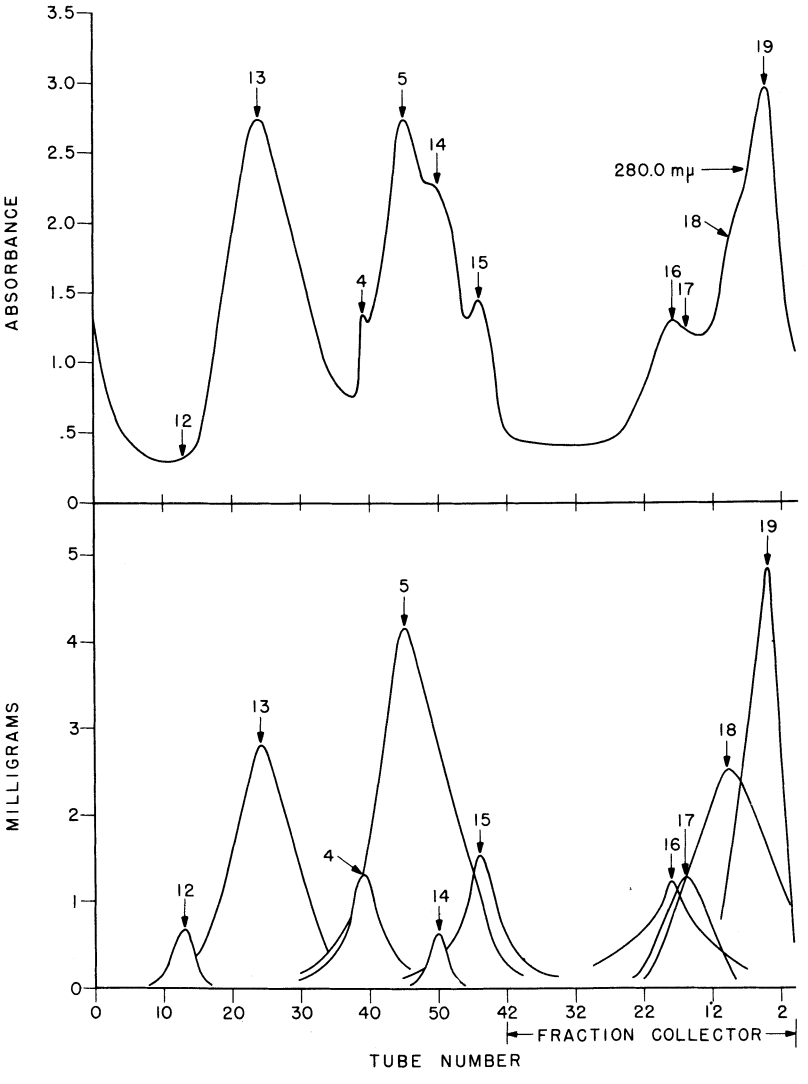


FIGURE 17.—Countercurrent Distribution of Tar Acids Boiling 251°–258°; 100 Transfers; pH 11.20.

TABLE 25.—*Countercurrent distribution of tar acids boiling 251°–258°; 100 transfers; pH 11.20*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
12	4-Indenol	----, 299.5, 287.8, 252.5 mμ, 14.45, 13.45, 13.42, 12.20, 11.10, 10.98, 10.60, 10.00, 6.42 μ.	[1] 0.13	11	13
13	5-Indenol	307.0, 290, 268, 258 mμ, 14.60, 14.48, 13.65, 13.00, 10.52 9.40, 9.00, 8.25, 6.42, 6.29, 6.27 μ.	.31	----	24
4	4-Indanol	276.4, 271.0, 268.7 mμ	[1] .68	41	39
5	5-Indanol	289.6, 283.3, 280.2 mμ	[1] .79	45	45
14	Unknown II	(No distinctive bands.)	.96	----	50
15	3,4,5-trimethylphenol	284.7, 280.0, 276.0 mμ, 14.33, 13.52, 12.04, 8.82, 8.44, 8.06 μ.	[1] 1.2	55	56
16	1-, 2-, or 3-Methyl-5-indanol (1-Methyl-5-indanol(?)).	288.8, 284.0, 280 mμ, 12.54, 12.32, 11.95, 10.68, 9.24, 8.55 μ.	3.3	----	[2] 18FC
17	1-, 2-, or 3-Methyl-4-indanol (3-Methyl-4-indanol(?)).	276.5, 271.5, 269.0 mμ, 14.27, 13.12, 12.98, 10.21, 8.73, 8.34 μ.	3.8	----	16FC
18	3,5-Dialkylphenol (3-Methyl-5-n-propylphenol)	280.3, 276.6, 273.4 mμ, 14.47, 12.04, 11.95, 10.38, 8.72 μ.	6.0	----	10FC
19	3,4-Dialkylphenol (4-Ethyl-3-n-propylphenol)	285, 278.3 mμ, 14.34, 13.60, 12.84, 12.45, 12.35, 11.87, 10.53, 10.37, 8.70 μ.	15	----	4FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube.
[2] Tube in fraction collector.

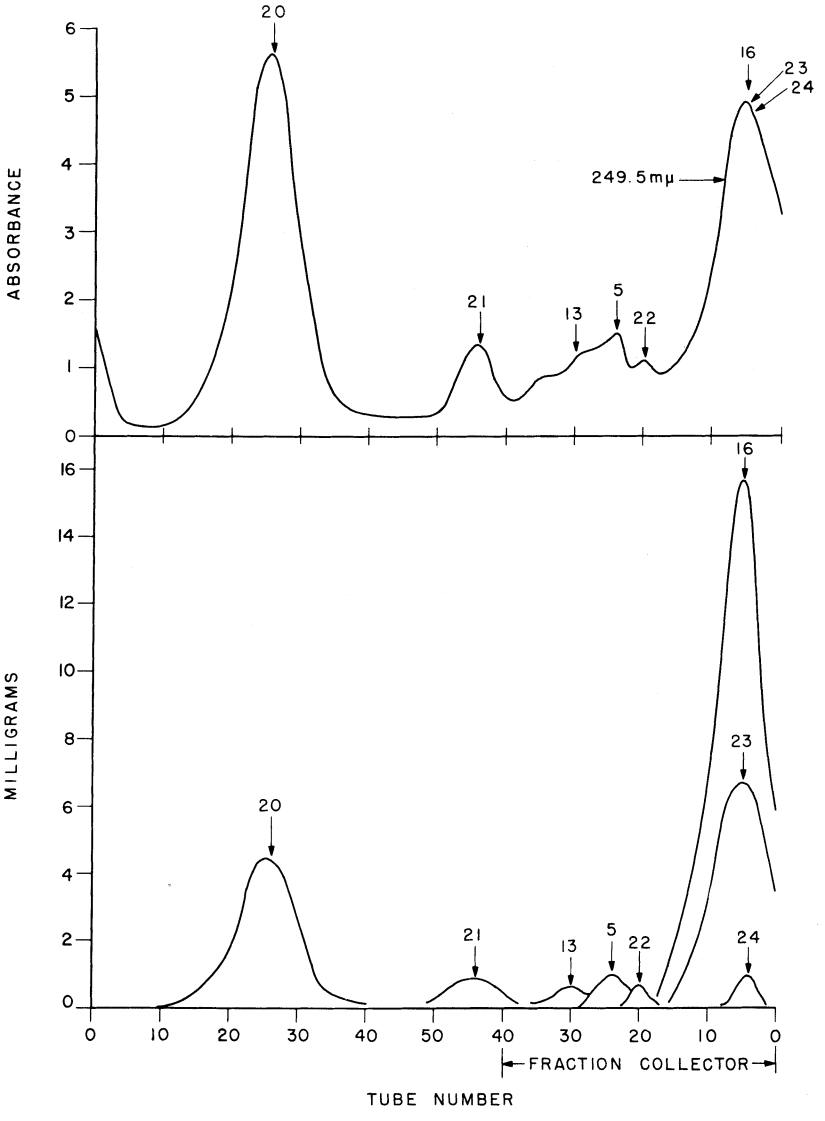


FIGURE 18.—Countercurrent Distribution of Tar Acids Boiling 258°–260°; 100 Transfers; pH 10.49.

TABLE 26.—*Countercurrent distribution of tar acids boiling 258°–260°; 100 transfers; pH 10.49*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
20	Methyl-1-indanone (4-Methyl-1-indanone(?))	314.0, 302.5, 296.0, 278.0, 257.4, 253,5. 249.5, 245.6, 242.0 mμ, 12.95, 8.65, 5.92 μ.	0.35		26
21	Methyl-1-indanone (6-Methyl-1-indanone(?))	314.0, 278.0, 271.0, 257.5, 253,5. 249.7, 242.0 mμ, 5.93 μ	1.0		56
13	5-Indenol	307.0, 290.0, 280.0, 268.0, 258 mμ, 14.60, 13.00, 10.52, 10.38, 8.25, 6.27 μ.	2.0		[2] 30FC
5	5-Indanol	289.5, 284.0, 280.0 mμ, 14.45, 13.47, 12.55, 12.32, 10.68, 9.25, 8.82, 8.55 μ.	[1] 2.9	20FC	24FC
22	2,3- or 2,6-Alkylalken-1-ylphenol (3-Methyl-2-propen-1-ylphenol).	296.4 mμ, 14.10, 12.88, 10.20 μ	3.0		20FC
16	1-, 2-, or 3-Methyl-5-indanol (1-Methyl-5-indanol (?)).	288.5, 282.9, 279.4, 274.5 mμ, 14.45, 12.07, 12.30, 9.24, 8.55 μ.	13		5FC
23	3,4-Dialkylphenol (3-Ethyl-4-n-propylphenol)	280.5, 273.5 mμ, 14.35, 13.61, 12.37, 11.88, 9.21, 9.02, 8.90, 8.68 μ.	13		5FC
24	2-Phenylphenol	14.25, 13.90, 13.70, 13.32, 13.02, 12.04 μ	[1] 34	2FC	4FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube.
[2] Tube in fraction collector.

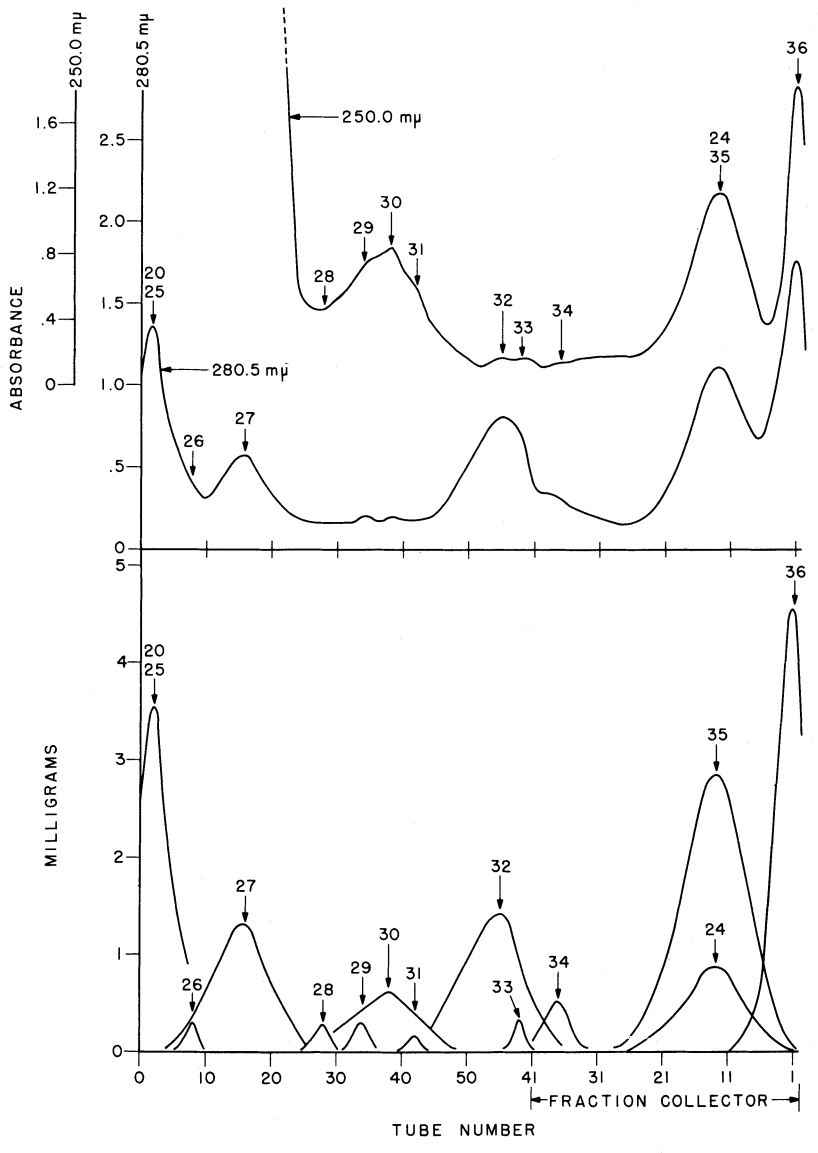


FIGURE 19.—Countercurrent Distribution of Tar Acids Boiling 260°–270°; 101 Transfers; pH 11.86.

TABLE 27.—*Countercurrent distribution of tar acids boiling 260°–270°; 101 transfers; pH 11.86*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
20	Methyl-1-indanone (4-Methyl-1-indanone)	314.0, 302.0, 257.0, 253.0, 249.0, 246.0 mμ	0.020		2
25	3,4-Dinuclearphenol	284.8, 280.7, 275.5 mμ	.020		2
26	Alkenylphenol I	292.0 mμ	.086		8
27	1-,2-, or 3-Methyl-4-indenol	309.6, 299.7, 288.6, 265.0, 260.7, 254.5, 249.3 mμ, 14.14, 13.15, 13.00, 12.89, 12.77, 12.42, 10.72, 10.51, 9.85, 9.15, 7.25, 6.28, 6.17, 6.14 μ.	.19		16
28	Unknown III	303.0, 240.0 mμ	.38		28
29	Cycloalkenylphenol I ?	253.0 mμ	.51		34
30	Methylindenol	296.5, 261.0, 254.5, 249.3 mμ, 10.42, 8.71, 8.45 μ	.60		38
31	Alkenylphenol II	308.0 mμ	.71		42
32	7-Methyl-5-indanol	287.8, 283.0, 279.5 mμ, 14.47, 13.10, 12.07, 10.53, 10.20, 9.87, 8.92, 8.47, 8.07, 7.58, 7.52, 7.26, 6.22 μ.	1.2		55
33	Methyl-5-indanol (6-Methyl-5-indanol)	287.8, 283.0, 279.5 mμ, 14.45, 13.60, 12.60, 12.50, 12.10, 11.97, 10.52, 10.05 μ.	1.4		58
34	2,4- or 3,4-Dialkylphenol (?)	287.5, 281.5, 277.0, 272.5 mμ	1.6		[2] 37FC
35	2,4- or 3,4-Dialkylphenol (4-Isopropyl-3-n-propylphenol).	287.5, 280.5, 273.4 mμ	4.5		13FC
24	2-Phenylphenol	283.0, 245.5 mμ, 14.25, 13.90, 13.70, 13.32, 13.02, 12.04, 8.49 μ.	[1] 4.5	13FC	13FC
36	2,4- or 3,4-Dialkylphenol (2,4-Di-n-propylphenol).	285.0, 279.0, 273.0 mμ, 12.45 μ	59		1FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube. [2] Tube in fraction collector.

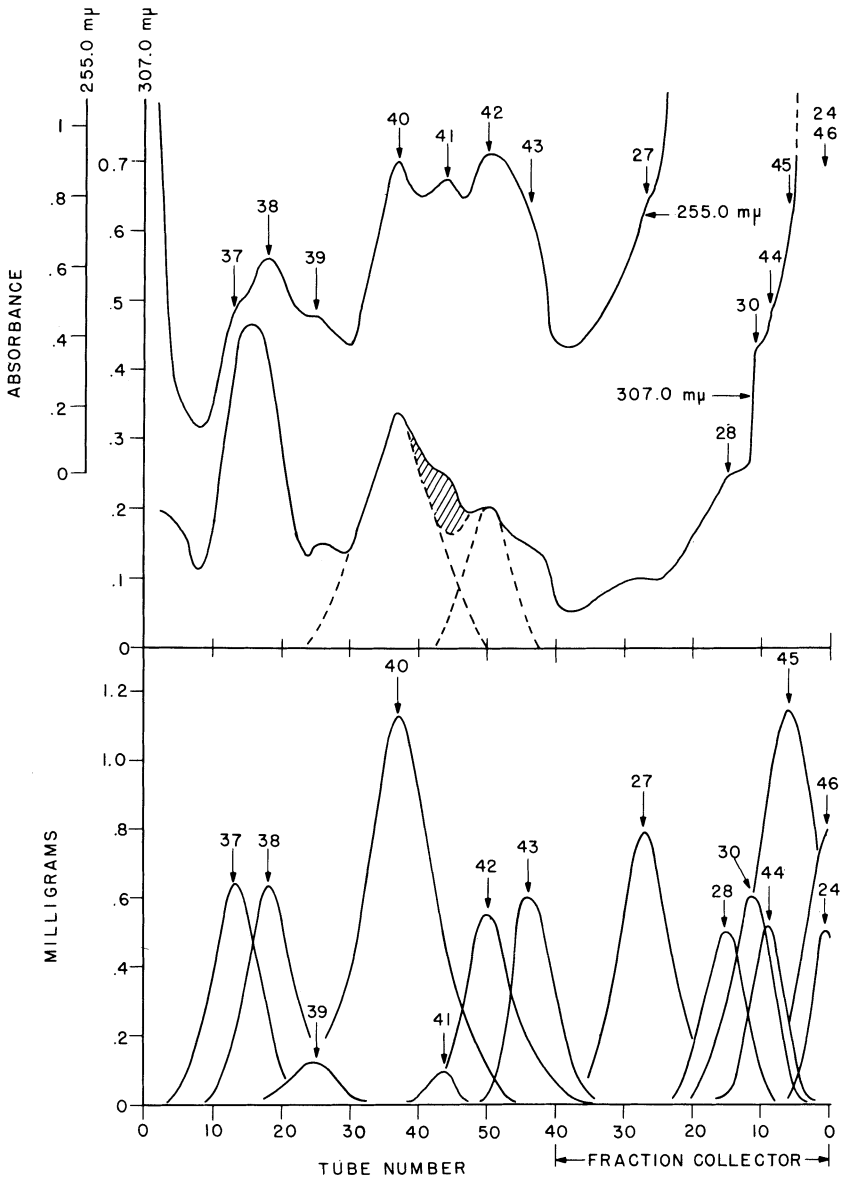


FIGURE 20.—Countercurrent Distribution of Tar Acids Boiling 270°–280°; 100 Transfers; pH 10.28.

TABLE 28.—*Countercurrent distribution of tar acids boiling 270°–280°; 100 transfers; pH 10.28*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
37	Unknown IV	248.0 mμ	0.15		13
38	Unknown V	307.5, 301.0, 296.0, 286.0, 265.4, 256.5 mμ, 14.57, 13.50, 13.00, 12.50, 10.84, 9.24, 9.15, 9.07, 9.02, 8.78, 8.52, 8.32, 8.12, 6.34 μ.	.22		18
39	Unknown VI	243.5 mμ, 14.69, 12.74 μ	.33		25
40	2-Naphthol	328.6, 324.0, 321.0, 314.0, 310.0, 307.0, 301.0, 285.4, 273.8, 263.5, 254.0 mμ, 13.47, 12.52, 12.41, 11.97, 10.42, 8.95, 8.75, 8.60, 6.60, 6.22, 6.12 μ.	[1] .59	37	37
41	Unknown VII	(No distinctive bands.)	.79		44
42	Ketone (Alkyl indanone)	314, 263.8, 259.0, 255.0, 248.0 mμ, 5.92 μ	1.0		50
43	Alkenylphenol III	301.0 mμ	1.2		56
27	1-, 2-, or 3-Methyl-4-indenol	309.6, 299.7, 288.6, 265.0, 254.5, 249.3 mμ, 14.14, 13.15, 13.00, 12.89, 12.77, 12.42, 10.72, 10.51, 9.85, 9.15, 6.28, 6.17, 6.14 μ.	2.2		[2] 27FC
28	Unknown III	303.0, 240.0 mμ, 14.55, 10.87, 10.10, 8.54 μ	3.9		15FC
30	Methyl indenol	296.5, 254.5, 249.0 mμ	5.4		11FC
44	5,6,7,8-Tetrahydro-2-naphthol	287.8, 279.5 mμ, 14.45, 13.60, 12.60, 12.50, 12.10, 11.97, 10.52 μ.	[1] 6.7	9FC	9FC
45	Unknown VIII	256.0 mμ, 10.40, 10.25, 8.92, 8.70, 8.50 μ	9.8		6FC
46	5,6,7,8-Tetrahydro-1-naphthol	279.0, 273.0 mμ, 14.10, 13.04, 12.07 μ	(*117*) 25	2FC	1FC
24	2-Phenylphenol	283.5, 245.5 mμ, 14.25, 13.90, 13.70, 13.32, 13.02, 12.04, 8.49 μ.	[1] 51	1FC	1FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube. [2] Tube in fraction collector.

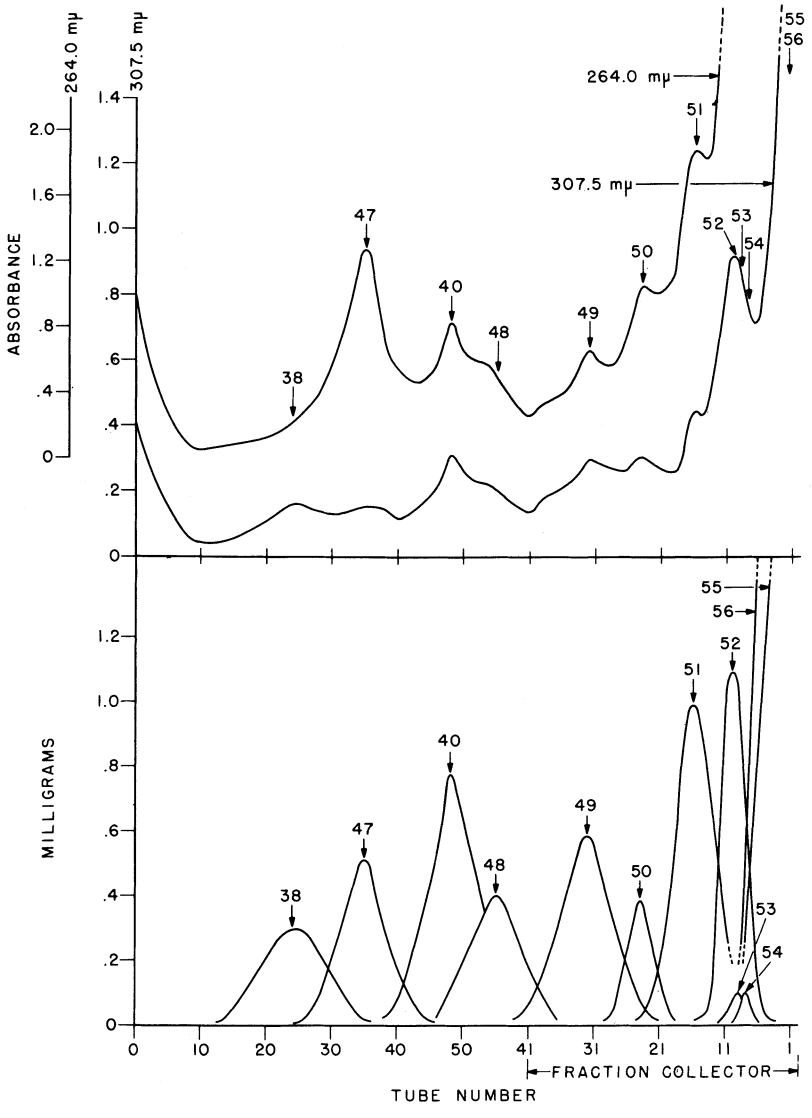


FIGURE 21.—Countercurrent Distribution of Tar Acids Boiling 280°–297°; 101 Transfers; pH 9.94.

TABLE 29.—*Countercurrent distribution of tar acids boiling 280°–297°; 101 transfers; pH 9.94*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
38	Unknown V	307.5, 296.3, 265.0, 255.8, 243.5 mμ	0.31		24
47	Cycloalkenylphenol II (?)	304.5, 292.5, 273.7, 264.5, 256.5 mμ, 13.30 μ	.53		35
40	2-Naphthol	328.6, 324.0, 321.0, 314.0, 310.0, 307.0, 301.0, 285.4, 273.8, 263.5, 254.0 mμ, 13.47, 12.52, 12.42, 11.98, 10.42, 8.94, 8.80, 8.60, 6.60, 6.24, 6.12 μ.	[1] .91	48	48
48	Unknown IX	(No distinctive bands)	1.2		55
49	1-, 2-, or 3-Polyalkyl-4-indenol	312 (sh), 307.5, 299.5, 296.3, 265.0, 256.0 mμ, 14.65, 13.12, 12.40, 9.13, 6.33, 6.14 μ.	1.8		[2] 32FC
50	Methyl-2-naphthol (4-Methyl-2-naphthol (?))	331.5, 327.0, 324.2, 317.0, 290.5, 276.0, 267.0, 258.0 mμ	2.5		24FC
51	Dimethyl-1-naphthol (5,7- Dimethyl-1-naphthol (?))	327.4, 320.0, 312.0, 306.0, 303.0, 265.0 mμ	3.7		16FC
52	4-Methyl-1-naphthol	326.0, 319.0, 312.0, 303.0, 290.0 mμ, 13.15, 12.40, 6.30 μ	[1] 5.5	11FC	10FC
53	Methyl-2-naphthol (3-Methyl-2-naphthol (?))	331.5, 317.0, 290.0, 278.0 mμ	6.6		9FC
54	1-Methyl-2-naphthol	335.0, 320.0, 304.0, 265.0 mμ, 13.48, 13.72, 12.45, 12.34, 10.55, 10.10, 9.83, 9.45, 8.82, 7.45, 6.63, 6.24, 6.15 μ.	7.4		8FC
55	Alkyl-1-naphthol (2-Ethyl-1-naphthol (?))	328.2, 321.0, 314.0, 300.0, 290.0 mμ, 12.52 μ	30		2FC
56	2-Cyclohexylphenol	279 mμ, 13.30 μ	(*117*) 2400	0–1FC	1FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube. [2] Tube in fraction collector.

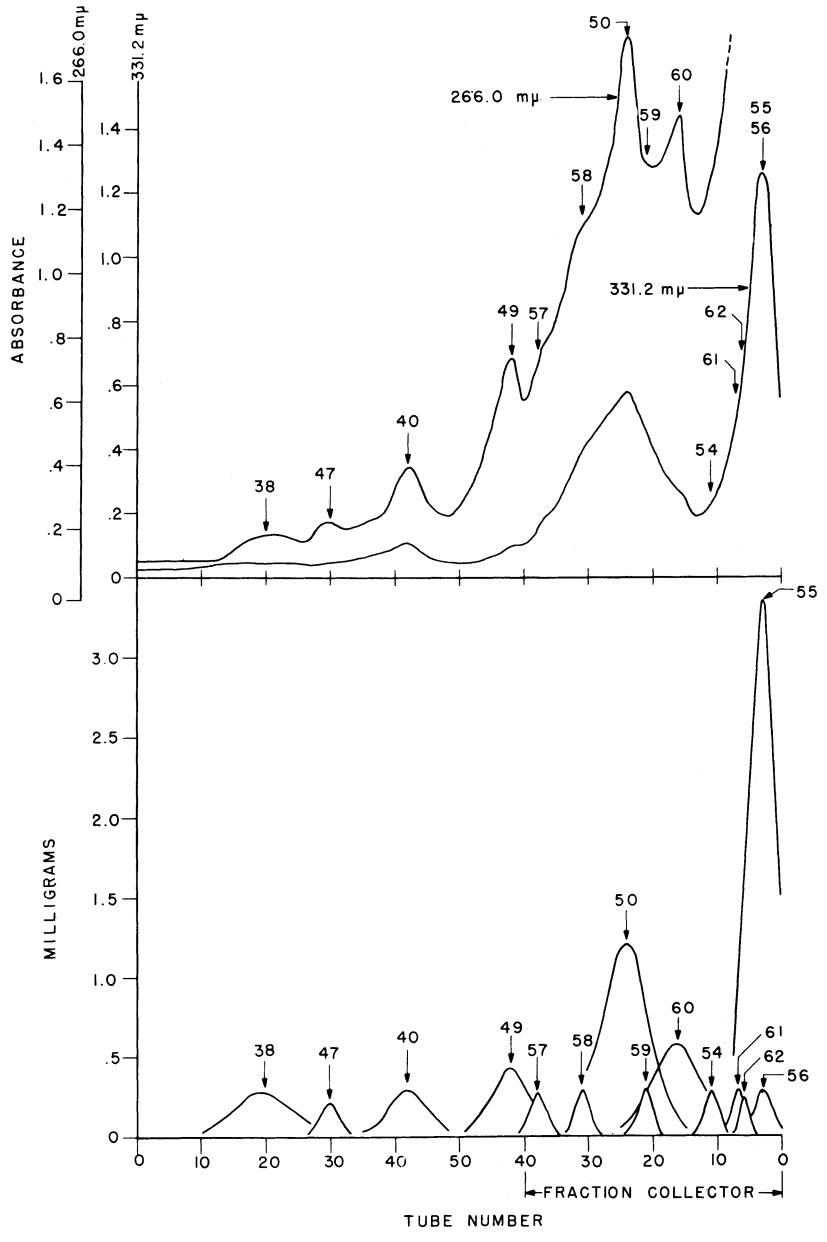


FIGURE 22.—Countercurrent Distribution of Tar Acids Boiling 297°–300°; 100 Transfers; pH 10.10.

TABLE 30.—*Countercurrent distribution of tar acids boiling 297°–300°; 100 transfers; pH 10.10*

Constituent		Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube	
No.	Identity			Calculated	Experimental
38	Unknown V	307.5, 296.3, 265.0, 255.8, 243.5 mμ	0.25		20
47	Cycloalkenylphenol II(?)	304.5, 292.5, 273.7, 264.5, 256.5 mμ, 13.30 μ	.43		30
40	2-Naphthol	328.6, 324.0, 321.0, 314.0, 310.0, 307.0, 301.0, 285.4, 273.8, 263.5, 254.0 mμ, 13.48, 12.52, 12.42, 11.98, 10.42, 8.60 μ.	[1].72	42	42
49	1-, 2-, or 3-polyalkyl-4-indenol	312 (sh), 307.5, 299.5, 296.3, 265.0, 256.5 mμ, 14.65, 13.12, 12.40, 9.13, 6.33, 6.14 μ.	1.4		58
57	Unknown X	(No distinctive bands.)	1.6		38
58	Unknown XI	309.0, 303.0, 297.0, 285.0, 276.0 mμ	1.9		[2] 31FC
50	Methyl-2-naphthol (4-methyl-2-naphthol(?))	331.5, 327.0, 324.2, 317.0, 290.5, 276.0, 267.0, 258.0 mμ, 13.40 μ.	2.5		24FC
59	Unknown XII	(No distinctive bands.)	2.9		21FC
60	4-Phenylphenol	255.6 mμ, 14.60, 14.05, 13.20, 12.05 μ	[1] 3.7	16FC	16FC
54	1-Methyl-2-naphthol	335.0, 320.0, 304.0, 265.0 mμ	5.5		11FC
61	Dimethyl-1-naphthol (2,5- or 2,7-dimethyl-1-naphthol(?)).	327.0, 311.0, 303.0, 290.0, 280.0 mμ	7.9		7FC
62	Dimethyl-1-naphthol (2,6-dimethyl-1-naphthol(?)).	331.5 mμ	9.3		6FC
55	Alkyl-1-naphthol (2-ethyl-1-naphthol (?)	328.2, 321.0, 314.0, 300.0, 290.0 mμ, 12.52 μ	20		3FC
56	2-Cyclohexylphenol	279 mμ, 13.30 μ	(117)2100	0–1FC	2FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube. [2] Tube in fraction collector.

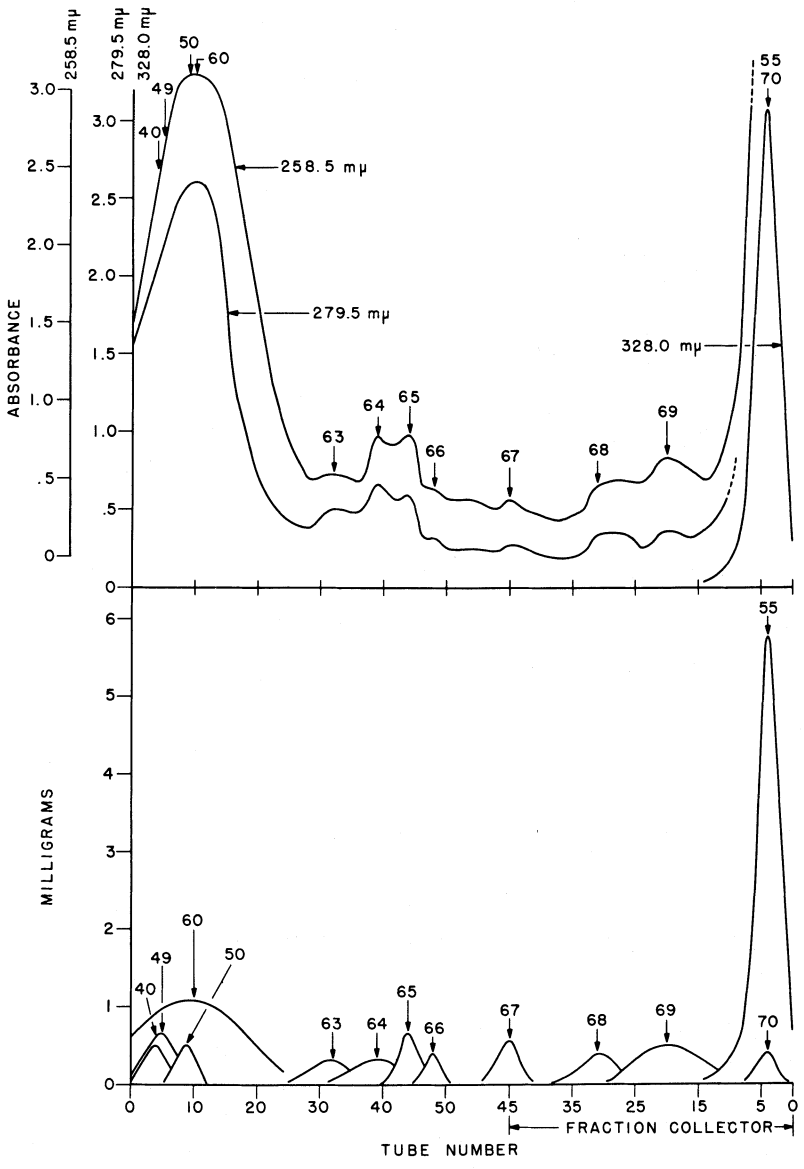


FIGURE 23.—Countercurrent Distribution of Tar Acids Boiling 300°–325°; 105 Transfers; pH 11.85.

TABLE 31.—*Countercurrent distribution of tar acids boiling 300°–325°; 105 transfers; pH 11.85*

No.	Constituent: Identity	Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube: Calculated	Peak tube: Experimental
40	2-Naphthol	328.6, 314.0, 285.0, 273.8 mμ, 13.48 μ	[1] 0.040	5	4
49	1-, 2-, or 3-Polyalkyl-4-indenol	307.5, 299.5, 296.3, 256.5 mμ	.050		5
50	Methyl-2-naphthol (4-Methyl-2-naphthol(?))	331.0, 317.0, 290.5, 276.0, 267.0, 258.0 mμ, 13.40 μ	.094		9
60	4-Phenylphenol	255.6 mμ, 14.60, 14.05, 13.20, 12.05, 11.02, 9.30, 8.97, 7.95 μ.	[1] .11	10	10
63	Unknown XIII	303.0, 296.0, 290.0 mμ	.44		32
64	Methyl-2-naphthol (7-Methyl-2-naphthol(?))	331.0, 317.0, 275.0, 266.3 mμ	.59		39
65	Unknown XIV	258.5 mμ	.72		44
66	Unknown XV	305.5 mμ	.84		48
67	Unknown XVI	304.0, 294.0 mμ	1.3		[2] 45FC
68	Unknown XVII	261.5, 255.0 mμ	1.9		31FC
69	Unknown XVIII	260 mμ	3.0		20FC
55	Alkyl-1-naphthol (2-Ethyl-1-naphthol(?))	328.2, 321.0, 314.0, 300.0, 290.0 mμ, 14.53, 13.48, 12.52, 12.12, 10.07 μ.	15		4FC
70	2-Alkylcycloalkylphenol I	287.0 mμ, 13.30 μ	15		4FC

[1] Partition coefficient determined from authentic specimen, other values calculated from experimental peak tube. [2] Tube in fraction collector.

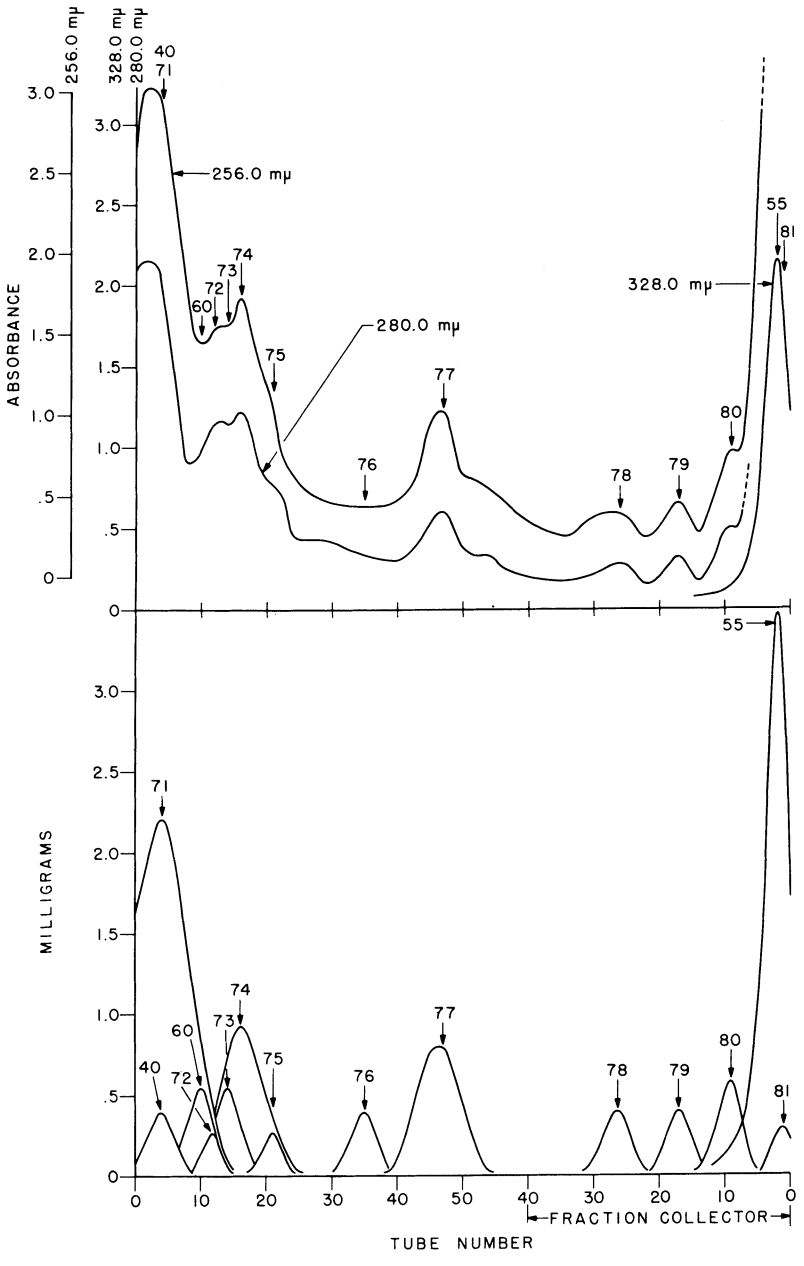


FIGURE 24.—Countercurrent Distribution of Tar Acids Boiling 325°–331°; 100 Transfers; pH 11.85.

in tube 52, which should place the peak at tube 37. This agrees with the total absorbance peak at tube 37. With the distribution curve for constituent 6 firmly established, constituents producing small shoulders in the total absorbance curve could have their distribution curves delineated. Thus, constituent 8, 4-n propylphenol, first appears in tube 39 and last in tube 43, as indicated by its characteristic bands at 285.4 and 278.9 mμ. This places its distribution peak at tube 41 in agreement with the position of the shoulder in the total absorbance curve.

The milligrams of each phenol in each tube were determined from the extinction coefficients at characteristic wavelengths, as obtained from authentic specimens or literature data. In those instances where such extinction coefficients were not available, an average extinction coefficient was obtained from phenols with the most similar structure or, for constitutents of unknown structure, from phenols with the most

TABLE 32.—*Countercurrent distribution of tar acids boiling 325°–331°; 100 transfers; pH 11.85*

No.	Constituent: Identity	Observed analytical wavelengths (UV in mμ, IR in μ)	Partition coefficient	Peak tube: Calculated	Peak tube: Experimental
40	2-Naphthol	328.6, 286.0, 279.5, 273.0 mμ, 14.00, 13.48, 12.52, 12.42, 11.98, 10.42 μ.	[1]0.042	5	4
71	Unknown XIX	306.0, 299.0, 294.0, 275.2 mμ	.042		4
60	4-Phenylphenol	256 mμ, 14.60, 14.05, 13.20, 12.05, 9.30, 8.97, 7.95 μ	[1].11	10	10
72	Methyl-2-naphthol (6-Methyl-2-naphthol(?))	331.0 mμ	.14		12
73	3-Phenylphenol	281.0, 249.5 mμ, 14.40, 13.25, 8.67, 8.56 μ	[1].16	15	14
74	Methyl-2-, 3-, or 4-fluorenol	311.0, 298.5, 282.5, 277.0, 258.0 mμ	.20		16
75	Unknown XX	278.5 mμ	.27		21
76	Unknown XXI	280.0, 260.7, 254.8 mμ	.54		35
77	Unknown XXII	302.0, 282.0, 268.0, 260.5, 255.0, 249.0 mμ	.89		47
78	8-Methyl-2-naphthol(?)	14.30, 13.76, 13.16 μ	2.3		[2] 26FC
79	Unknown XXIII	(No distinctive bands.)	3.5		17FC
80	Unknown XXIV	(No distinctive bands.)	6.6		9FC
55	Alkyl-1-naphthol (2-Ethyl-1-naphthol(?))	328.2, 321.0, 314.0, 300.0, 290.0 mμ, 14.53, 13.48, 12.52, 12.12, 10.07 μ.	29.5		2FC
81	2-Alkylcycloalkylphenol II	13.27 μ	59		1FC

[1] Partition coefficient determined from authentic specimen; other values calculated from experimental peak tube. [2] Tube in fraction collector.

similar absorption bands and boiling point. Plots of milligrams versus tube number were prepared, as shown in the lower halves of figures 16 to 24, inclusive. One useful technique was to construct the distribution curve for the compound on the plot of absorbance versus tube number, as previously described, and as illustrated for constituent 40, 2-naphthol, in the upper half of figure 20. The absorbance value for each tube number was read off of this distribution curve and divided by the specific extinction coefficient for 2-naphthol at this wavelength, 307 mμ. The resulting value of milligrams per milliliter was multiplied by 40 to obtain the milligrams of 2-naphthol in each tube. This technique could be used even for small amounts of phenols of unknown structure. For example, having established the distribution curve for constituent 40, 2-naphthol (upper half of fig. 20), the curve for constituent 42, a ketone, was similarly obtained. The sum of the absorbances in the overlapping portions of these two curves was subtracted from the total absorbance curve to give the shaded portion in the figure. This gives the absorbance at 307 mμ due to constituent 41 (a phenol of unknown structure) in each tube.

Partition coefficients for the cyclohexane: phosphate buffer system were obtained for a large number of authentic specimens of phenols at a wide variety of pH values. These were used to calculate the peak tube number, using the following equations:

$$N = n\frac{k}{k+1}, \qquad N_{FC} = \frac{59}{k},$$

where N = peak tube number in the instrument,
N_{FC} = peak tube number in the fraction collector,
n = number of transfers, and
k = partition coefficient.

The first equation is the one presented by Williamson and Craig (*116*); the second equation is self-evident. The tubes are numbered from 0 to 59 in the direction of transfer in the instrument and from zero up as used in the fraction collector. Thus, if the last tube used in the fraction collector is number 40, it will immediately follow tube 59 in the plot of milligrams versus tube number.

If the calculated peak tube agreed well with the experimental peak tube, this constituted additional proof of identity, as demonstrated in tables 24 to 32, inclusive. In those instances where the authentic specimen was not available, the partition coefficients of the many other available phenols were the basis of partition coefficient-structural correlations, which were frequently quite useful and reliable in establishing the general structure of constituents.

The weight-percentages of each high-boiling constituent in the distillable tar acids (3.62 weight-percent of the tar) were calculated from the milligrams versus tube-number distribution curves and the amounts of the various distillate fractions. For completeness certain data were included, which were obtained by other techniques. It was found that the tar acids boiling from 231°–238° could be analyzed essentially as well by the method of fractional distillation followed by infrared spectrophotometry. In addition, some of the constituents in this range have been included in the gas-liquid chromatographic analysis of the tar acids boiling up to 234°. Five phenols were identified in the 231°–238° fractions, which were not found in either the gas-liquid chromatography work or the countercurrent distribution fractionations. These are 3-ethyl-2-methylphenol, 2-methyl-5-isopropylphenol, 3-n-propylphenol, 4-isopropylphenol, and 2,3,6-trimethylphenol; evidence for the presence of the last two is good but not as good as for the other three. In addition, 5-ethyl-2-methylphenol, which was the struc-

ture proposed for an unknown phenol found in the gas-liquid chromatography work (table 22), was positively identified on the basis of published infrared spectral data (*49*).

1-Naphthol was readily determined to be present in the tar acids by means of the ultraviolet and infrared spectra of the distillate fractions. However, this phenol is easily oxidized in the presence of air when it is dissolved in alkaline solutions, and none of it could be detected in the countercurrent fractions. 2-Naphthol occurred in two distillate fractions in such relatively large amounts that some of it crystallized out. The pure 2-napththol isolated in this manner was not added to the charge to the countercurrent instrument. The amounts of 1-naphthol and 2-naphthol therefore were based on the distillate fractions.

Aliphatic carboxylic acids were found in every countercurrent fractionation. From their infrared spectra these acids were seen to be mostly long-chain saturated aliphatic carboxylic acids. There could have been a small amount of terminal unsaturation, but there definitely was no internal unsaturation, since this gives a strong C=C stretching band, which could not be detected in any of the fractions. These acids have such low partition coefficients that they always were restricted to the first few tubes in the instrument and did not interfere with the determination of the phenols. The weight-percent of total aliphatic carboxylic acids in each boiling range was determined by using the intensity of the C=O stretching band at about 5.85 μ. A plot of extinction coefficient versus boiling point for various aliphatic and externally unsaturated carboxylic acids in the range 237°–305° showed an exact linear relationship; that is, $\epsilon = -0.305t + 133$, where ϵ=extinction coefficient for a 0.1-mm. sodium chloride cell and t=boiling point in ° C. The results of this quantitative procedure are presented in table 33.

TABLE 33.—*Quantitative analysis of the high-boiling aliphatic carboxylic acids*

Constituent	Wt.-pct.[1]
Boiling 238°–251°	0.04
Boiling 251°–258°	.14
Boiling 258°–260°	.02
Boiling 260°–270°	.12
Boiling 270°–280°	.08
Boiling 280°–297°	.03
Boiling 297°–300°	.02
Boiling 300°–325°	.05
Boiling 325°–331°	.06
Total	.56

[1] On the basis of the distillable tar acids, which constitute 3.62 wt.-pct. of the tar.

USE OF SPECTRAL-STRUCTURAL CORRELATIONS AND PARTITION COEFFICIENT-STRUCTURAL CORRELATIONS FOR HIGH-BOILING TAR ACIDS

With respect to identification, the high-boiling tar acids fell into one of three groups. The first group consisted of those compounds for which authentic specimens were available. For these compounds the Low-Temperature Tar Laboratory's own ultraviolet and infrared spectra and partition coefficients were available. The second group consisted of those compounds for which ultraviolet and/or infrared spectra were available from the literature and, in a few instances, partition coefficients also. The third group consisted of those compounds for which only the literature boiling point was available. Compounds in the first two groups were nearly always identified with complete certainty. Compounds in the third group were almost never identified with complete certainty as to the specific isomer, but by the cautious application of spectral-structural correlations, partition coefficient-structural correlations, and boiling range-structural correlations the general structure of the compound could be established. In some instances the name of a specific isomer is given in parentheses in the tables. These individual compounds were selected as being most representative of the constituent on the basis of the combined spectral, partition coefficient, and boiling-range data. These selections must be considered to be only tentative. A somewhat detailed description of the identification of the compounds in this third group is presented here as a general guide for other investigators.

1. Alkylphenols: The spectra of constituent 10 indicated that it was a 2,6-dialkylphenol. Its partition coefficient of about 10 at pH 11.58 is only slightly lower than the 15 for 2,6-di-n-propylphenol, indicating that it could be very similar in structure. Both 2,6-di-n-propylphenol and 2-methyl-6-n-propylphenol were excluded as possibilities since authentic specimens of these compounds were available for comparison. It was concluded, therefore, that constituent 10 could be 2-ethyl-6-n-propylphenol, b. 240°.

Constituent 18, a 3,5-dialkylphenol, had a partition coefficient of 6.0 at pH 11.20, calculated from its concentration peak in tube 10 FC. The partition coefficient of 3-ethyl-5-methylphenol is 1.1, which would place its peak in tube 55. Therefore, the degree of n-alkylation must be greater than in 3-ethyl-5-methylphenol; 3,5-diethylphenol was excluded, since its infrared spectrum was available. It was concluded that constituent 18 could be 3-methyl-5-n-propylphenol (b. p., 254°).

Constituent 19, a 3,4-dialkylphenol, had a partition coefficient of 15 at pH 11.20, only slightly lower than the 20 for 2,6-di-n-propylphenol. The degree of n-alkylation must, therefore, be only slightly less; taking into consideration the boiling range of the distillate, constituent 19 could be 4-ethyl-3-n-propylphenol (b. p., 258°).

Constituent 23, a 3,4-dialkylphenol, had a partition coefficient of 13 at pH 10.49, whereas the value for 3-methyl-4-ethylphenol is 5.0. Since four major infrared absorption bands in the hydrogen out-of-plane deformation vibration region are essentially identical to major bands for constituent 19, this suggests that these compounds are closely isomeric but not identical, as shown by the ultraviolet spectra. Constituent 23 could, therefore, be 3-ethyl-4-n-propylphenol (b. p., 263°).

Constituent 35, a 2,4- or 3,4-dialkylphenol, had a partition coefficient of 4.5 at pH 11.86, which indicates the alkyl groups must have structures and locations on the ring that would give only a moderately high partition coefficient; for example, there could not be two long chains close to the OH group. 2,4-Diisopropylphenol (b. p., 248°) is too low boiling to be present, but 4-isopropyl-3-n-propylphenol (b. p., 262°), is a distinct possibility. Constituent 36, also a 2,4- or 3,4-dialkylphenol, had a very high partition coefficient of 59 at pH 11.86, requiring two n-alkyl groups, with at least one in the ortho position. 2,4-Di-n-propylphenol (b. p., 263°) is a likely possibility.

2. Alkenylphenols: Constituent 22, a 2,3- or 2,6-dialkylphenol, had an ultraviolet absorption band at 296.4 mμ, indicative of an unsaturated side chain, probably an orthopropenyl group, conjugated with the benzene ring (*6*). 2-Propen-1-ylphenol has a partition coefficient of 3.5 at pH 10.49, which is quite close to the 3.0 for constituent 22. 2-Methyl-6-propen-1-ylphenol (b. p., 243°) is too low boiling to be present, but 3-methyl-2-propen-1-ylphenol (b. p., 256°) could be present. Constituent 29 has the low partition coefficient of an unsaturated phenol and an absorption band at 253.0 mμ in common with 2-cyclopenten-1-ylphenol (b. p., 272°).

3. Cycloalkylphenols: Constituent 70 has the 13.30 μ absorption band in the infrared indicative of mono-ortho substitution. The very high partition coefficient of 15 at pH 11.85 is of the same order of magnitude as that for 2-cyclohexylphenol, constituent 56. The higher boiling range for constituent 70 and the bathochromic shift for the ultraviolet absorption band indicate alkylation on the cycloalkyl ring. Constituent 81 is similar to 70 but not identical, as indicated by the slight shift in the mono-ortho band to 13.27 μ and the slight change in peak tube at pH 11.85 from 4 FC to 1 FC.

4. Indanones: Constituent 20 had no OH band in its infrared spectrum and had a strong band at 5.92 μ for the C=O group. The ultraviolet spectrum was that of a benzene-ring-substituted 1-indanone (*37*). An infrared band at 12.95 μ for three adjacent hydrogens on the benzene ring indicated that constituent 20 could be either 4- or 7-methyl-1-indanone. Constituent 21 was very similar to 20, except that there was no evidence for three adjacent hydrogens on the benzene ring. Since the partition coefficient of constituent 21 is appreciably greater than that of constituent 20, the methyl substituent must be situated in the latter so as to decrease the extent of keto-enol tautomerism as compared to the former. This suggests that constituent 20 is 4-methyl-1-indanone and constituent 21 is 6-methyl-1-indanone.

5. Indanols: Constituent 16 had ultraviolet and infrared spectra, which clearly indicated a 5-indanol structure. There were infrared bands for out-of-plane deformation vibrations of two adjacent hydrogens and also a single hydrogen. This indicated that the indanol was substituted in the saturated ring, and most likely the substituent would be a single methyl group to place this compound in the same distillate fraction in which 5-indanol itself (constituent 5) is the major component. In a similar manner, it was indicated that constituent 17 was a 4-indanol with a single methyl group in the saturated ring. Whereas the partition coefficients of 4- and 5-indanol at pH 11.20 are 0.68 and 0.79, respectively, the values for the methyl-4- and 5-indanol are 3.8 and 3.3, respectively; that is, they are reversed with respect to the parent compounds. This would seem to require the methyl group in the 1-position of the 5-indanol for the minimum increase of partition coefficient and the methyl group in the 3-position of the 4-indanol for the maximum increase.

Constituents 32 and 33 are both 5-indanols. In the infrared bands for out-of-plane hydrogen deformation there is a good match between 4-indanol and 2,3-xylenol, as well as between 5-indanol and 3,4-xylenol. Constituent 32, 7-methyl-5-indanol, identified by the ultraviolet and infrared spectra of an authentic specimen, has a good match with 3,4,5-trimethylphenol for seven bands in the out-of-plane region, whereas constituent 33 has a good match with 2,4,5-trimethylphenol for six bands in the out-of-plane region, indicating 6-methyl-5-indanol (b.p., 263°). Orthoalkylated isomers invariably have the highest partition coefficients, a fact that is in agreement with the relative positions of these two constituents.

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6. Indenols: Constituent 13 is a meta-substituted phenol, with split bands at 6.27 and 6.29 μ indicative of a conjugated olefinic group. Although this split band is not unique for conjugated olefins the absorption at 290 and 307 mμ indicates a dinuclear system, such as in indenes, which absorb in the range 290–295 mμ. There is a 16-mμ increase in the longest wavelength band in going from indan to 5-indanol. From this it might be expected that the longest wavelength band of 5-indenol would be 293+16=309 mμ as compared with the 307 mμ band observed. The longest wavelength band of a 2,3-disubstituted-6-indenol has been given as 305 mμ (*105*). From all of this evidence it seems certain that constituent 13 is 5-indenol (b.p., 259°) or its nearly identical isomer, 6-indenol. The partition coefficient of 0.31 at pH 11.20 is considerably lower than the 0.79 for 5-indanol, as would be expected upon introducing an olefinic group.

Constituent 27 had an infrared spectrum, which showed the split at 6.14, 6.17, and 6.28 μ indicative of an olefinic group conjugated with a benzene ring (*30*). Also, a band at 7.25 μ indicated an indene-type structure, and a band at 14.14 μ indicated a 2,3-substituted phenol. Thus, this constituent must be a 4-indenol with no additional substitution on the benzene ring. However, since 4-indenol boils around 250°, this constituent must have a methyl group on the five-membered ring. The methyl-4-indenol structure was confirmed by comparison of the ultraviolet bands at 309.6, 299.7, 288.6, 265, 260.7, and 254.5 mμ with the bands obtained with a sample of 4-indenol synthesized from 4-indanol by R. E. Dean, Coal Tar Research Association, Leeds, England. This sample consisted of more indanol than indenol, but characteristic bands at 306, 300, 289.0, 265, 260, and 252.0 mμ could be picked out. Constituent 12 was clearly 4-indenol itself, for although the longest wavelength band was obscured, there were three other ultraviolet bands and nine infrared bands that checked well with the synthetic material. A synthetic sample of 5-indenol was also available, which likewise consisted of more indanol than indenol. The longest wavelength band of this impure sample was 304.4 mμ rather than the 307.0 mμ found for constituent 13. This discrepancy may be due to a difference in the ratio between 5- and 6-indenol, both of which could be produced from 5-indanol. However, two other ultraviolet bands and nine infrared bands checked well with the synthetic material. The relative positions of 4-indenol (constituent 12) and 5-indenol (constituent 13) are the same as for 4- and 5-indanol. The sample of 4-indenol had long wavelength bands completely isolated from the rest of the spectrum, which allowed determination of the partition coefficient even though the sample had more indanol than indenol. Using this value, a good check between calculated and experimental peak tube was obtained.

7. Naphthols: The spectra of only a relatively small number of the alkylated 1- and 2-naphthols were available for comparison with those of samples isolated by countercurrent distribution. However, the ultraviolet spectra of a large number of alkylated naphthalenes were available, and it was found that the longest wavelength absorption bands of the alkylated naphthols could be estimated quite closely from the spectra of the corresponding naphthalenes. For example, the value of the band for 3-methyl-2-naphthol can be estimated by adding to the value for 2-naphthol the value of the bathochromic increment in going from 2-methylnaphthalene to 2,3-dimethylnaphthalene. These estimated values could not, of course, be used for positive proof of identity of individual isomers.

The naphthols were all readily identified as either 1- or 2-naphthols from the highly characteristic shapes and relative intensities of the ultraviolet absorption bands; these were altered very little by the presence of alkyl groups. The degree of bathochromic shift of these bands from the wavelength values for the parent compounds was an immediate indication of either monomethyl or dimethyl substitution. The hydrogen out-of-plane deformation vibration region around 11 to 15 μ was useful in determining possible arrangements of hydrogen atoms and hence of methyl groups.

Constituent 55, a dimethyl (or ethyl)-1-naphthol, had a strong infrared band at 12.52 μ, indicative of two adjacent hydrogens and suggesting 2-alkyl substitution as in 2-methyl-1-naphthol, 12.52 μ. This constituent almost certainly had ortho substitution in order to have a partition coefficient as high as 30 at pH 9.94. It is not 2-methyl-1-naphthol itself, because its prominent analytical band is only 324.4 mμ, determined with an authentic specimen, as compared with 328.2 mμ for constituent 55. Strong infrared bands at 14.53 and 13.48 μ indicate four adjacent hydrogens as in 2-methyl-1-naphthol, 14.55 μ, and 4-methyl-1-naphthol (constituent 52), 13.52 μ. From this it appears that constituent 55 must be a 2-alkyl-1-naphthol and could be 2-ethyl-1-naphthol.

There were six distinct countercurrent distribution peaks that were readily determined to be due to monomethyl-2-naphthols. The 5-isomer was immediately excluded on the basis of the available infrared spectrum of this compound, leaving equal numbers of constituents and isomers. Constituent 54 was positively identified as 1-methyl-2-naphthol by means of

the available infrared spectrum of this compound. Constituent 53, which immediately preceeds 1-methyl-2-naphthol in the countercurrent distribution, must also have orthosubstitution to have such a large partition coefficient. Thus, constituent 53 appears to be 3-methyl-2-naphthol (b.p., 302°). Constituent 50 had a strong band at 13.40 μ, indicating four adjacent hydrogens. The low partition coefficient of 2.5 at pH 9.94 confirmed the exclusion of the 1- and 3-methyl isomers already proposed for other constituents. Thus, constituent 50 appeared to be 4-methyl-2-naphthol. Constituent 78 had strong bands at 14.30 and 13.16 μ, indicative of three adjacent hydrogens. Since the 5-isomer was excluded, it appeared that constituent 78 was 8-methyl-2-naphthol (b. p., 320°).

8. Fluorenols: Constituent 74 has ultraviolet absorption bands very similar to those for 8-methyl-2-fluorenol (*78*). However, the longest wavelength band in the region around 311 mμ is held in common by other methyl-2-fluorenols and also methyl-3(and 4)-fluorenols. The longest wavelength bands for methyl-1-fluorenols are at wavelengths at least 10 mμ lower. Thus, constituent 74 is a methyl-2-, 3-, or 4-fluorenol.

SUMMARY OF TAR ACIDS AND TAR BASES IDENTIFIED AND THEIR AMOUNTS

GENERAL RESULTS

The results of the qualitative and quantitative analytical procedures for the tar acids and tar bases are summarized in table 34. The compounds have been arranged in this table according to groups involving the same fundamental ring structures. Approximately 130 individual compounds were identified, mostly with respect to individual isomers, and the amounts were determined, or estimated, in nearly all instances.

NATURE OF TAR ACIDS

Seven different fundamental ring structures were observed among the tar acids. These were:

1. Phenol
2. Indanol
3. Indenol
4. Tetrahydronaphthol
5. Phenylphenol
6. Naphthol
7. Fluorenol

In addition, aliphatic carboxylic acids were present in all boiling ranges, and indanones were present as impurities in a few fractions. The latter were apparently capable of functioning as acids in alkaline solutions, probably through a keto-enol mechanism.

The individual tar acids identified consisted of these seven fundamental structures; mostly methyl groups and some ethyl groups were attached. About 3 tar acids had isopropyl groups, and about 10 had n-propyl groups, but no phenols with butyl groups or higher could be found. Cyclohexyl groups and probably also cycloalkenyl groups were present. A small proportion of alkenyl groups, like propenyl, were likewise present. Alkylphenols with a total of more than 6 carbon atoms in alkyl groups were apparently absent. The most prevalent class of phenol among the high-boiling tar acids was the naphthols.

TABLE 34.—*Summary of tar acids and tar bases identified in a low-temperature bituminous-coal tar, and their amounts*

Tar acids (distillable tar acids, wt.-pct.) [1]	Tar bases (distillable tar bases, wt.-pct.) [2]	
Phenol (2.3)		Aniline (0.26).
o-Cresol (5.6)		
m-Cresol (7.2)		3-Methylaniline (0.48).
p-Cresol (4.9)		
o-Ethylphenol (1.5)		2-Ethylaniline (0.22).
m-Ethylphenol (2.5)		
p-Ethylphenol (2.5)		
2,3-Xylenol (1.3)	2,3-Dimethylpyridine (0.01)	
2,4-Xylenol (9.1)	2,4-Dimethylpyridine (0.45)	
2,5-Xylenol (3.7)		2,5-Dimethylaniline (0.22).
2,6-Xylenol (1.4)		2,6-Dimethylaniline (0.60).
3,4-Xylenol (3.7)		
3,5-Xylenol (5.9)	3,5-Dimethylpyridine (0.04)	3,5-Dimethylaniline (0.77).
		N,N-Dimethylaniline (0.06).
		N-Methyl-2-methylaniline (0.16).
2,3,5-Trimethylphenol (3.3)	2,3,5-Trimethylpyridine (0.58)	
2,3,6-Trimethylphenol (0.01)		
2,4,6-Trimethylphenol (1.4)	2,4,6-Trimethylpyridine (0.87)	
3,4,5-Trimethylphenol (0.13)		
3-Ethyl-2-methylphenol (0.01)		
3-Ethyl-4-methylphenol (0.01)	3-Ethyl-4-methylpyridine (0.88)	
3-Ethyl-5-methylphenol (2.1)		
4-Ethyl-2-methylphenol (4.5)	4-Ethyl-2-methylpyridine (0.11)	
5-Ethyl-2-methylphenol (0.01)	5-Ethyl-2-methylpyridine (0.48)	
2-n-Propylphenol (0.01)		
3-n-Propylphenol (0.01)		
4-n-Propylphenol (0.13)		
4-Isopropylphenol (0.01)	4-Isopropylpyridine (0.09)	
	2,3,4,6-Tetramethylpyridine (0.99)	
2,3,5,6-Tetramethylphenol (0.04)	2,3,5,6-Tetramethylpyridine (0.24)	
	2,6-Dimethyl-4-ethylpyridine (0.45)	
	3,4-Diethylpyridine(?) (0.63) [3]	
3-Methyl-5-n-propylphenol(?) (0.29)		
2-Methyl-5-isopropylphenol (0.01)		
2-Ethyl-6-n-propylphenol(?) (0.26)		
3-Ethyl-4-n-propylphenol(?) (0.12)		
4-Ethyl-3-n-propylphenol(?) (0.24)		
4-Isopropyl-3-n-propylphenol(?) (0.14)	(4)	
2,4-Di-n-propylphenol(?) (0.13)		

See footnotes at end of table.

TABLE 34.—*Summary of tar acids and tar bases identified in a low-temperature bituminous-coal tar, and their amounts*—Continued

Tar acids (distillable tar acids, wt.-pct.) [1]	Tar bases (distillable tar bases, wt.-pct.) [2]	
2,4- or 3,4-Dialkylphenol(?) (0.02)		
3-Methyl-2-propen-1-ylphenol(?) (0.003).		
Alkenylphenol I (0.005)		
Alkenylphenol II (0.001)		
Alkenylphenol III (0.03)		
2-Cyclohexylphenol (0.20)		
2-Alkylcycloalkylphenol I (0.02)		
2-Alkylcycloalkylphenol II (0.01)		
Cycloalkenylphenol I(?) (0.005)		
Cycloalkenylphenol II(?) (0.04)		
4-Indanol (0.53)	2,3-Cyclopentenopyridine (0.16)	
5-Indanol (0.49)		
1-Methyl-5-indanol(?) (0.36)		
3-Methyl-4-indanol(?) (0.09)		
	4-Methyl-1-indanone (?) (0.15)	
6-Methyl-5-indanol (?) (0.005)	6-Methyl-1-indanone (?) (0.01)	
7-Methyl-5-indanol (0.10)	Alkyl indanone (0.03)	
4-Indenol (0.03)		
5-Indenol (0.27)	[4]	
1-, 2-, or 3-Methyl-4-indenol (0.14)		
Methyl indenol (0.08)		
1-, 2-, or 3-Polyalkyl-4-indenol (0.13)		
3,4-Dinuclearphenol (0.06)		
5, 6, 7, 8-Tetrahydro-1-naphthol (0.02)		
5,6,7,8-Tetrahydro-2-naphthol (0.02)		
	Alkyl-5,6,7,8-tetrahydroquinolines (?).	
2-Phenylphenol (0.08)	2-Phenylpyridine (1.03)	
3-Phenylphenol (0.03)		
4-Phenylphenol (0.37)	4-Phenylpyridine (1.21)	
	2-Methyl-6-phenyl-pyridine (?) (0.72).	Alkylphenylanilines (?).
		N-Benzyl-2-methylaniline (0.19).
		N-Benzyl-4-methylaniline (0.29).
1-Naphthol (0.20)	Quinoline (1.86)	
2-Naphthol (1.54)		2-Naphthylamine (0.63).
1-Methyl-2-naphthol (0.02)		
3-Methyl-2-naphthol (?) (0.008)	2-Methylquinoline (2.36)	
4-Methyl-1-naphthol (0.04)	4-Methylquinoline (3.21)	
4-Methyl-2-naphthol (?) (0.11)		
6-Methyl-2-naphthol (?) (0.01)	6-Methylquinoline (0.44)	
7-Methyl-2-naphthol (?) (0.05)	7-Methylquinoline (1.02)	
8-Methyl-2-naphthol (?) (0.02)	8-Methylquinoline (0.33)	
2-Ethyl-1-naphthol (?) (0.85)		
	2,4-Dimethylquinoline (5.92)	
2,5- or 2,7-Dimethyl-1-naphthol (?) (0.008).		
2,6-Dimethyl-1-naphthol (?) (0.008)	2,6-Dimethylquinoline (1.95)	
	2,7-Dimethylquinoline (1.36)	
	2,8-Dimethylquinoline (1.89)	
	3,4-Dimethylquinoline (?) (1.33)	
	4,6-Dimethylquinoline (?) (1.32)	
5,7-Dimethyl-1-naphthol (?) (0.05)		
	2,4,6-Trimethylquinoline (3.41)	
	2,4,7-Trimethylquinoline (2.85)	
	2,4,8-Trimethylquinoline (2.81)	
	2,6,8-Trimethylquinoline (2.25)	
Methyl-2-, 3-, or 4-fluorenol (0.06)		
	Acridine (2,3-benzoquinoline) (0.13).	
	2,4-Dimethylbenzo[g]quinoline (?).	
[5]	Phenanthridine (3,4-benzoquinoline) (0.48).	
	Benzo[f]quinoline (5,6-benzoquinoline) (2.13).	
	Benzo[h]quinoline (7,8-benzoquinoline) (1.64).	
	2,4-Dimethylbenzo[f]quinoline (?).	
	2,4-Dimethylbenzo[h]quinoline (?).	

[1] The distillable tar acids constitute 3.62 wt.-pct. of the tar.
[2] The distillable tar bases constitute 0.31 wt.-pct. of the tar.
[3] (?) indicates uncertainty as to which isomer is present.
[4] No data available on tar bases in these groups because of lack of spectra of pure compounds.
[5] Tar acids in these groups were not distillable.

Nine individual tar acids were identified; each comprised more than 3 weight-percent of the total tar acids and together comprised nearly one-half of the total tar acids. All were low-molecular-weight alkylphenols, as follows: o-, m-, and p-cresol, 2,4-, 2,5-, 3,4-, and 3,5-xylenol, 2,3,5-trimethylphenol, and 4-ethyl-2-methylphenol.

NATURE OF TAR BASES

Eight different fundamental ring structures were observed among the tar bases. These were:

1. Pyridine
2. Cyclopentenopyridine
3. Phenylpyridine
4. Quinoline
5. Benzoquinoline
6. Aniline
7. N-benzylaniline
8. Naphthylamine

Two other ring structures appeared to be present, although no individual compounds could be identified; these were tetrahydroquinoline and phenylaniline. These structures covered the boiling range from initial boiling point to about 355° C. It would appear to be certain that the polycyclic structures also would be present in the distillation residue or "pitch."

The individual tar bases identified consist of these eight fundamental structures, with mostly methyl and some ethyl groups attached. One compound with an isopropyl group was identified, but no alkyl groups with chain lengths greater than 2 carbon atoms were observed. Under the conditions of formation of the tar (500° C.), alkyl chains of three or four carbons could conceivably cyclize to form fused saturated rings, as exemplified by cyclopentenopyridines and tetrahydroquinolines. The spectra of alkyl derivatives of these compounds were not available but 2,3-cyclopentenopyridine was definitely identified, and tar-base-distillate fractions 10 to 20 (fig. 7) appeared to contain appreciable amounts of alkyl-5,6,7,8-tetrahydroquinolines. There was no doubt, from the ultraviolet spectra of these fractions, that they were rich in some kind of pyridine, that is, compounds with a pyridine ring but no other unsaturated ring in the molecule. Yet the boiling range of these fractions was above the boiling points of the known highly alkylated pyridines. On the other hand, the boiling points of the known alkyl-5,6,7,8-tetrahydroquinolines, which have a pyridine ring but no other aromatic ring, covered the boiling range for fractions 10 to 20 quite closely.

Eight individual tar-base compounds were identified; each comprised more than 2 weight-percent of the total tar bases and together they comprised fully one-fourth of the total tar bases. All were quinolines, as follows: 2- and 4-methyl-quinoline, 2,4-dimethylquinoline, 2,4,6-, 2,4,7-, 2,4,8-, and 2,6,8-trimethylquinoline, and benzo[f]quinoline. From this standpoint one can say that quinolines, especially those alkylated in the 2- and 4-positions,are the compounds that best typify the tar bases from low-temperature bituminous coal tar and not pyridines, as might have been assumed.

CORRELATION OF TAR ACID AND BASE COMPOSITION WITH COAL STRUCTURE

GENERAL CONSIDERATIONS

Availability of the results of an extensive characterization of both the tar acids and tar bases in a single low-temperature tar rather naturally led to consideration of the possibility of correlating tar composition with coal structure.

Not much is known about the dependence of tar composition on coal structure. It has been demonstrated by Orning and Greifer (*86*) that if a coal sample is heated at 510° C. under conditions of molecular distillation, the distillate has an identical infrared spectrum and therefore the same general molecular configuration as the coal. Under these conditions, once the molecules (radicals) are released from the pores of the coal particles they do not enter into any collisions with each other or the walls of the vessel until they strike the condensing surface. Therefore secondary reactions are limited to those occurring before release from the coal particle and after condensation, and these must not be extensive. Under the conditions of commercial or experimental low-temperature carbonization there are many collisions of released molecules or radicals with each other, the surface of the char particles, and the walls of the vessel. The longer the residence time the less "primary" the tar is at the same carbonization temperature. Modern fluidized-bed, low-temperature carbonization can involve relatively short average residence times (down to some seconds, only) and when conducted at 500° C. or lower presumably produces a tar with significant primary characteristics.

It is known that coal is heterogeneous and frequently contains organic residues, which are little altered from the original plant material. These are typically water-insoluble, relatively heat-stable compounds, such as natural waxes. From available evidence there seems little reason to doubt that such substances are distilled with little alteration under conditions of true low-temperature carbonization. Vahrman (*111*) showed that the chloroform eluates from an alumina column of both coal extracts and their respective low-temperature tars were similar ester fractions with a pinelike odor. The yields of ester fractions from the coals were paralleled by smaller but approximately proportionate amounts of ester fractions from the respective tars. In the present report it is shown that there are long-chain aliphatic carboxylic acids throughout the entire high boiling range from about 240°–330° C.; these include compounds like myristic acid, which are widespread in plant esters.

The "resinols," namely the benzene-soluble, petroleum ether-insoluble materials of a low-temperature bituminous coal tar, were examined by Vahrman (*112*). Upon either pyrolysis or hydrogenation of the resinols it was found that the main product was a mixture of lower phenols. These resinols had molecular weights of 300 to 600, were thermoplastic resins, and from their infrared spectra and other considerations were thought to be linear polymers of monocyclic rings linked by ether oxygen. This is a structure that is related in a broad sense to the structure commonly assigned lignin.

By means of X-ray scattering intensities, Ergun (*32*) has shown that both the high-vacuum distillate and the residue from a bituminous coal vitrinite contained aromatic layers. The vitrinite contained 36 percent volatile matter and was conceived as a polymer of planar aromatic nuclei with 1 to 3 rings, which depolymerizes upon heating, setting some of the structural entities free as vapor. This finding appears to be analogous to that of Vahrman with respect to the resinols.

From the extensive studies by many investigators of the oxidation reactions and products of coal, recently reviewed by Yohe (*121*), the firm conclusion is drawn that coal is comprised of high-molecular-weight substances, containing single and condensed aromatic rings, and aliphatic structures (including oxygen linkages) as connecting chains between aromatic nuclei or as parts of hydroaromatic units. It is clear that depolymerization of these high-molecular-weight substances would produce mainly alkylated and hydroxylated aromatics rather than the parent hydrocarbons, and it is indeed observed that under these conditions the parent hydrocarbons are found only in small amounts. For example, whereas coke-oven tars contain around 10 percent naphthalene, true low-temperature tars contain only about 0.1 percent naphthalene but do contain a significant amount of combined alkylated naphthalenes.

There is no question about the fact that, although the bituminous low-temperature tar acids and bases were rich in alkylated derivatives, there were no aromatic rings among the tar acids and bases that had long alkyl groups attached to them. The Low-Temperature Tar Laboratory researchers were unable to detect a single normal-butylated compound among about 130 tar acids and bases with aromatic rings, although an excellent collection of authentic specimens and spectra of these compounds was available to them. It is conceivable that cyclization reactions leading to structures of the indan and tetrahydronaphthalene type have accounted for the lack of n-butylated aromatics and the presence of these hydroaromatic structures in the tar. However, there is every reason to believe that the hydroaromatics could have been released from the coal; in addition, identification of about 10 phenols with n-propyl groups is difficult to explain if cyclization is occurring so extensively. The tentative conclusion might be reached that the connecting aliphatic chains in the coal polymers are limited essentially to 3 carbon atoms. Once again this is suggestive of the polymeric structure usually assigned to lignin. Another observation about the low-temperature tar acids and bases is that one can apparently expect to find the same fundamental ring structures whether they are in the tar acids or tar bases (table 34). (Lack of authentic specimens and their spectra prevented this interesting comparison from being complete in all details.) This suggests a common origin in the form of repetitive units in a polymeric structure.

THERMODYNAMIC AND KINETIC DISTRIBUTIONS OF ISOMERS

The tar acids and bases obtained by low-temperature (500° C.) carbonization of coal may be examined either from the standpoint of chemical thermodynamic equilibria or chemical kinetics (*55*). In the former case, if thermodynamic equilibrium has been achieved under the conditions of carbonization, the proportions of various isomers will be the same as those predicted by theory. In the latter case, if thermodynamic equilibrium is far from being obtained, owing to insufficient time (residence time at 500° C.), then the most abundant isomers would be those predicted from the relative rates of formation. At thermodynamic equilibrium the more abundant isomers would be the more stable isomers, while at times relatively short, compared with those required to approach equilibrium, the more abundant isomers would be the ones formed at the fastest rates. These could be the same isomers in both cases, although this generally should not be expected.

Not a great deal of precise information is available on the proportions of isomers at equilibrium at various temperatures, as determined by studies in chemical thermodynamics. Data required for the present comparison were obtained from experiments by others in isomerization and other reactions in which the investigators concluded that equilibrium distribution of isomers had been approached. An example of this would be the work by Pigman, Del Bel, and Neuworth (*91*) on the silica-alumina catalyzed isomerization of xylenols at 344° C. Catalysts may be utilized to speed up the approach to equilibrium at a given temperature without distorting the proportions of isomers, as shown experimentally by Rossini, Mair, and Streiff (*98*). The relative amounts of the four C_8 alkylbenzenes in five different catalytically cracked gasolines were shown to be very close to the amounts predicted for thermodynamic equilibrium. This does not mean, of course, that all data on catalytic reactions represent equilibrium conditions; in fact, in most cases thermodynamic equilibrium probably is not reached. In the ideal case, if it can be shown that independent of the nature or proportions of the reactants and independent of the nature of the catalyst the same distribution of isomers is obtained, then it can be assumed that thermodynamic equilibrium has been obtained at the temperature stated.

Whereas the reaction mechanisms need not be known in a consideration of the thermodynamic equilibria, a knowledge of them is required in an examination of products obtained under nonequilibrium conditions. The compounds involved in the present comparisons probably should be considered as having been formed in a free radical process. These isomeric compounds would all be in the gas phase at 500° C., and at these conditions of phase and temperature it is generally assumed that a free radical mechanism is predominant. An ionic mechanism at 500° C. would almost certainly imply that the reactions were dominated by powerful, specific catalysts, that is, that conditions were predominantly those encountered in intentionally catalytic processes. The metal walls of the carbonizing equipment and the char (or the minerals in the char) at 500° C. probably exert a relatively mild, nonspecific catalytic effect on the reactions being discussed. This seems quite likely to be limited to radical initiation on the surface of the metal or the char by the removal of a hydrogen atom, the radical chain then being propagated in the gas phase.

It is generally accepted that a rate-determining factor in free radical substitution on

an aromatic nucleus is the free valence index, F_r, at each carbon atom, r. A simplified concept of the free valence index is that it is equal to the percentage importance of a structure containing a lone electron on a carbon atom; the values of F_r for the carbon atoms of a given aromatic structure are obtained by molecular orbital calculations. Isomeric compounds, structurally related to the reactant isomers of largest values of F_r, will be formed at the fastest rates and thus will predominate in the nonequilibrium mixture. Thus, among given disubstituted benzenes, like cresols or dialkyl benzenes, those with 1,2-substitution are formed the most rapidly because the 2-position of a benzene ring has the largest F_r value (*63*). Conversely, among these same dialkyl benzenes, those with 1,3-substitution are more stable (*107*) at 500° C. If for a given set of disubstituted benzene isomers in a low-temperature coal tar the 1,2-isomer is predominant, then thermodynamic equilibrium was far from being achieved, and approximate isomeric distributions should be predictable from the free valence indices. On the other hand, if for this set of disubstituted benzene isomers the 1,3-isomer is predominant, then thermodynamic equilibrium was approached fairly closely, and approximate isomeric distributions should be predictable from whatever useful information on chemical thermodynamic equilibria happens to be available.

Kooyman and Farenhorst (*63*) have experimentally established that

$$F_{max}=a \log K'_r+b \quad (1)$$

for a series of aromatic hydrocarbons, where F_{max} is the highest free valence number calculated for each molecule by the molecular orbital method and K'_r is the reactivity for the CCl_3 radical reaction. The differences between the free valence numbers within each molecule are so considerable that reactivity can be expected to be mainly due to the most reactive positions; that is, F_{max} is in effect F for the most reactive position, which is the ortho position for a monosubstituted benzene ring. K'_r is evaluated by determining the relative reactivity of the aromatic hydrocarbon, that is, by comparing the rate constant for the hydrocarbon to the rate constant for some standard in a competitive reaction with the CCl_3 radical. The values of K'_r are independent of the numerical value for the rate constant of the standard, so that the relative reactivity of each hydrocarbon is directly proportional to the rate constant for that hydrocarbon. It can be assumed that the slope of the line would remain nearly the same for the closely analogous CH_3 radical. In addition it can be assumed that alkylbenzenes would be very similar to benzene, phenylpyridines to biphenyls, methylquinolines to naphthalenes, and so on, in these free radical reactions, so that these compounds would fall fairly close to Kooyman and Farenhorst's plot and the same value of a would apply to them.

Since $K'_r=k_A/c$, where k_A can be the rate constant for isomer A in the free radical reaction and c is a constant, and since F_{max} is in effect F for the most reactive position, equation 1 may be rewritten as $F_A=a \log (k_A/c)+b$, F_A being the free valence number for isomer A, or

$$k_A/c=10^{(F_A-b)/a}. \quad (2)$$

From this,

$$k_A/k_B=(10^{F_A/a})/(10^{F_B/a}). \quad (3)$$

The ratios of isomers will be independent of the concentrations of the reacting species, as shown by Ingold and Shaw (*48*) for competitive substitution reactions. This means that at any given time in the initial period of reaction the mole-percent of any of the isomers is directly proportional to its rate constant.

With the inclusion of a term (p) for the number of equivalent positions, the following relationship is obtained:

$$\text{Mole-percent } A/\text{mole-percent } B=p_Ak_A/p_Bk_B$$
$$=(p_A10^{F_A/a})/(p_B10^{F_B/a}). \quad (4)$$

This equation has the same form as those that can readily be derived from equations presented by Glasstone, Laidler, and Eyring (*39*) for determining the relative amounts of ortho-, meta-, and para-substitution in ionic reactions. Comparison of these equations with equation 4 shows that the term a is directly proportional to the absolute temperature, which is, of course, required by the general theory of absolute reaction rates. Kooyman and Farenhorst have experimentally determined the value of a at 91° to be about 0.022; at 500° a should be 0.047.

The approximate isomeric distributions can be obtained from the free valence numbers or indices by means of equation 4. These could be called the "kinetic" distributions, compared with the thermodynamic equilibrium distributions. The values for these two types of isomeric distributions are listed in table 35 for 28 tar acids and bases and their amounts found in the low-temperature bituminous coal tar produced at 500° C. by fluidized carbonization.

The accuracy of the quantitative determinations of the tar components was generally quite adequate for the comparisons made in table 35. These quantities were determined by infrared analysis, or gas-liquid chromatography, or both.

TABLE 35.—*Isomeric distributions of tar acids and bases, compared with thermodynamic equilibrium and kinetic distributions*

Compounds	Isomeric distribution in tar, mole-percent	Thermodynamic equilibrium distribution, mole-percent	Free valence, F_r, of position substituted	Kinetic distribution, mole-percent
			Pyridine: [2]	
2-Phenylpyridine	46	[1] 53	Ortho, 0.091	51
3-Phenylpyridine	0	[1] 32	Meta, 0.079	29
4-Phenylpyridine	54	[1] 15	Para, 0.086	20
			Quinoline: [3]	
2-Methylquinoline	32		2-position, 0.344	23
3-Methylquinoline	0		3-position, 0.290	1.5
4-Methylquinoline	44		4-position, 0.356	43
5-Methylquinoline	0		5-position, 0.338	17
6-Methylquinoline	6		6-position, 0.290	1.5
7-Methylquinoline	14		7-position, 0.296	2
8-Methylquinoline	4		8-position, 0.331	12
			Aniline: [4]	
2,5-Dimethylaniline	14		Ortho, 0.425	50
2,6-Dimethylaniline	38		Meta, 0.397	40
3,5-Dimethylaniline	48		Para, 0.415	10
			N-Methylaniline: [4]	
N-Benzyl-2-methylaniline	40		Ortho, 0.431	62
N-Benzyl-3-methylaniline	0		Meta, 0.399	13
N-Benzyl-4-methylaniline	60		Para, 0.426	25
			Phenol: [7]	
o-Cresol	31	[5] 18	[6] 21	Ortho, 0.410	49
m-Cresol	41	[5] 60	[6] 61	Meta, 0.399	28
p-Cresol	28	[5] 22	[6] 18	Para, 0.408	23
2,3-Xylenol	5	[8] 9	[9] 10		16
2,4-Xylenol	36	[8] 30	[9] 26		30
2,5-Xylenol	15	[8] 24	[9] 22		16
2,6-Xylenol	6	[8] 11	[9] 2		10
3,4-Xylenol	15	[8] 12	[9] 17		22
3,5-Xylenol	23	[8] 14	[9] 23		6
o-Ethylphenol	23		[9] 21		49
m-Ethylphenol	38		[9] 60		28
p-Ethylphenol	38		[9] 19		23

[1] At 105° C.; (*45*).
[2] (*28*).
[3] (*101*).
[4] (*90*).
[5] At 164° C. with $AlCl_3$; (*77*).
[6] At 380° C.; (*58*).
[7] (*72*).
[8] At 344° C.; (*91*).
[9] At 450° C. with AlF_3; (*82*).

The infrared values had maximum deviations of about ±5 percent from the true values for distillate fractions containing only about three components and deviated up to about ±10 percent for fractions containing about six or more components; that is, a value of 20 percent for a component in such a fraction was actually 20 ±2 percent. The gas-liquid chromatography values were demonstrated to have deviated not more than ±3 percent from the true values when the peaks were essentially completely resolved and up to about ±5 percent for typical overlapping peaks. The reliability of the thermodynamic values is perhaps best indicated by the fair agreement between Given's values at 380° C. and Pigman, Del Bel, and Neuworth's values at 344° C. for the xylenols, and the good agreement between Given's values at 380° C. and Meissner and French's values at 164° C. for the cresols. The values of F_r are probably fairly reliable, since in several cases these were calculated by two different methods with fairly good agreement. The kinetic distribution values, however, should be considered as approximations, although a twofold change in the value of a, for example, would generally have little effect on the distribution values.

Examination of table 35 shows no overall agreement of isomeric distributions in the tar with either thermodynamic equilibrium distributions or kinetic distributions, although some isolated instances of fair agreement can be picked out, as for the thermodynamic distributions of the xylenols or the kinetic distributions of the methyl quinolines. This cannot be explained solely on the basis of inaccuracies, in view of the previously discussed accuracy of these values. Of particular significance is the large proportion of tar values that fall completely outside of the range presented by the combined thermodynamic and kinetic systems.

Most striking of all was the number of instances in which the para isomer predominated. Referring to tables 34 and 35 the para isomers of phenylpyridine, N-benzylaniline, n-propylphenol, and phenylphenol were present in the greatest amount. Only the para isomers of isopropylphenol and isopropylpyridine could be detected. In addition, the para isomers of cresol and ethylphenol, although not quite present in the greatest amount, were present in considerably larger amounts than would be expected from the thermodynamic distribution, which predicts a predominance of meta isomer, or the kinetic distribution, which predicts a predominance of the ortho isomer.

A particularly clear-cut example of the predominance of the para isomer among both the cresols and the ethylphenols can be seen for all four subbituminous tars listed in table 1.

These tars were obtained under very carefully controlled carbonization temperatures in a fluidized-bed carbonizer with relatively short residence time. The temperaures were as follows: Stansbury, 510° C.; Hanna, 510° C.; Big Horn, 499° C.; Wyodak, 482° C.

Here again, the structure usually assigned to lignin can be called upon for a plausible explanation. The products of depolymerization of lignin are generally explained by the assumption that the main building block in lignin is something comparable to 1-n-propyl-3-methoxy-4-hydroxybenzene (*16*). The oxygen in the hydroxy group is derived from an ether linkage between the benzene ring and one of the chain carbons, which is fundamental to the polymeric nature of the lignin, whereas the methoxy group exists as such in the polymer. In going from lignin to lignite to bituminous coal, oxygen is lost, and it is evident that one process involved could be the loss of these methoxy groups or their equivalent in the lignin-derived polymers. This is shown by the fact that catechol derivatives are the major phenolic compounds obtained upon depolymerization of lignin and are also present in somewhat smaller but still relatively large amounts in low-temperature lignite and brown-coal tars, whereas the low-temperature tars from bituminous coals contain only small or trace amounts of catechols. From these considerations it might be expected that something comparable to 1-n-propyl-4-hydroxybenzene would be a significant building block in the lignin-derived polymeric structures of the subbituminous coals, and that para isomers would be the most prevalent among the monoalkyl phenols released upon depolymerization.

SYNTHESIS OF AUTHENTIC SPECIMENS OF TAR ACIDS AND TAR BASES

PURPOSE OF SYNTHESIS PROGRAM

Authentic specimens of tar acids and tar bases were required for ultraviolet and infrared spectra, retention times in gas-liquid chromatography, partition coefficients in countercurrent distribution, and boiling points in fractional distillation. A few pure compounds were synthesized to meet these essential needs at least partially. Lack of available man-hours prevented the synthesis program from being as extensive as dictated by the requirements of the characterization research.

SYNTHESIS OF PHENOLS

Hawthorne has presented a procedure for converting aryl halides to the corresponding phenols, in which he demonstrated good yields for phenol, 1-naphthol, and 4-methylphenol (*42*). Since a relatively large number of aryl halides has been made available for purchase in recent years, this apparently general method of synthesizing phenols seemed to offer an appealingly ready route for preparing authentic specimens. However, it was soon discovered that most of the higher molecular-weight aryl halides gave little or no phenol according to the procedure described by Hawthorne.

The difficulty was readily shown to lie in lack of oxidation of the arylboronic acid with 10 percent hydrogen peroxide. Good yields of the arylboronic acid could be obtained from the action of methyl borate with the arylmagnesium halide, but the subsequent oxidation to the phenol failed to take place. Kuivila (*68*) has demonstrated that the reaction of hydrogen peroxide with benzene-boronic acid proceeds by way of the hydroperoxide ion, HOO^-, which attacks the boron atom. The rate of the reaction depends on concentration of hydroperoxide ion, as shown by Kuivila; it is also logical to assume that an increase in reaction temperature will increase the reaction rate. Therefore, 30 percent hydrogen peroxide was used in place of 10 percent hydrogen peroxide; and, possibly of more importance, the original refluxing ether solution employed by Hawthorne during the oxidation step was replaced by a refluxing benzene solution. This meant an increase of about 45° C. in the reaction temperature. Under these conditions most of the high-molecular-weight arylboronic acids were readily oxidized to the corresponding phenols (*119*).

Preparation of the Grignard reagents was straightforward, although some of the aryl halides, such as 2-bromofluorene and 5-bromoacenaphthene, were insufficiently reactive and required introduction of ethyl bromide to keep the magnesium active (*35*). After the Grignard reagent was added to the ether solution of the trimethyl borate, as described by Hawthorne, the reaction mixture was refluxed 15 minutes as recommended by Seaman and Johnson for increased yields of arylboronic acid (*103*). Nearly all of the ether was removed by evaporation over a water bath, and an equivalent volume of benzene was added. This benzene solution was heated to reflux, and 30 percent hydrogen peroxide was added slowly in a nitrogen atmosphere and the reaction mixture refluxed for 45 minutes. The remainder of the procedure was essentially that described by Hawthorne. Yields were based on the aryl halides.

2-Fluorenol. Yield, 23 pct. M.p., 169°-170° [lit. (*43*) 171°]; $\lambda_{max}^{cyclohexane}$ 315.2, 308.3, 304.0, 282.3, 276.5, 271.0, 267.0, 262.0 mμ (log ε 3.76, 3.72, 3.74, 4.18, 4.25, 4.33, 4.30, 4.22). Reported (*37*), $\lambda_{max}^{cyclohexane}$ 315.2, 308.3, 304.0, 282.3, 276.5, 271.0, 267.0, 262.0 mμ (log ε 3.75, 3.70, 3.74, 4.17, 4.24, 4.32, 4.31, 4.26).

Anal. Calculated for $C_{13}H_{10}O$: C, 85.69, H, 5.53. Found: C, 85.69; H, 5.54.

Acetate, m.p. 129°–130° [lit. (*73*) 130°].

Benzoate, m.p. 169.5°–171° (not previously reported).

Anal. Calculated for $C_{20}H_{14}O_2$: C, 83.89, H, 4.93. Found: C, 83.83; H, 5.01.

5-Acenaphthenol. Yield, 15 percent. M.p. 121.5°–123° [lit. (*96*) 125°–126°].

Anal. Calculated for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.68; H, 6.00.

Picrate, m.p. 173°–174° (dec.) (not previously reported).

Anal. Calculated for $C_{18}H_{13}O_8N_3$: C, 54.14; H, 3.28. Found: C, 54.02; H, 3.26.

2-Methyl-1-naphthol. Yield, 51 percent. M.p. 61°–63° [lit. (*100*) 62.4°].

Anal. Calculated for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.28; H, 6.37.
Benzoate, m.p. 97°–99° [lit. (*43*) 94°–95°].
Picrate, m.p. 131°–133° [lit. (*43*) 133°–134°].

4-Methyl-1-naphthol. Yield, 33 percent. M.p. 83°–85° [lit. (*43*) 84°–85°).

Anal. Calculated for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.46; H, 6.44.
Benzoate, m.p. 79.8°–80.5° [lit. (*43*) 80.6°–81°].
Picrate, m.p. 165°–167° [lit. (*84*) 163°–165°].

3-Phenylphenol. Yield, 61 percent. M.p. 72°–74° [lit. (*117*) 72°–76°]; $\lambda_{max}^{cyclohexane}$ 290.0, 281.0, 249.0 mμ (log ε 3.50, 3.60, 4.21). Reported (*95*), λ_{max}^{EtOH} 290, 287, 249 (log ε 3.52, 3.58, 4.20).

Anal. Calculated for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.91; H, 5.86.
Phenylurethane, m.p. 131°–133° [lit. (*117*) 132.5°–134°].

3,4,5-Trimethylphenol was synthesized from isophorone using the procedure described by Beringer and Geering (*10*). In this reaction bromine at 0° C., in the presence of 1,2,4-trichlorobenzene as solvent, dehydrogenates isophorone and induces rearrangement of the methyl groups, producing mostly 3,4,5-trimethylphenol and small amounts of 2,3,5-trimethylphenol and other phenols. The purification procedure outlined by Beringer and Geering was followed.

3,4,5-Trimethylphenol. Yield, 24.1 percent. M.p. 107° [lit. (*43*) 107°].

Employing the method of Smith and Opie (*106*), 3,5-dimethyl-2-ethyl- and 2,3-dimethyl-6-ethylphenol were prepared. The experimental details were as follows:

3,5-Dimethylphenyl acetate (I) (70 g., 85 percent yield, b.p. 120°/19mm.) was prepared from 3,5-dimethylphenol in the usual way, using acetic anhydride and sulfuric acid.

2-Hydroxy-4,6-dimethyl-acetophenone (II) was prepared from (I) by a Fries rearrangement using aluminum trichloride as catalyst. A light yellow solid (20 g., 60 percent-yield, m.p. 58°, b.p. 142°-144°/13 mm.) was obtained. Smith and Opie reported a 67-percent yield of material that melted at 57°–58.5° C. The molecular weight of (II) was determined by the ebullioscopic method to be 164.6; the calculated value is 164.2.

3,5-Dimethyl-2-ethylphenol (III) was prepared from (II) by a Clemmensen reduction, using zinc amalgam and hydrochloric acid. This yielded the white, crystalline phenol, 8.5 g.

3,5-Dimethyl-2-ethylphenol. Yield, 57 percent. B.p. 90°–93°/1 mm. M.p. 75°–76.5° [lit. (*106*) 74°–76°].

2,3-Dimethylphenyl acetate (IV), (colorless liquid, 102.3 g., 77-percent yield, b.p. 112°–113°/12.5 mm.) was prepared from 2,3-dimethylphenol.

2-Hydroxy-3,4-dimethyl-acetophenone (V) was prepared by rearrangement of (IV). A yellow-liquid (53.7 g., 51-percent yield, b.p. 120°–126°/8 mm.) was obtained.

2,3-Dimethyl-6-ethylphenol (VI) was prepared by Clemmensen reduction of (V). A pale-yellow crystalline phenol was obtained, 13.9 g.

2,3-Dimethyl-6-ethylphenol. Yield, 62 percent. B.p. 115°–117°/12 mm. M.p. 47°–50° [lit. (*54*) 53°–54°].

Seven phenols were synthesized from the corresponding acetophenone, or propiophenone, by Clemmensen reduction, using the method of Brewster and Harris (*18*), with some modifications in the separation procedures.

3-Ethylphenol. B.p. 115°/20 mm. [lit. (*54*) 114.5°/20 mm.].

2-Ethyl-4-methylphenol. B.p. 118°–120°/23 mm., n_D^{20} 1.5317.

4-Ethyl-2-methylphenol. B.p. 125.5°/17 mm. n_D^{20} 1.5320 [lit. (*54*) n_D^{25} 1.5372].

4-Ethyl-3-methylphenol. B.p. 140°/52 mm. [lit. (*54*) 122°/15 mm.].

3-n-Propylphenol. B.p. 109°/12 mm. [lit. (*54*)127°/20 mm.].

2-Ethylresorcinol. M.p. 97°.

2-Ethylhydroquinone. M.p. 112.3° [lit. (*8*) 112°–113°].

SYNTHESIS OF QUINOLINES

2,8-Dimethylquinoline, 2,5,7-trimethylquinoline, 2,5,8-trimethylquinoline, 2,6,8-trimethylquinoline, and 2,7,8-trimethylquinoline were all synthesized according to the general procedure outlined by Bowen and coworkers for preparation of the 2,5,8-isomer (*14*). The 2,5,7- and 2,7,8-isomers are apparently previously unreported. The "Handbook" (*46*) lists 2,5,7-trimethylquinoline, m.p. 43°, very soluble in water, whereas the pure 2,5,7-isomer was found to be liquid at room temperature and essentially insoluble in water, as are the other known trimethylquinolines. Since 2,5,7-trimethylquinoline is not listed in Chemical Abstracts, Beilstein, etc., it was assumed that the "Handbook" entry is probably in error.

2,4,6-Trimethylquinoline, 2,4,7-trimethylquinoline, 2,4,8-trimethylquinoline, 2,4,5,8-tetramethylquinoline, and 2,4,7,8-tetramethylquinoline were all synthesized according to the general procedure outlined by Adams and Campbell for preparing the 2,4,7-isomer (*1*). In this procedure the intermediate imine is prepared and purified. 2,4,7,8-Tetramethylquinoline and its imine precursor, 4-(2,3-

dimethylbenzimino)-pentan-2-one, are both apparently previously unreported.

2,5,8-Trimethylquinoline. A 41-percent yield of oil, b.p. 143°–145° at 15 mm. [lit. (*14*) 144–146° at 15 mm.], was obtained. Upon redistillation this yielded a main cut b.p. 90°–91° at 0.98 mm., 250.4° at 746 mm.; n_D^{21} 1.5941; picrate, m.p. 177°–178.5° [lit. (*14*) n_D^{21} 1.5958; picrate, m.p. 181°–182°].

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.12; H, 7.69.

2,8-Dimethylquinoline. A 37-percent yield of oil, b.p. 89°–90° at about 2 mm. [lit. (*74*) 93°–95° at 2 mm.], was obtained. Upon redistillation, this yielded a main cut b.p. 85°–86° at 1.79 mm., 249.1° at 740 mm. [lit. (*4*) 245–252° at 760 mm.]; n_D^{20} 1.5999; picrate, m.p. 183° [lit. (*43*) n_D^{20} 1.6022; picrate, m.p. 183°].

Anal. Calculated for $C_{11}H_{11}N$: C, 84.04; H, 7.05. Found: C, 84.24; H, 7.09.

2,6,8-Trimethylquinoline. A 46-percent yield of the quinoline, b.p. 142°–144° at 15 mm., was obtained. Upon redistillation this yielded a main cut b.p. 94°–95° at 1.27 mm., 267.4° at 746 mm.; picrate, m.p. 185°–186.5° [lit. (*43*) b.p. 266°–267° at 780 mm.; picrate, m.p. 185°].

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.34; H, 7.80.

2,5,7-Trimethylquinoline. A 51-percent yield of viscous oil, sparingly volatile with steam, b.p. 152°–153.5° at 15 mm., was obtained. Upon redistillation this yielded a main cut b.p. 107°–108° at 1.2 mm., 286.6° at 746 mm.; n_D^{20} 1.5980; picrate, m.p. 204.5°–205.5°d.

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.35; H, 7.60.

2,7,8-Trimethylquinoline. A 22-percent yield of crystals, very sparingly volatile with steam, b.p. 144°–146° at 15 mm., was obtained. Upon recrystallization from 95-percent ethanol this yielded white needles, m.p. 41°; b.p. 276.1° at 740 mm.; picrate, m.p. 186°. The melting point of the recrystallized quinoline was not altered upon sublimation.

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.20; H, 7.64.

4-(3-Methylbenzimino)-pentan-2-one. A 74-percent yield of pale yellow oil, b.p. 109°–109.5° at 1 mm., n_D^{20} 1.6100 [lit. (*1*) b.p. 125°–126° at 2 mm., n_D^{20} 1.6105], was obtained.

Anal. Calculated for $C_{12}H_{15}NO$: C, 76.15; H, 7.99. Found: C, 76.26; H, 8.02.

2,4,7-Trimethylquinoline. Cyclodehydration of the above imine in sulfuric acid gave a 67-percent yield of the quinoline, b.p. 116°–117.5° at 2 mm. [lit. (*1*) 103°–104° at 1.5 mm.], b.p. 282.9° at 742 mm. [lit. (*43*) 280°–281° at 760 mm.]; n_D^{20} 1.6000 [lit. (*1*) n_D^{20} 1.5997]; picrate, m.p. 229.5°–231° d. [lit. (*43*) 232° d.].

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.09; H, 7.72.

4-(4-Methylbenzimino)-pentan-2-one. Upon recrystallization of the crude product from n-hexane a 74-percent yield of white crystals, m.p. 66.8°–67.3° [lit. (*13*) 65°–66°], was obtained.

Anal. Calculated for $C_{12}H_{15}NO$: C, 76.15; H, 7.99. Found: C, 76.15; H, 8.01.

2,4,6-Trimethylquinoline. The method of Adams and Campbell for the 2,4,7- isomer had to be modified for the 2,4,6- isomer in that the sulfate of the quinoline was isolated by pouring the cyclodehydration reaction mixture onto cracked ice and collecting the precipitate. If the sulfate was not isolated before neutralization no quinoline was obtainable. Upon recrystallization of the crude-free quinoline from 95 percent ethanol, a 76-percent yield of white crystals (containing some water of hydration) was obtained, m.p. 52° C. This was further purified by sublimation to give white crystals, m.p. 41.5° [lit. (*97*) 43°–45°]; b.p. 286.9° at 742 mm. [lit. (*66*) 287° at 758 mm.]; picrate, m.p. 191.5°–192.5° [lit. (*43*) 189°].

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 81.58; H, 7.81.

This microanalysis indicates that sublimation did not yield a completely water-free product, since the carbon content is slightly low and the hydrogen content very slightly high.

4-(2-Methylbenzimino)-pentan-2-one. Upon drying and distillation of the crude product, a 57-percent yield of a very pale yellow oil, b.p. 125.5° at 1 mm., n_D^{20} 1.6032, was obtained.

Anal. Calculated for $C_{12}H_{15}NO$: C, 76.15; H, 7.99. Found: C, 76.28; H, 7.98.

2,4,8-Trimethylquinoline. The quinoline was isolated as the sulfate. The crude-free quinoline (64-percent yield) was recrystallized from 95 percent ethanol, giving white crystals, m.p. 42°; b.p. 275.8° at 740 mm.; picrate, m.p. 192.5°–193.0° [lit. (*43*) m.p. 42°; b.p. 280° at 746 mm.; picrate, m.p. 193°].

Anal. Calculated for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.18; H, 7.67.

4-(2,5-Dimethylbenzimino)-pentan-2-one. Upon drying and distilling the crude product, a 46-percent yield of imine was obtained. Redistillation gave the pure imine, b.p. 109°–110° at 0.65 mm. [lit. (*15*) about 170° at 12 mm.]; n_D^{20} 1.5940.

Anal. Calculated for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.80; H, 8.21.

2,4,5,8-Tetramethylquinoline. The cyclodehydration procedure of Adams and Camp-

bell yielded neither the quinoline nor its sulfate when applied to the above imine. However, it was observed that, by slowly distilling the imine, a slightly higher boiling fraction was obtained at the end of the distillation, which formed colorless crystals upon cooling. This material proved to be the quinoline in an impure state and had been formed in small yield by cyclodehydration induced solely by heating the imine around 110° C. at about 1 mm. pressure. Recrystallization from 95 percent ethanol gave white crystals of the quinoline, which still contained large amounts of the imine. Further purification was not successful. The literature (*15*) values for 2,4, 5,8-tetramethylquinoline are b. p. 168°–172° at 12 mm.; m.p. 48°. By comparing the infrared spectra of the imine and the quinoline contaminated with imine, several wavelengths were determined to be characteristic of the quinoline.

4-(2,3-Dimethylbenzimino)-pentan-2-one. Upon recrystallization of the crude product from n-hexane a 60-percent yield of white crystals, m.p. 88.0°, was obtained.

Anal. Calculated for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.92; H, 8.45.

2,4,7,8-Tetramethylquinoline. The quinoline was isolated as the sulfate. The crude-free quinoline (88-percent yield) was recrystallized from 95 percent ethanol, giving white needles, m.p. 30°; b.p. 295.5° at 742 mm.; picrate, m.p. 180°–180.5°d.

Anal. Calculated for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.26; H, 8.28.

In addition to carbon and hydrogen, nitrogen analyses were desired for the synthesized quinolines. It was decided to establish the Kjeldahl nitrogen method as a reliable elemental analytical procedure for heterocyclic nitrogen compounds (the predominant form in which nitrogen occurs in tars). Previous investigations, made mostly by the petroleum industry, were limited almost entirely to reproducibility studies with little work on individual heterocyclic compounds. The procedures recommended in the literature were found to work well enough on some individual heterocyclics, such as carbazole, but gave very low yields on most quinolines. After a thorough investigation of all pertinent factors such as digestion temperature, digestion time, and various digestion catalysts, it was found that most quinolines have a very high decomposition threshold temperature, that is, for decomposition of the type yielding ammonium ion. The commercial electrical digestion apparatus being used had to be discarded for a Fisher burner in order to reach the required temperature of 370° C. It was necessary to increase the standard salt to acid ratio several-fold in order to get a mixture that would reflux at this high a temperature. It was also necessary to keep a constant check on the temperature of the digestion mixture by means of a thermocouple, which was incased in a glass tube that was closed at the bottom and filled with a suitable high-boiling liquid. It was, incidentally, found to be advantageous to mix up the indicator just before making the titration for easier detection of the endpoint. Following these new procedures excellent results were obtained on all quinolines examined, as shown in table 36.

TABLE 36.—*Results of microanalysis of synthesized quinolines with modified Kjeldahl procedure*

Compound	Nitrogen, wt.-pct.	
	Calculated	Found [1]
Quinoline	10.84	10.86
2,8-Dimethylquinoline	8.91	8.90
2,4,6-Trimethylquinoline	8.18	[2] 8.00
2,4,7-Trimethylquinoline	8.18	8.20
2,4,8-Trimethylquinoline	8.18	8.13
2,5,7-Trimethylquinoline	8.18	8.16
2,5,8-Trimethylquinoline	8.18	8.10
2,6,8-Trimethylquinoline	8.18	8.16
2,7,8-Trimethylquinoline	8.18	8.19
2,4,7,8-Tetramethylquinoline	7.56	7.55

[1] Average of two determinations.
[2] This microanalysis indicates that the sublimed product did not yield a completely water-free product, since the nitrogen content is slightly low.

APPENDIX

The appendix of this report contains the ultraviolet and infrared spectra of 189 individual tar acids and tar bases. For the most part, these are the compounds that were identified in the low-temperature bituminous coal tar along with their isomers, which did not happen to be detected in this particular tar but could very well be present in other tars in significant amounts.

These compounds have been grouped according to isomers, making it easy to see at a glance which isomers are represented from each group. The groups of isomers have been arranged according to increasing complexity; that is, first cresols, then xylenols, and so forth.

Each of the compounds has been assigned a number, which is shown in center right of the page. These same numbers have been listed in the indices of individual tar acids and bases based on boiling point. Since fractional distillation is frequently used as an intermediate or even final separatory procedure, these indices can be used for rapid location of the spectra of the compounds that could be present in a particular boiling-range fraction. In addition these indices have some application to gas-liquid chromatographic fractionation, since there is generally a predictable relationship between log relative retention and normal boiling point for the members of a homologous series; that is, it is frequently observed that the members of a homologous series generally are eluted from the column in the order of increasing boiling point, especially when using less polar substrates, such as Apiezon L grease.

The numbers in parentheses refer to the items in the bibliography that are references for boiling points or spectra. Spectra and boiling points without reference numbers were obtained in this laboratory with authentic specimens.

INDEX OF INDIVIDUAL TAR ACIDS BASED ON BOILING POINT

Compound	*Boiling point, ° C./760 mm.*	*No.*	*Page*
Phenol	182	1	64
2-Methylphenol	190.8	2	65
2,6-Dimethylphenol	201	8	71
4-Methylphenol	202.1	4	67
3-Methylphenol	202.2	3	66
2-Ethylphenol	207	11	74
2,4-Dimethylphenol	210	6	69
2,5-Dimethylphenol	210	7	70
2-Ethyl-6-methylphenol	212–214	16	78
3-Ethylphenol	214	12	75
2-Isopropylphenol	214/745	32	92
2-Ethyl-4-methylphenol	216–218	14	77
2,3-Dimethylphenol	218	5	68
4-Ethylphenol	219	13	76
3,5-Dimethylphenol	219.5	10	73
2,3,6-Trimethylphenol	[1] [220] 100/14	25	85
2-n-Propylphenol	220	29	89
4-Ethyl-2-methylphenol	222	21	81
2,4,6-Trimethylphenol	222	27	87
5-Ethyl-2-methylphenol	223	19	79
2-Ethyl-5-methylphenol	224.2	15	78
3,4-Dimethylphenol	225	9	72
3-Ethyl-2-methylphenol	227	17	79
2,4-Dimethyl-6-ethylphenol	227–228	48	107
3-n-Propylphenol	228	30	90
3-Isopropylphenol	228	33	92
2-Isopropyl-3-methylphenol	228.5	35	94
2-Isopropyl-4-methylphenol	228–229/763	36	95
4-Isopropylphenol	228–229/745	34	93
4-Ethyl-3-methylphenol	228–230	22	82
2-(Propen-1-yl)phenol	230–231	60	118
2,4,5-Trimethylphenol	232	26	86
4-n-Propylphenol	232.6	31	91
2-Methyl-6-n-propylphenol	[233] 105–107/12	42	101

See footnote at end of table.

INDEX OF INDIVIDUAL TAR ACIDS BASED ON BOILING POINT—Continued

Compound	Boiling point, ° C./760 mm.	No.	Page
3-Ethyl-5-methylphenol	233	20	80
2,3,5-Trimethylphenol	233	24	84
2-Isopropyl-5-methylphenol	233.5	37	96
4-Isopropyl-2-methylphenol	230–234	39	98
3-Ethyl-4-methylphenol	234–235	18	79
2,3,4-Trimethylphenol	235–237	23	83
5-Isopropyl-2-methylphenol	236.8–237.4	41	100
4-Isopropyl-3-methylphenol	238	40	99
2,3-Dimethyl-6-ethylphenol	[1][240] 166/100	47	106
4-Methyl-2-n-propylphenol	[241] 121–123/18	43	102
3-Isopropyl-5-methylphenol	241	38	97
4-Indanol	245/764	69	124
Catechol	245	54	112
2,3,5,6-Tetramethylphenol	247–248	46	105
3,5-Diethylphenol	248	51	110
3-Methylcatechol	248	55	113
3,4,5-Trimethylphenol	248–249	28	88
3,5-Dimethyl-2-ethylphenol	[250] 90–93/1	50	109
3,4-Dimethyl-6-ethylphenol	[250]	49	108
6-Methyl-4-indanol	[250]	71	126
7-Methyl-4-indanol	[250]	72	127
2,3,4,6-Tetramethylphenol	250	45	104
5-Indanol	255	70	125
2,6-Di-n-propylphenol	256/764	53	111
4-Methylcatechol	258	56	114
3,5-Dimethyl-2(propen-1-yl)phenol	[260]	61	119
7-Methyl-5-indanol	[260]	73	128
2,3,4,5-Tetramethylphenol	260	44	103
5,6,7,8-Tetrahydro-l-naphthol	264.5–265/705	74	129
2-Ethylresorcinol	[265]	57	115
Pentamethylphenol	267	52	110
4-Ethylresorcinol	[270] 131/15	58	116
2-(Cyclopenten-2-yl)phenol	[270] 133–135/12	65	120
2-(Cyclopenten-1-yl)phenol	[272]	62	119
2-Phenylphenol	275	81	133
5,6,7,8-Tetrahydro-2-naphthol	275–276	75	130
4-Methyl-5,6,7,8-tetrahydro-l-naphthol	[280]	76	131
4-Methyl-2-phenylphenol	[280] 101–105/2	80	132
2-Cyclohexylphenol	282.5–283.5	67	122
2-(Cyclopenten-2-yl)-4-methylphenol	[284] 105–108/1.3	64	119
2-Fthylhydroquinone	[285]	59	117
1-Naphthol	288.01	84	136
3-Methyl-5,6,7,8-tetrahydro-2-naphthol	[290]	77	131
4-Methyl-5,6,7,8-tetrahydro-2-naphthol	[290]	78	131
4-(Cyclopenten-1-yl)phenol	[293]	63	119
4-(Cyclopenten-2-yl)phenol	[293] 114–117/1.5	66	121
2-Naphthol	294.85	85	137
2-Methyl-1-naphthol	[295]	86	138
4-Cyclohexylphenol	293.5–295.5/752	68	123
4-Methyl-1-naphthol	[298] 177–179/25	87	139
1-Methyl-2-naphthol	[300]	88	140
1,4-Dimethyl-5,6,7,8-tetrahydro-2-naphthol	[305]	79	132
5-Methyl-2-naphthol	[305]	89	140
3,4-Dimethyl-1-naphthol	[315] 205–210/15	90	141
4-Phenylphenol	319	83	135
7-Fthyl-4-methyl-1-naphthol	[320]	91	141
3-Phenylphenol	325	82	134
5-Acenaphthenol	[332] 221/40	97	146
4-Acenaphthenol	[338]	96	145
1-Fluorenol	[345]	92	142
2-Fluorenol	340–350	93	143
3-Fluorenol	[350]	94	144
8-Methyl-2-fluorenol	[355]	95	144

[1] Figures in brackets are atmospheric boiling points estimated from reduced-pressure data or from boiling-point data of isomers and homologs.

569705 O—61——5

INDEX OF INDIVIDUAL TAR BASES BASED ON BOILING POINT

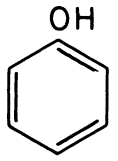
INDEX OF INDIVIDUAL TAR BASES BASED ON BOILING POINT—Con.

Compound	*Boiling point, ° C./760 mm.*	*No.*	*Page*
2,4,6-Trimethylquinoline	287/758	148	187
2-Naphthylamine	294	189	224
2,4,7,8-Tetramethylquinoline	295.5/742	155	194
1-Naphthylamine	300.8	188	223
2,4,5,8-Tetramethylquinoline	[1] [310] 168–172/12	169	204
N-Benzyl-2-methylaniline	[310] 176/10	185	220
N-Benzyl-3-methylaniline	312	186	221
N-Benzyl-4-methylaniline	312–313	187	222
7,8-Benzoquinoline	335	159	198
6,7-Benzoquinoline	[345] 200–205/14	160	199
2,3-Benzoquinoline	345–346	156	195
3,4-Benzoquinoline	349/769	157	196
5,6-Benzoquinoline	350/721	158	197
2,4-Dimethylbenzo[h]quinoline	355	168	204
1,3-Dimethylbenzol[f]quinoline	[358] 240/35	164	201
9-Methylacridine	359–360/740	161	199
2-Methylbenzo[g]quinoline	[360]	162	200
4-Methylbenzo[g]quinoline	[360]	163	200
2,3-Dimethylbenzo[f]quinoline	[360]	165	202
2,4-Dimethylbenzo[g]quinoline	[370]	166	203
3,4-Dimethylbenzo[g]quinoline	[370]	167	203

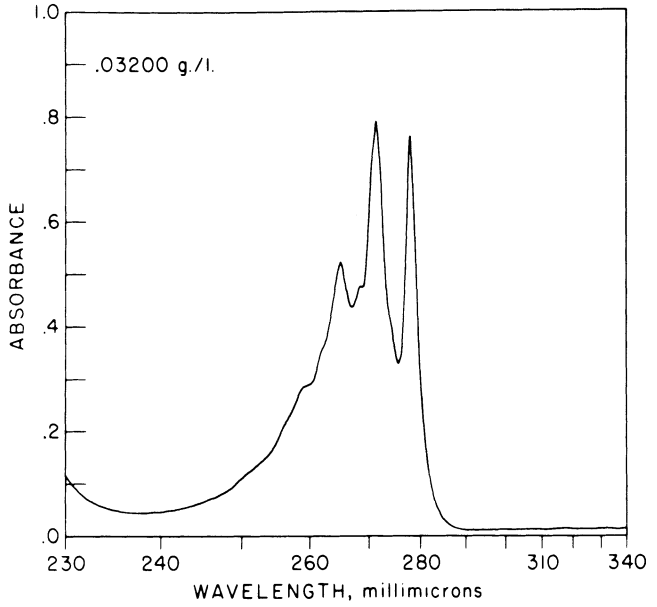
[1] Figures in brackets are atmospheric boiling points estimated from reduced-pressure data or from boiling-point data of isomers and homologs.

ULTRAVIOLET AND INFRARED SPECTRA OF INDIVIDUAL TAR ACIDS AND BASES

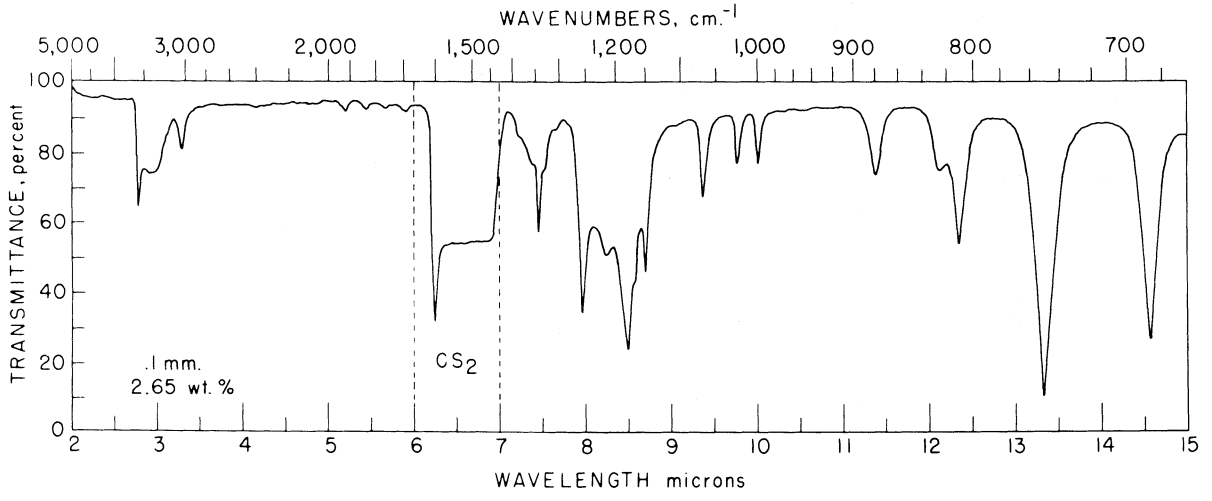
PHENOL



B. p. 182° (54)

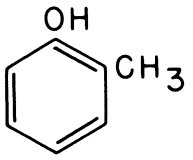


λ max, mμ cyclohexane	log ε
277.8	3.35
271.2	3.36
268.4	3.15
265.0	3.19
262.0	11.16
259.5	9.00
256.3	6.81

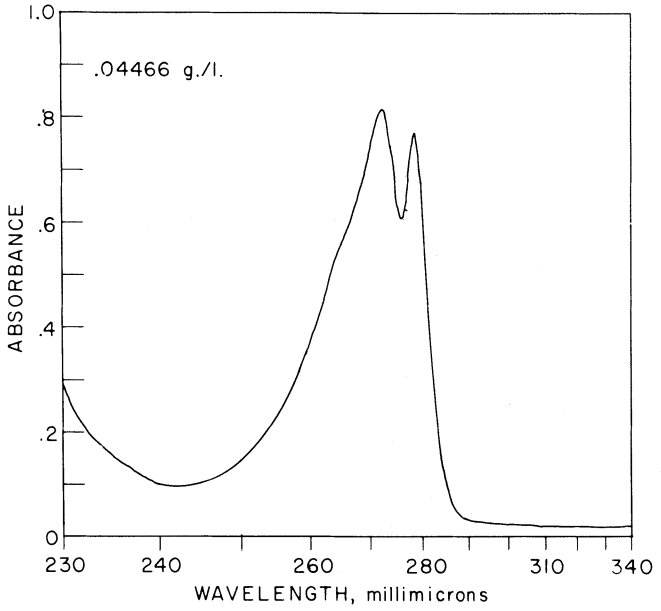


λ^{CS_2}: 14.57 (s), 13.33 (s), 12.35 (m), 12.12 (w), 11.37 (m), 10.02 (w), 9.77 (w), 9.37 (m), 8.70 (m), 8.57 (w), 8.50 (s), 8.25 (w). 7.97 (m), 7.46 (m).

2-METHYLPHENOL

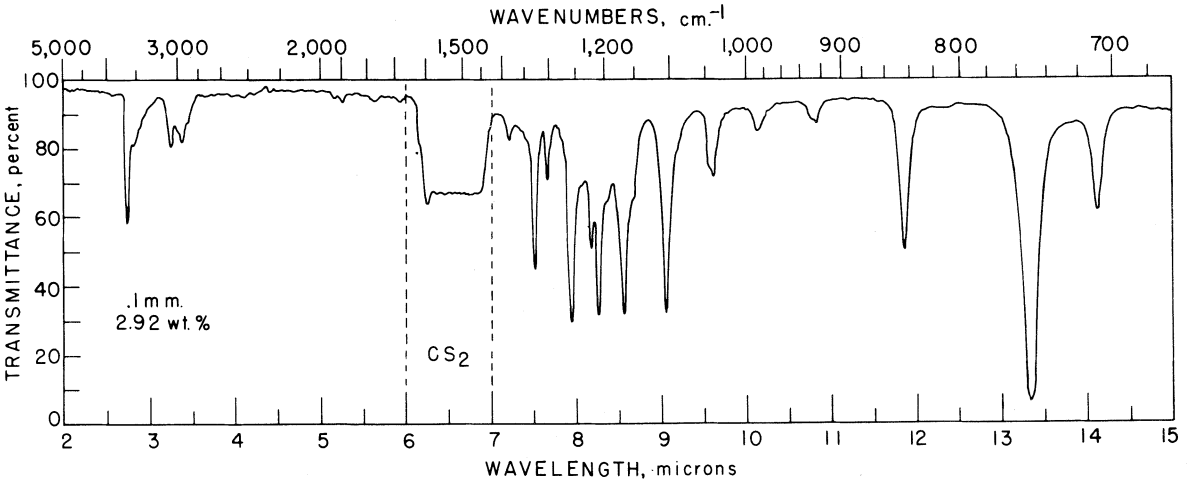


B. p. 190.8° (54)



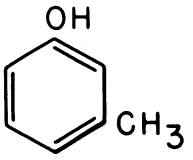
λ max, mμ (cyclohexane)	log ε
278.2	3.27
272.3	3.30

2

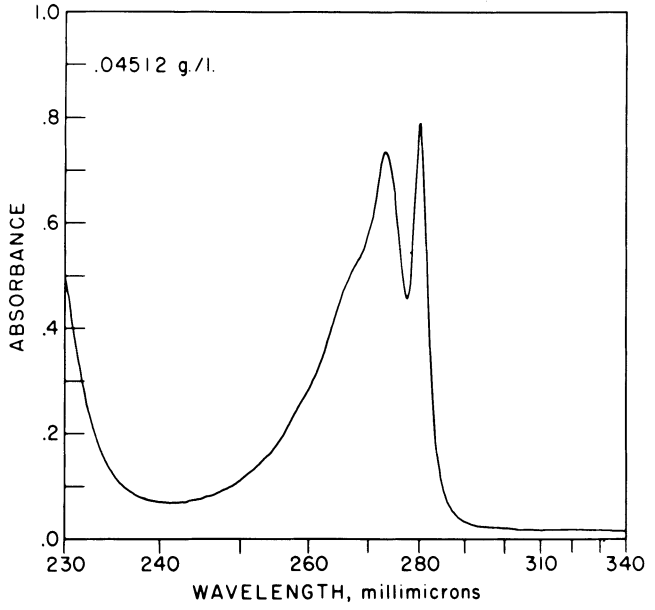


λ^{CS_2}: 14.12 (m), 13.35 (s), 11.86 (m), 10.83 (w), 10.77 (w), 10.14 (w), 9.63 (m), 9.59 (w), 9.08 (m), 8.59 (m), 8.28 (m), 8.20 (w), 7.97 (m), 7.69 (w), 7.54 (m), 7.24 (w).

3-METHYLPHENOL

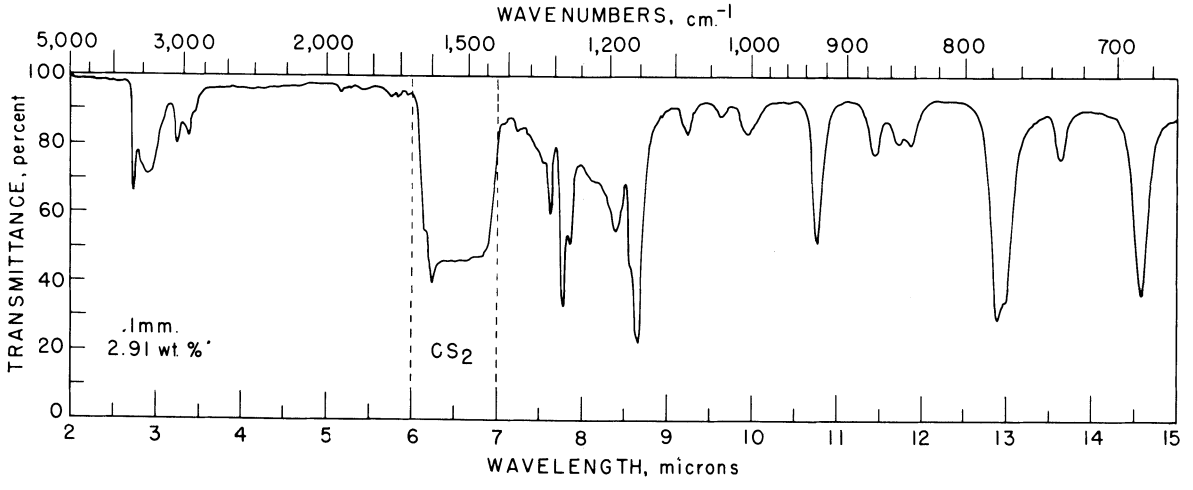


B. p. 202.2° (54)



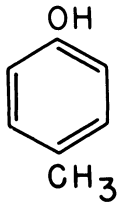
λ max, mμ (cyclohexane)	log ε
280.0	3.28
273.0	3.26
267.5	3.12

3

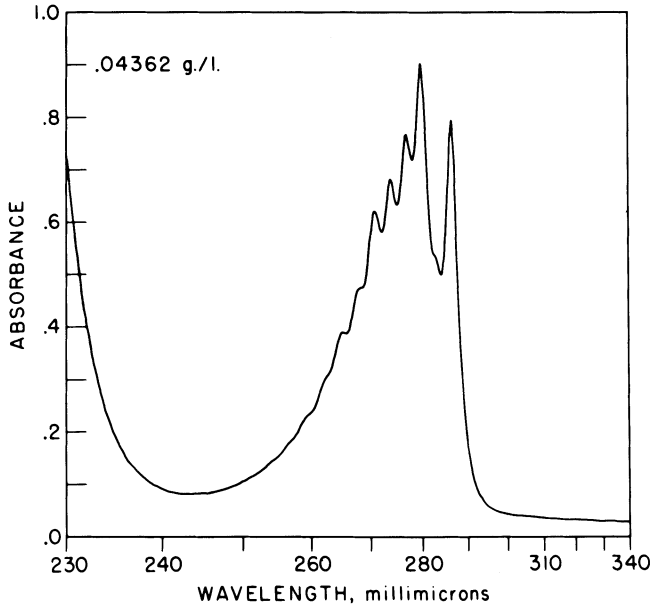


λ^{CS_2}: 14.58 (s), 13.64 (w), 12.98 (s), 12.88 (s), 11.88 (w), 11.72 (w), 11.45 (w), 10.77 (m), 9.97 (w), 9.64 (w), 9.25 (w), 8.68 (s), 8.58 (w), 8.40 (m), 8.15 (w), 7.87 (w), 7.79 (m), 7.63 (m), 7.55 (w), 7.25 (w).

4 - METHYLPHENOL

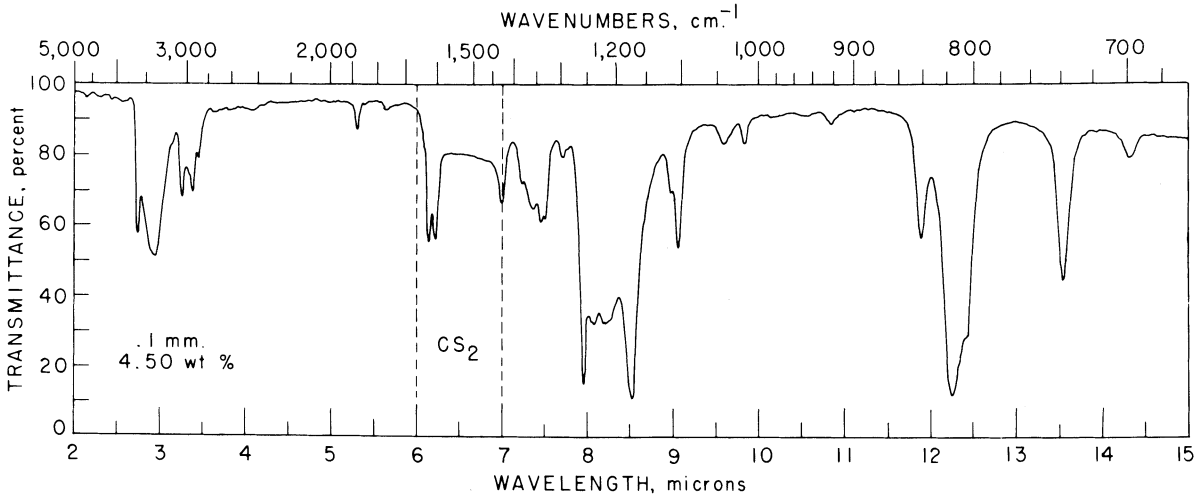


B.p. 202.1° (54)



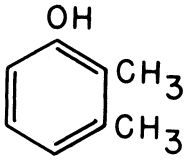
λ_{max}, mμ cyclohexane	log ε
286.2	3.31
279.8	3.36
276.8	3.29
273.7	3.24
270.6	3.20
267.8	3.09
264.9	3.01
262.4	2.90
259.5	2.80

4

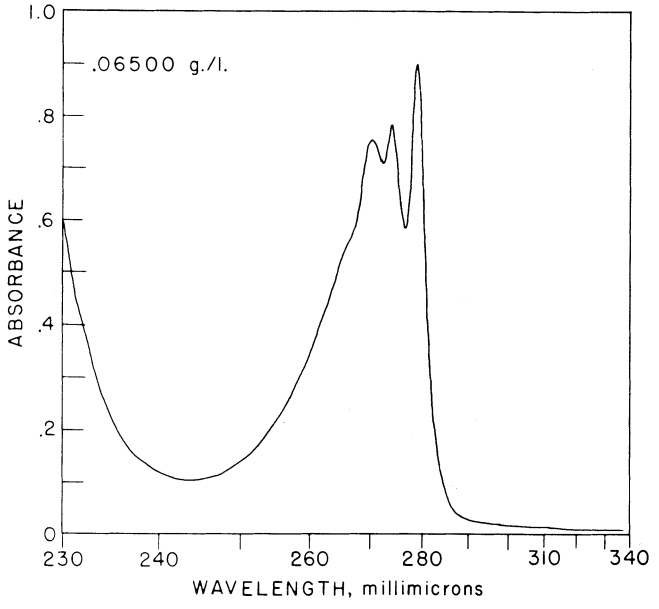


λ^{CS_2}: 14.32 (w), 13.54 (m), 12.42 (m), 12.25 (s), 11.89 (m), 10.85 (w), 9.84 (w), 9.60 (w), 9.07 (m), 8.98 (w), 8.54 (s), 8.25 (w), 8.10 (w), 7.98 (s), 7.72 (w), 7.53 (w), 7.47 (w), 7.38 (w), 7.25 (w).

2, 3 - DIMETHYLPHENOL

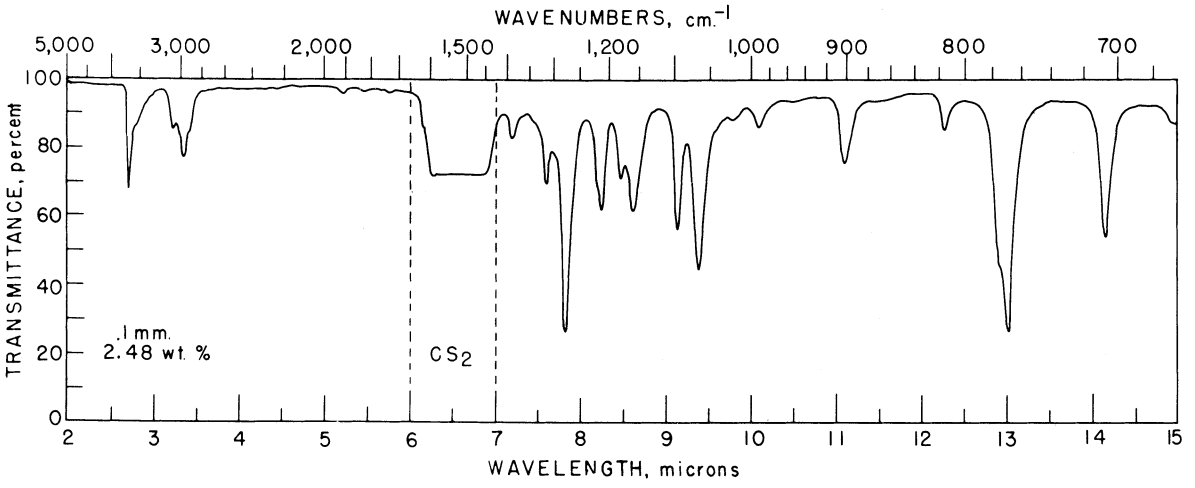


B. p. 218° (54)



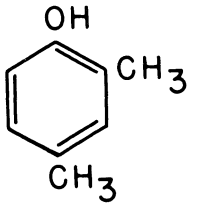
λ max, mμ (cyclohexane)	log ε
279.0	3.22
274.0	3.17
270.5	3.16

5

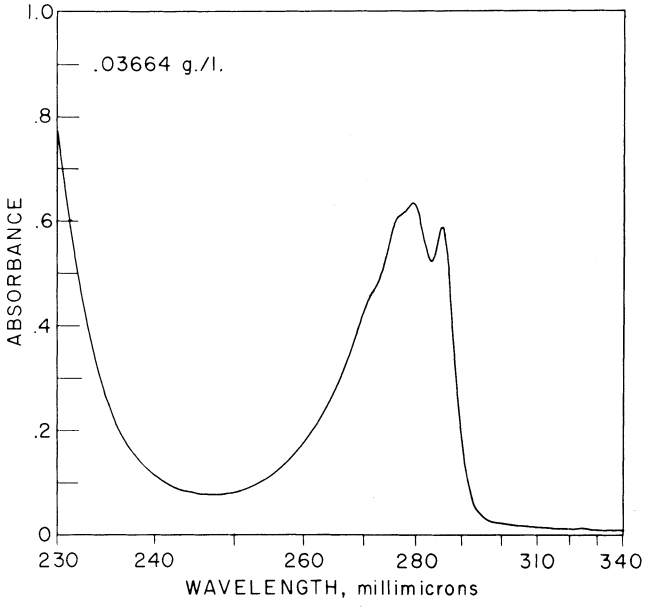


λ^{CS_2}: 14.96 (w), 14.17 (m), 13.02 (s), 12.93 (w), 12.28 (w), 11.12 (m), 10.12 (w), 9.80 (w), 9.40 (m), 9.16 (m), 8.64 (m), 8.50 (w), 8.27 (m), 7.84 (s), 7.62 (w), 7.22 (w).

2, 4 - DIMETHYLPHENOL

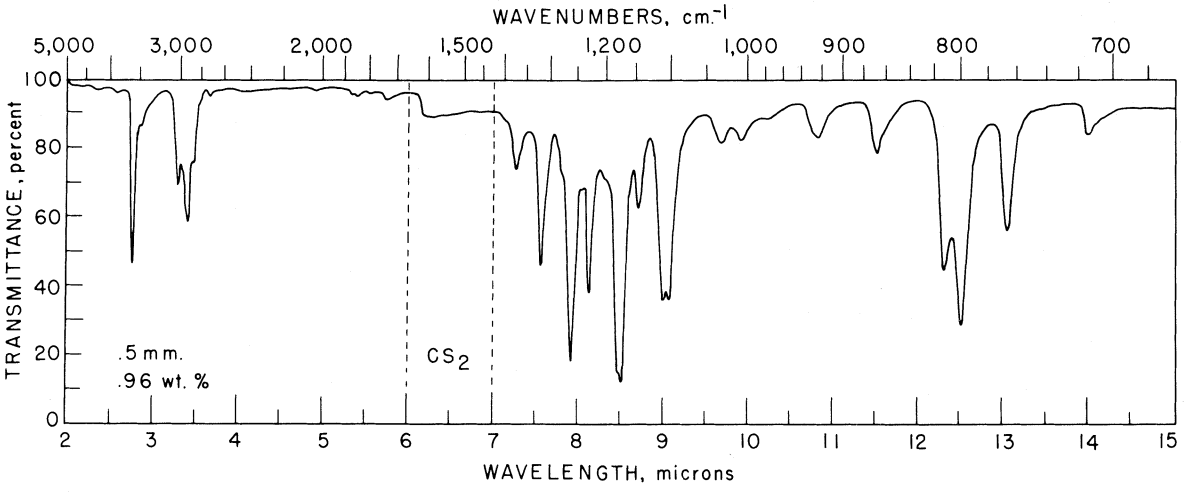


B. p. 210° (54)



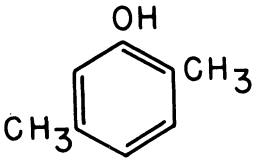
λ max, mμ (cyclohexane)	log ε
285.4	3.29
279.3	3.33
276.0	3.31

6

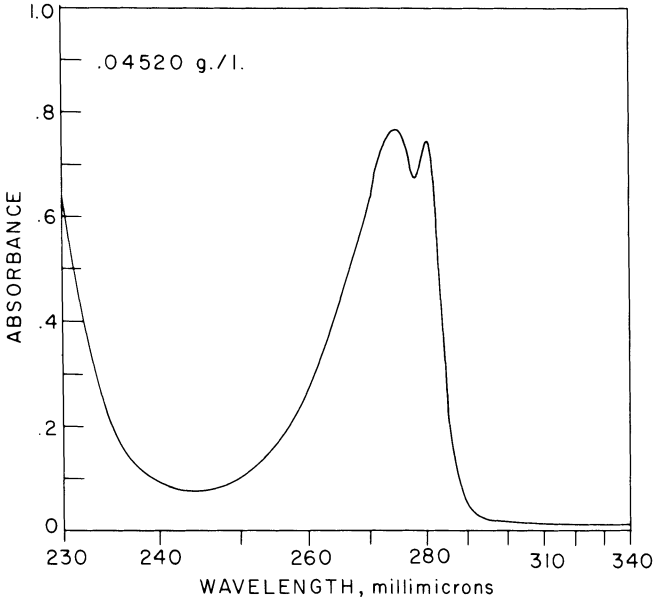


λ^{CS_2}: 13.97 (w), 13.03 (m), 12.50 (s), 12.30 (m), 11.49 (m), 10.82 (w), 9.92 (w), 9.67 (w), 9.07 (s), 9.00 (s), 8.72 (w), 8.52 (s), 8.48 (m), 8.33 (w), 8.14 (m), 7.93 (s), 7.80 (w), 7.57 (m), 7.27 (w).

2, 5 - DIMETHYLPHENOL

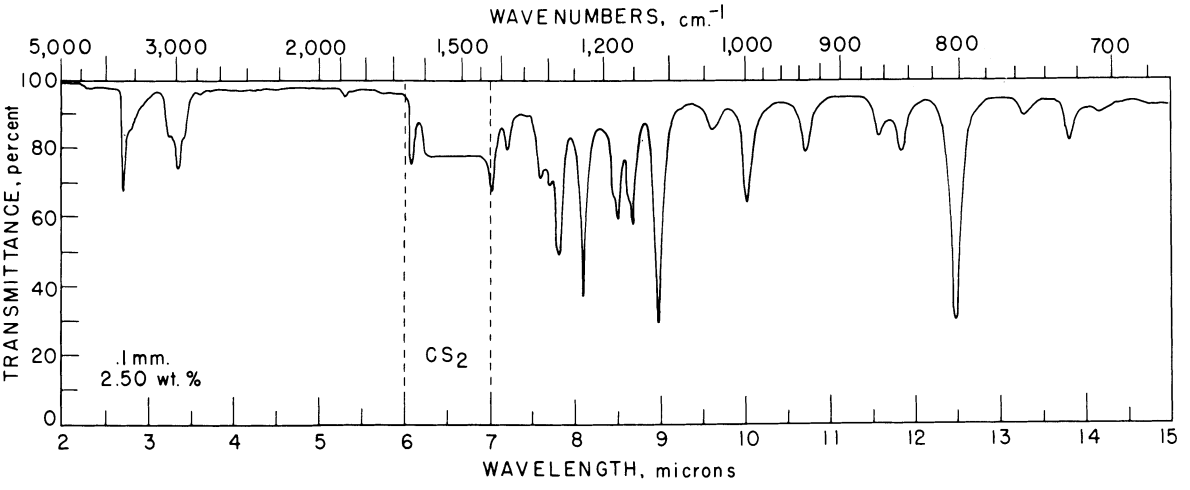


B. p. 210° (54)



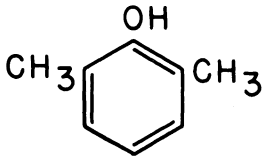
λ max, mμ (cyclohexane)	log ε
281.5	3.28
275.5	3.29

7

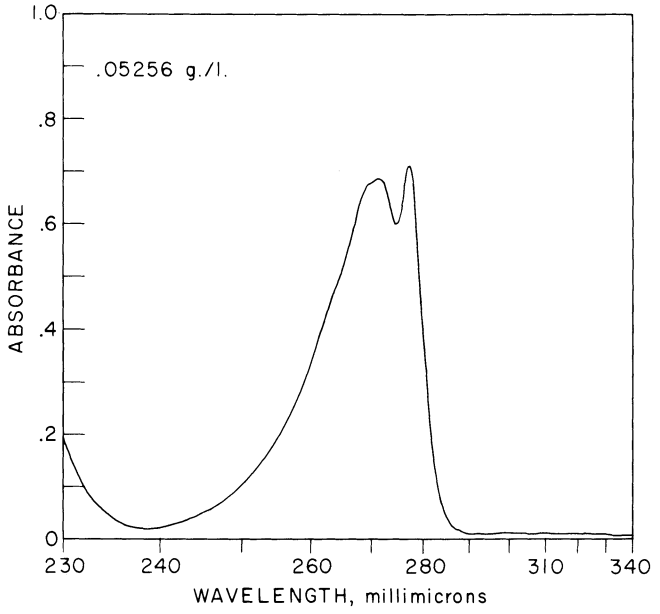


λ^{CS_2}: 14.15 (w), 13.82 (m), 13.28 (w), 12.48 (s), 11.85 (m), 11.58 (w), 10.72 (m), 10.04 (m), 9.64 (w), 9.00 (s), 8.70 (m), 8.65 (w), 8.52 (m), 8.48 (w), 8.13 (s), 7.84 (m), 7.74 (w), 7.62 (w), 7.23 (w), 7.04 (m).

2, 6 - DIMETHYLPHENOL

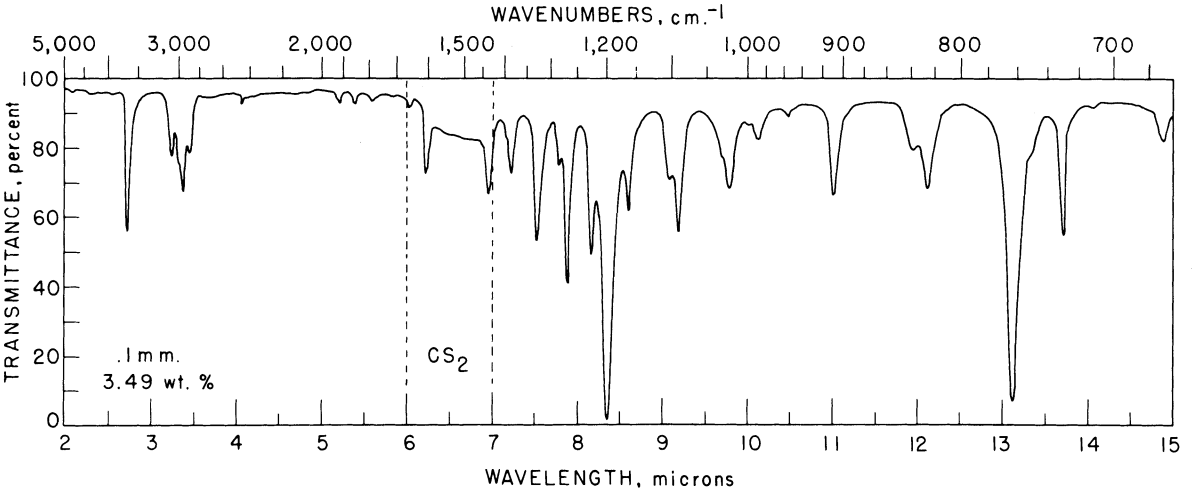


B. p. 201° (54)



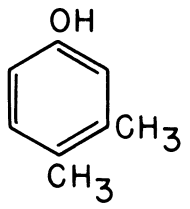
λ max, mμ (cyclohexane)	log ε
277.0	3.23
271.5	3.20

8

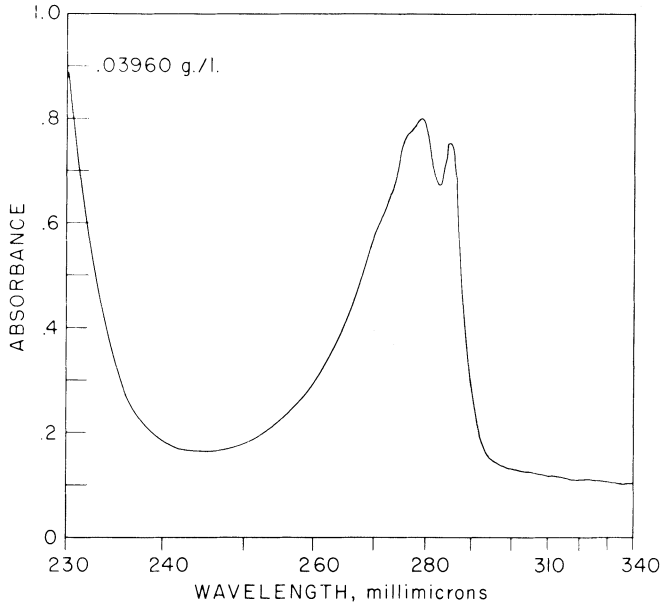


λ^{CS_2}: 14.88 (w), 13.72 (m), 13.33 (w), 13.12 (s), 12.11 (m), 11.94 (w), 11.02 (m), 10.49 (w), 10.13 (w), 9.79 (m), 9.72 (w), 9.20 (m), 9.09 (w), 8.61 (w), 8.36 (s), 8.18 (m), 7.88 (m), 7.80 (w), 7.54 (m), 7.24 (w).

3, 4 - DIMETHYLPHENOL

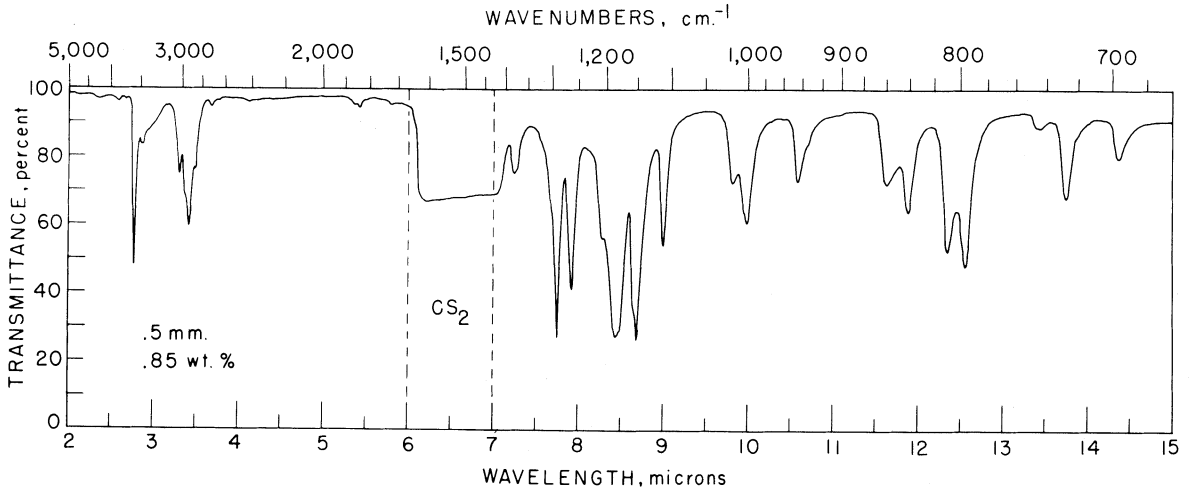


B. p. 225° (54)



λ max, mμ (cyclohexane)	log ε
285.0	3.39
278.7	3.41
276.4	3.40
270.5	3.41

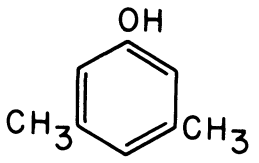
9



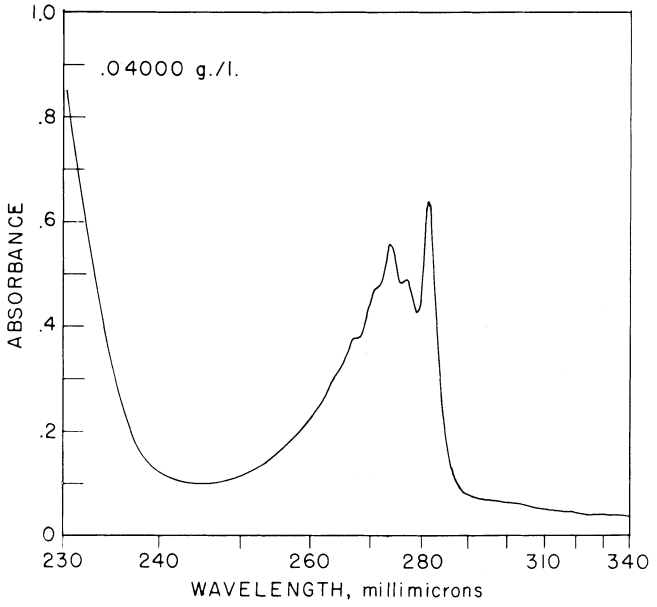
CS_2

λ : 14.37 (w), 13.74 (m), 13.42 (w), 12.56 (s), 12.35 (s), 11.88 (m), 11.62 (m), 10.69 (w), 10.58 (m), 9.98 (m), 9.82 (m), 9.00 (m), 8.69 (s), 8.65 (m), 8.44 (s), 8.29 (w), 7.92 (s), 7.76 (s), 7.67 (w), 7.25 (w).

3, 5 - DIMETHYLPHENOL

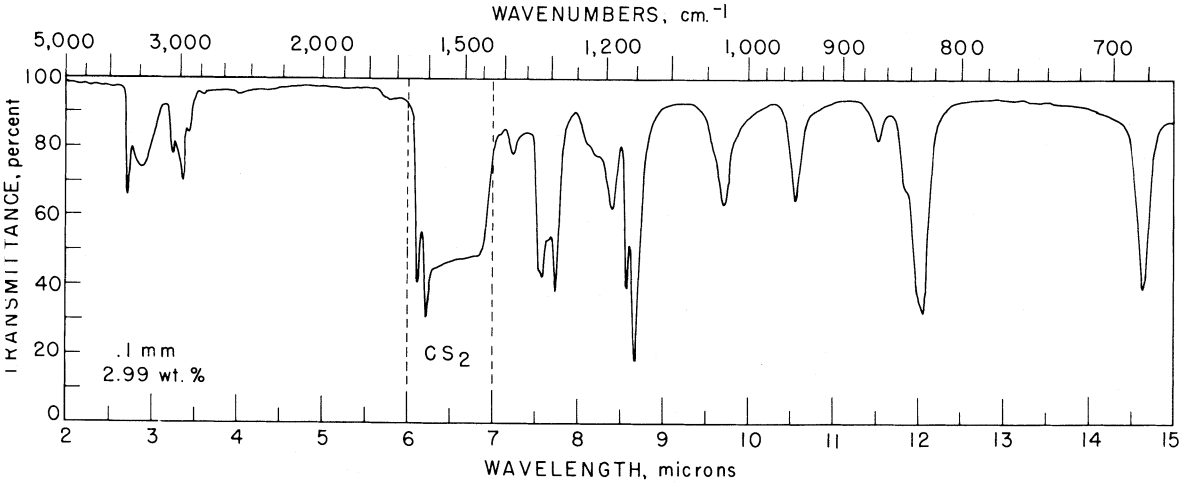


B. p. 219.5° (54)



λ max, mμ (cyclohexane)	log ε
281.2	3.29
276.8	3.18
273.8	3.23
271.0	3.16
267.3	3.07
264.0	2.98

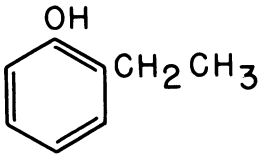
10



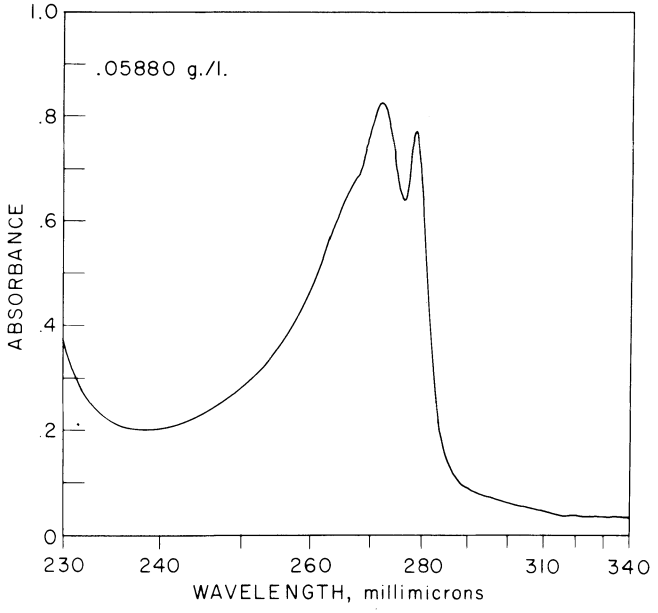
CS_2

λ : 14.64 (s), 12.06 (s), 11.86 (w), 11.54 (w), 10.56 (m), 9.73 (m), 8.68 (s), 8.58 (m), 8.42 (m), 8.22 (w), 7.75 (m), 7.60 (m), 7.56 (m), 7.25 (w).

2-ETHYLPHENOL

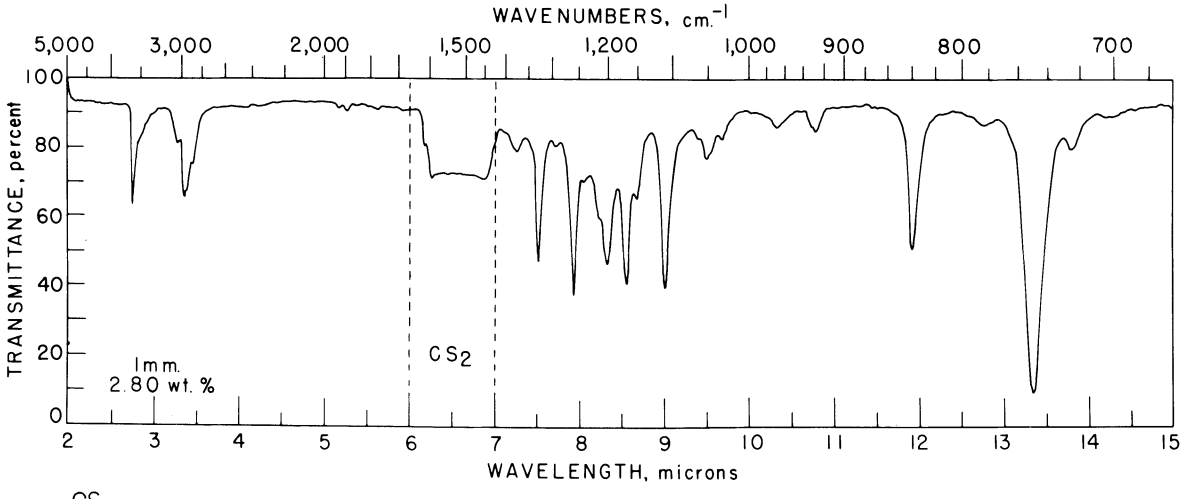


B. p. 207° (54)



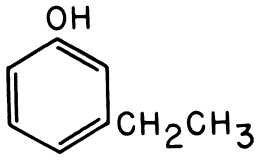
λ cyclohexane max, mμ	log ε
278.7	3.20
272.2	3.24
266.5	3.15

II

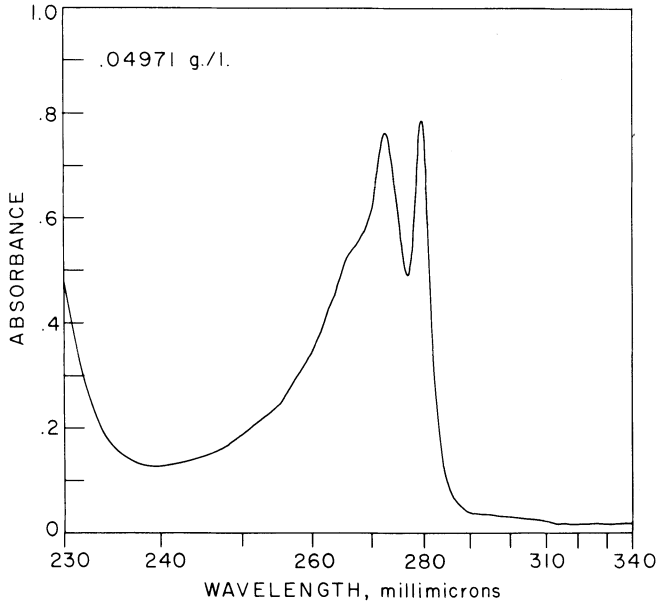


λ^{CS_2}: 14.25 (w), 13.82 (w), 13.37 (s), 12.78 (w), 11.94 (m), 10.82 (w), 10.75 (w), 10.35 (w), 9.70 (w), 9.52 (w), 9.42 (w), 9.03 (m), 8.70 (w), 8.57 (m), 8.35 (m), 8.27 (w), 8.08 (w), 7.96 (m), 7.75 (w), 7.55 (m), 7.30 (w).

3-ETHYLPHENOL

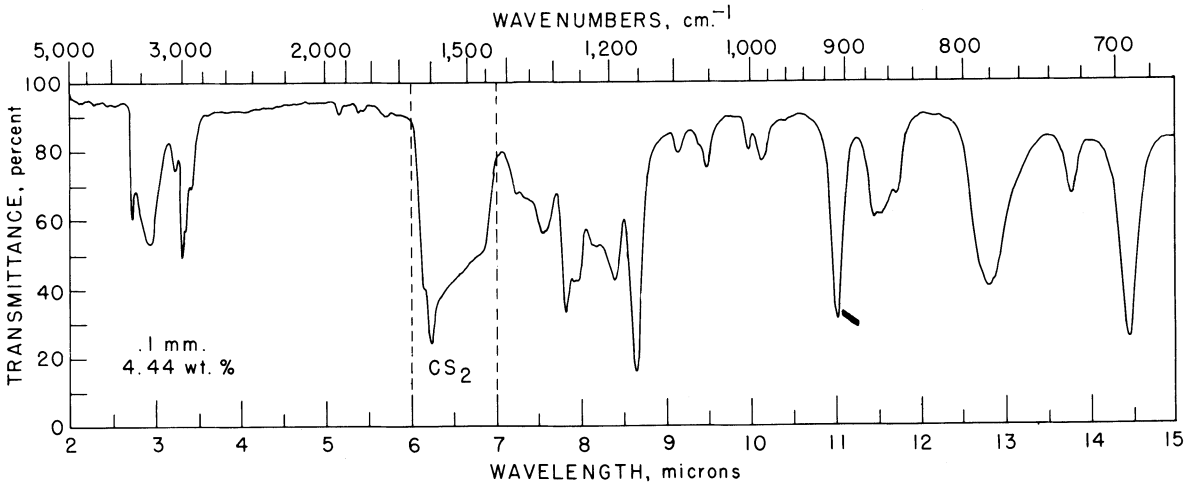


B. p. 214° (54)



λ max, mμ (cyclohexane)	log ε
279.5	3.29
272.3	3.27
267.0	3.13

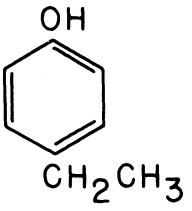
12



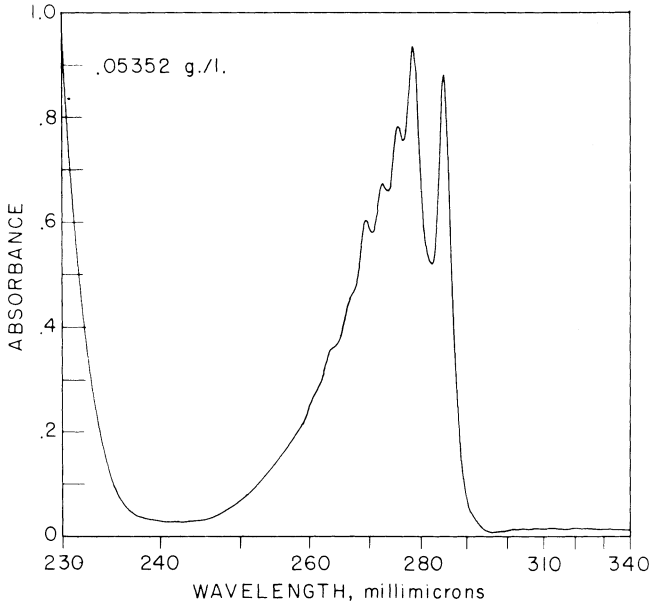
CS_2

λ : 14.48 (s), 13.80 (m), 12.84 (s), 11.75 (m), 11.57 (w), 11.48 (m), 11.04 (s), 10.15 (w), 10.00 (w), 9.51 (w), 9.42 (w), 9.18 (w), 8.68 (s), 8.42 (m), 8.20 (w), 7.97 (m), 7.84 (m), 7.58 (m), 7.28 (w).

4-ETHYLPHENOL

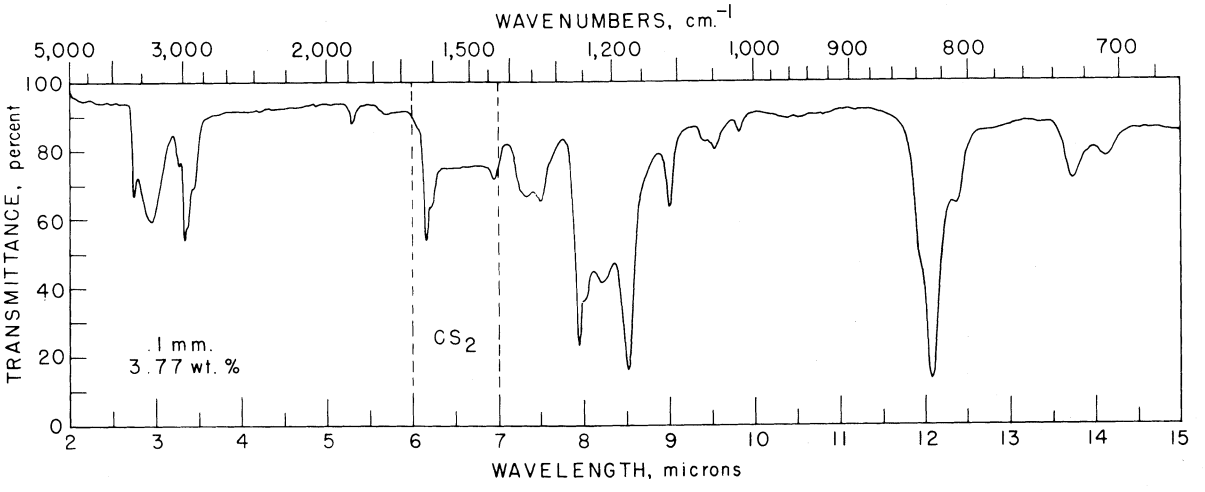


B. p. 219° (54)



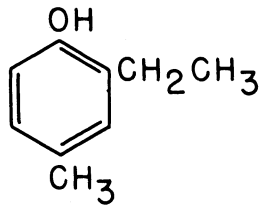
λ max, mμ (cyclohexane)	log ε
285.0	3.30
278.3	3.32
275.3	3.25
272.4	3.18
269.5	3.13
266.8	3.02
264.0	2.91
261.0	2.80

13

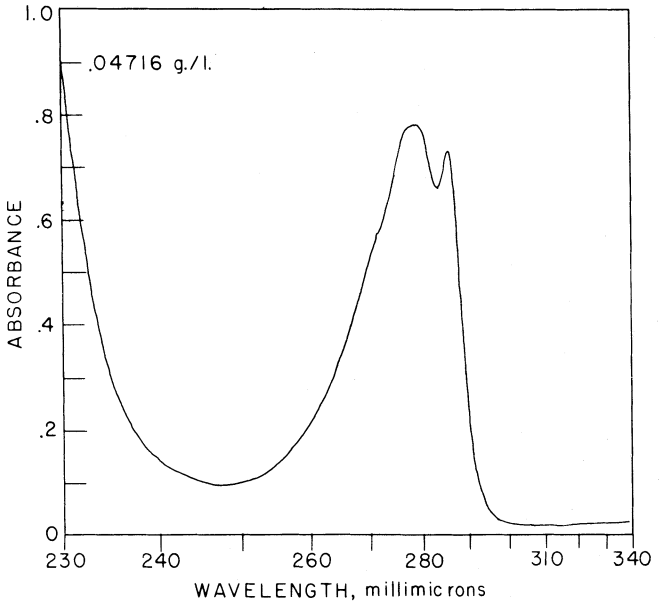


λ^{CS_2}: 14.13 (w), 13.75 (w), 12.38 (w), 12.08 (s), 9.84 (w), 9.55 (w), 9.43 (w), 9.02 (m), 8.54 (s), 8.24 (w), 8.02 (w), 7.96 (m), 7.52 (w), 7.35 (w).

2-ETHYL-4-METHYLPHENOL

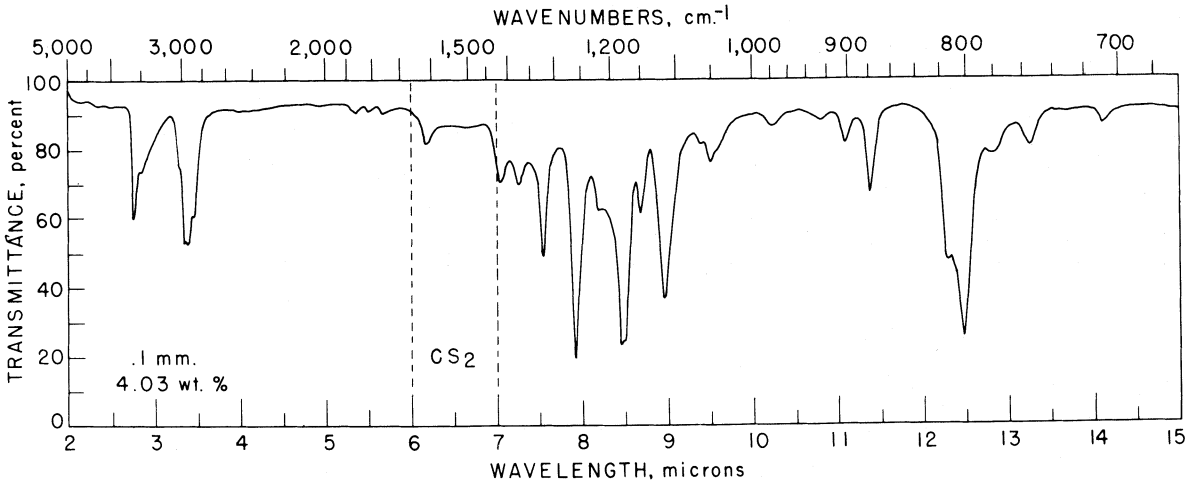


B. p. 216-218° (54)



λ max, mμ (cyclohexane)	log ε
285.4	3.35
279.0	3.38

14



λ^{CS_2}: 14.12 (w), 13.26 (w), 12.85 (w), 12.47 (s), 12.28 (m), 11.38 (m), 11.09 (w), 10.82 (w), 10.25 (w), 9.52 (w), 9.42 (w), 8.97 (s), 8.70 (w), 8.50 (s), 8.20 (w), 7.94 (s), 7.56 (m), 7.27 (w), 7.05 (w).

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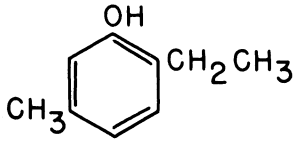
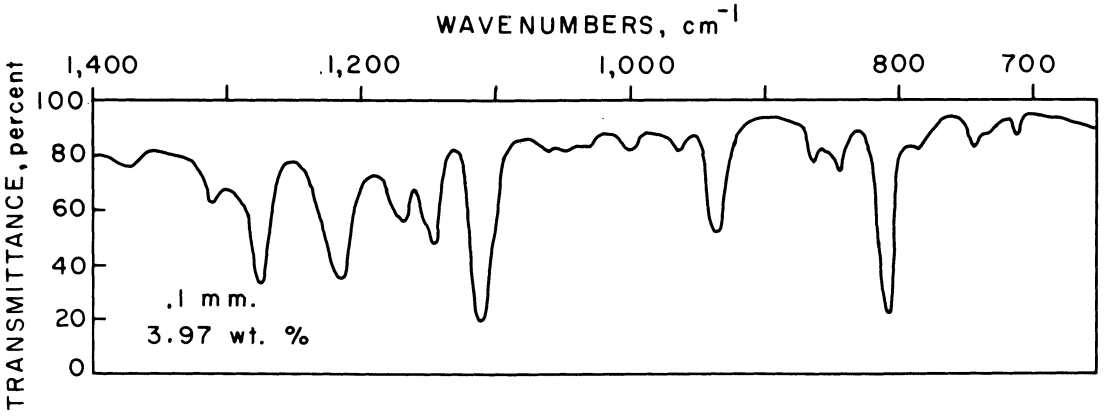
2-ETHYL-5-METHYLPHENOL



B.p. 224.2° (54)

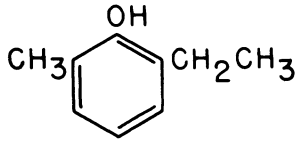


λ^{CS_2}: 14.04 (w), 13.66 (w), 13.40 (w), 12.74 (w), 12.38 (s), 11.85 (w), 11.50 (w), 10.70 (m), 10.35 (w), 10.00 (w), 9.69 (w), 9.52 (w), 9.42 (w), 8.99 (s), 8.73 (m), 8.63 (w), 8.53 (m), 8.21 (s), 7.84 (s), 7.63 (w), 7.29 (w). (11)

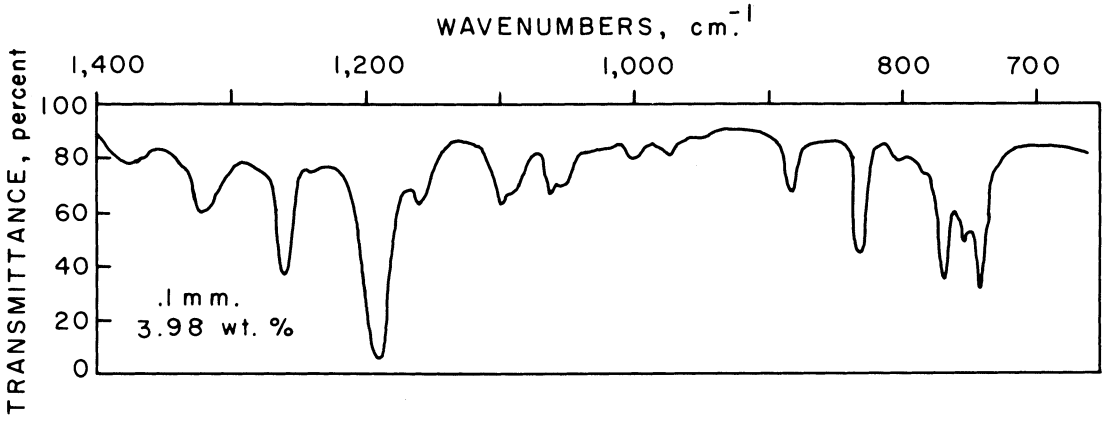
15

2-ETHYL-6-METHYLPHENOL

16

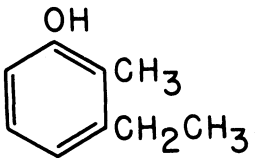


B.p. 212-214° (54)



λ^{CS_2}: 13.42 (s), 13.23 (m), 12.95 (s), 12.74 (w), 12.42 (w), 12.03 (s), 11.30 (m), 10.52 (w), 10.29 (w), 10.00 (w), 9.72 (w), 9.51 (w), 9.42 (m), 9.19 (w), 9.10 (m), 8.62 (m), 8.42 (s), 8.06 (w), 7.92 (s), 7.55 (m), 7.29 (w). (11)

3-ETHYL-2-METHYLPHENOL

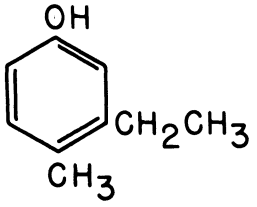


B.p. 227° (54)

Infrared bands, μ : 14.08 (s), 12.90 (s), 12.66 (s), 12.21 (w), 11.35 (s), 11.21 (s), 10.34 (m), 9.71 (s), 9.35 (s), 9.18 (s), 9.03 (s), 8.55 (s), 8.42 (s), 8.10 (m), 7.85 (s), 7.72 (s), 7.38 (s), 7.25 (m). (49)

17

3-ETHYL-4-METHYLPHENOL

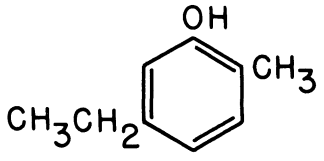


B.p. 234-235° (54)

Infrared bands, μ : 12.42 (s), 11.49 (s), 10.81 (s), 10.10 (w), 9.85 (m), 9.61 (w), 9.43 (m), 8.91 (m), 8.61 (s), 8.31 (s), 8.10 (s), 7.95 (s), 7.70 (s), 7.52 (m), 7.25 (m). (49)

18

5-ETHYL-2-METHYLPHENOL

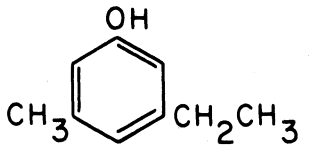


B.p. 223° (54)

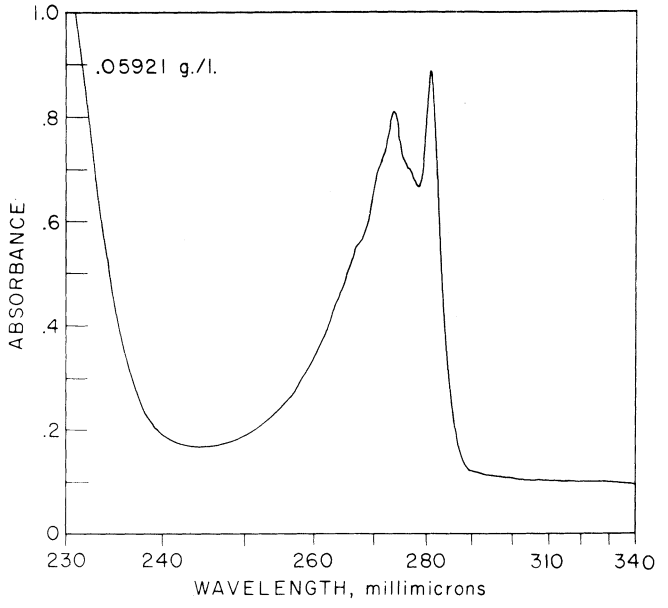
19

Infrared bands, μ : 11.90 (s), 10.99 (m), 10.31 (m), 9.70 (m), 9.35 (m), 8.77 (s), 8.12 (m), 7.89 (m), 7.69 (s), 7.50 (s), 7.30 (s). (49)

3-ETHYL-5-METHYLPHENOL

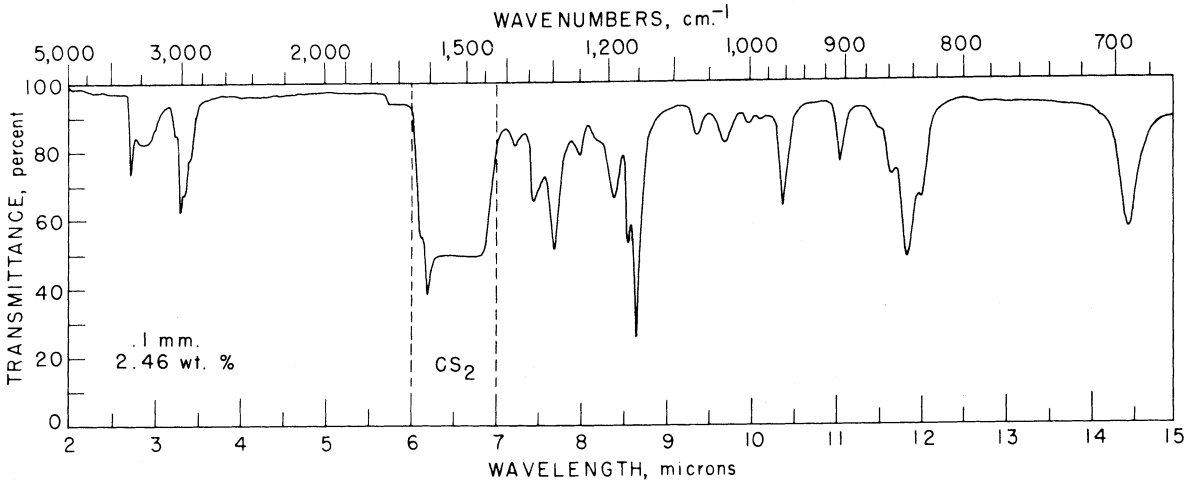


B. p. 233° (54)



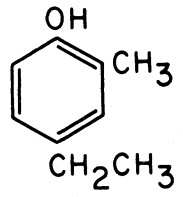
λ max, mμ (cyclohexane)	log ε
280.8	3.35
276.6	3.27
273.3	3.32
270.7	3.27
266.9	3.18
264.0	3.11

20

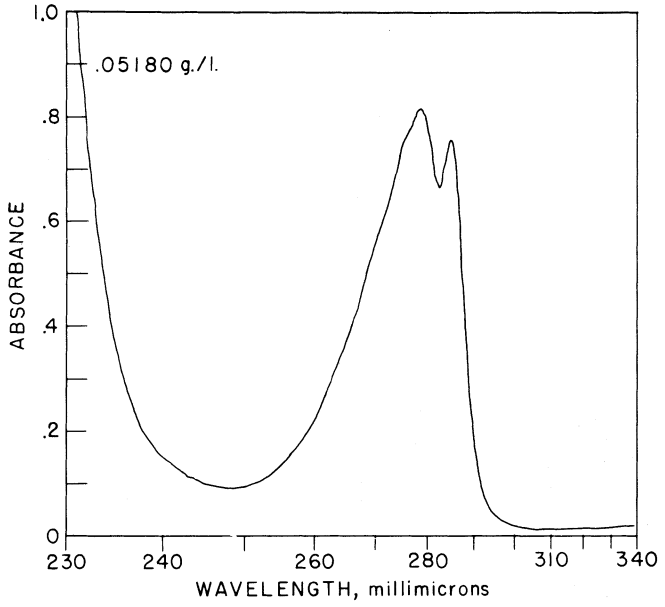


λ^{CS_2}: 14.47 (s), 12.02 (w), 11.86 (s), 11.67 (w), 11.52 (w), 11.07 (m), 10.40 (m), 10.12 (w), 9.72 (w), 9.38 (w), 8.68 (s), 8.58 (m), 8.42 (m), 8.20 (w), 8.01 (w), 7.72 (m), 7.47 (m), 7.25 (w).

4-ETHYL-2-METHYLPHENOL

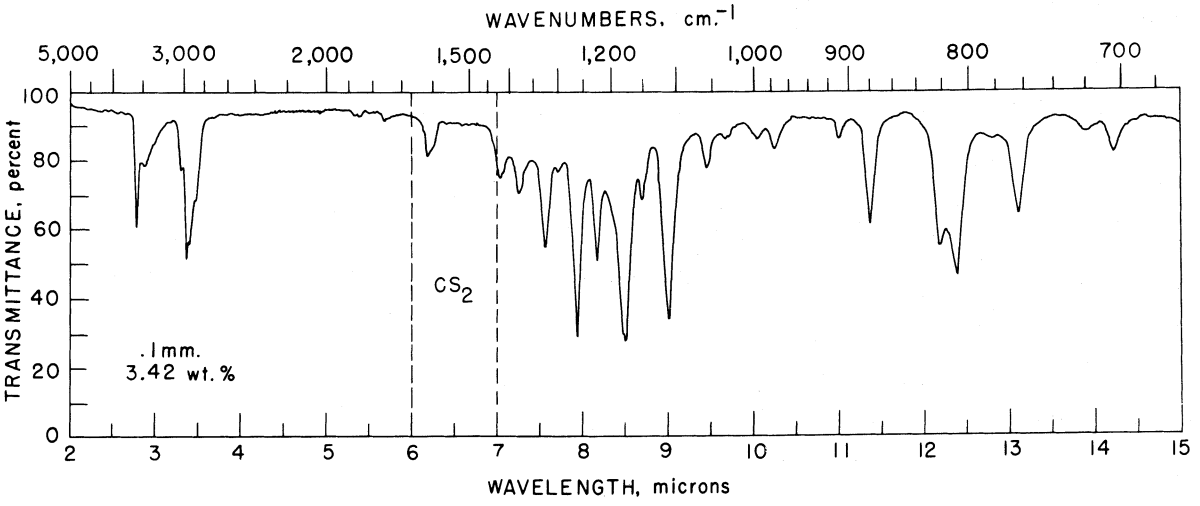


B. p. 222° (54)



λ max, mμ (cyclohexane)	log ε
285.0	3.30
278.5	3.33
275.4	3.30

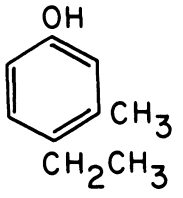
21



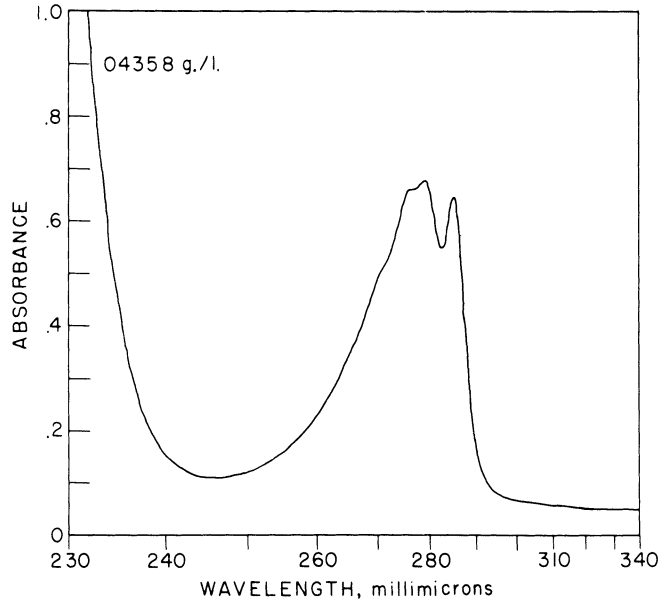
CS_2

λ : 14.22 (w), 13.90 (w), 13.10 (m), 12.36 (s), 12.17 (m), 11.35 (s), 11.00 (w), 10.25 (w), 10.02 (w), 9.65 (w), 9.45 (w), 9.00 (s), 8.70 (w), 8.50 (s), 8.47 (m), 8.15 (m), 7.92 (s), 7.72 (w), 7.55 (m), 7.26 (w).

4-ETHYL-3-METHYLPHENOL

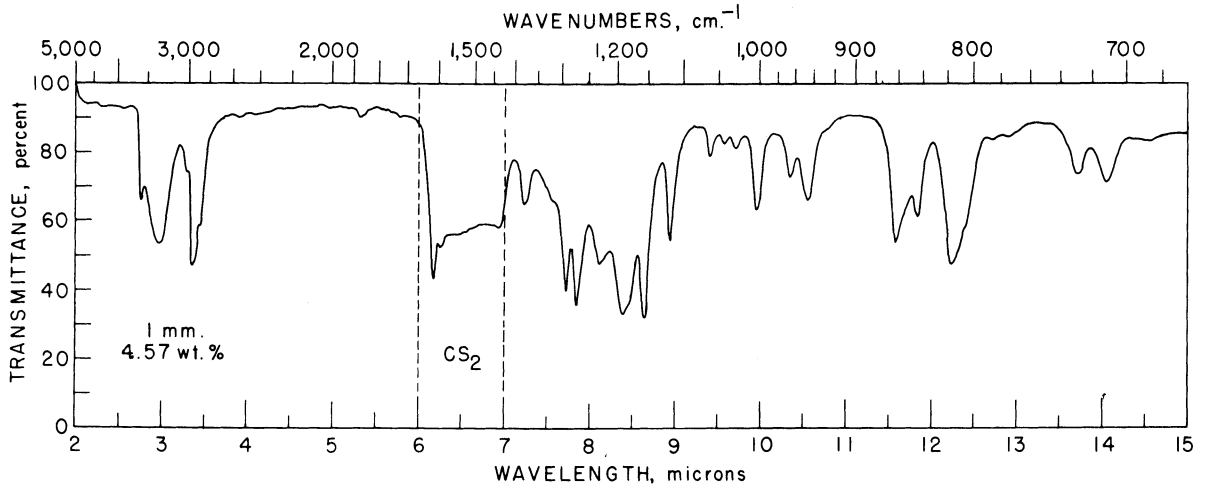


B. p. 228-230° (54)



λ max, mμ (cyclohexane)	log ε
285.0	3.31
279.0	3.33
276.0	3.32
271.0	3.21

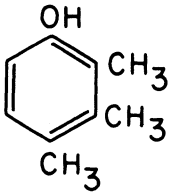
22



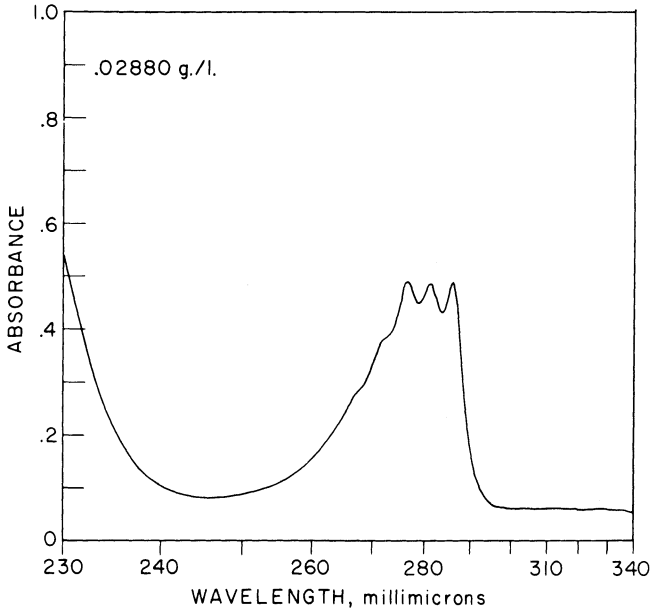
CS_2

λ : 14.06 (m), 13.72 (m), 12.88 (w), 12.72 (w), 12.40 (w), 12.24 (s), 11.84 (m), 11.59 (s), 10.56 (m), 10.35 (m), 9.97 (m), 9.72 (w), 9.58 (w), 9.42 (w), 8.94 (s), 8.65 (s), 8.40 (s), 8.12 (m), 7.86 (s), 7.74 (m), 7.58 (w), 7.25 (w).

2, 3, 4 - TRIMETHYLPHENOL

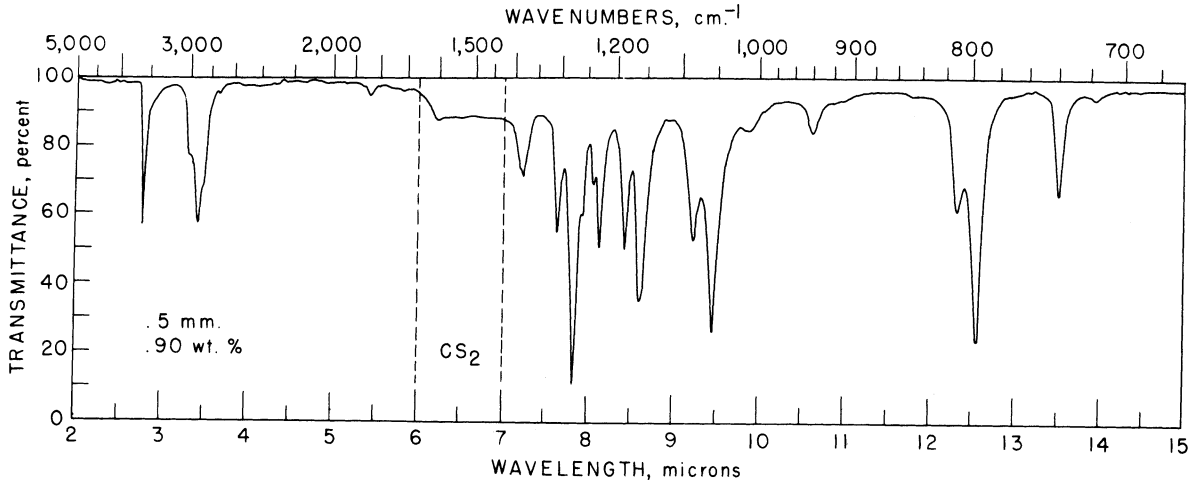


B. p. 235 - 237° (54)



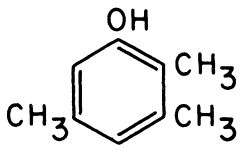
λ max, mμ (cyclohexane)	log ε
285.9	3.36
281.2	3.36
276.5	3.36
272.0	3.25
267.2	3.12

23

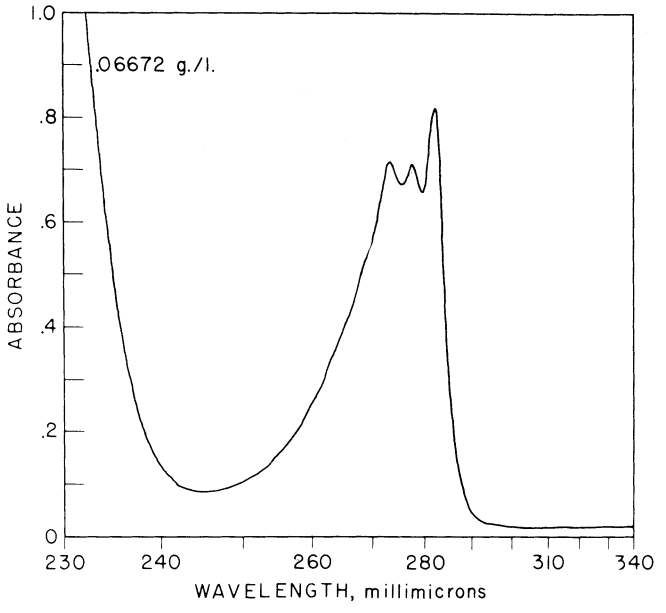


λ^{CS_2}: 13.97 (w), 13.54 (m), 12.57 (s), 12.34 (m), 10.65 (w), 9.92 (w), 9.49 (s), 9.26 (m), 8.64 (s), 8.46 (m), 8.17 (m), 8.08 (w), 7.95 (w), 7.86 (s), 7.67 (m), 7.26 (m).

2, 3, 5 - TRIMETHYLPHENOL

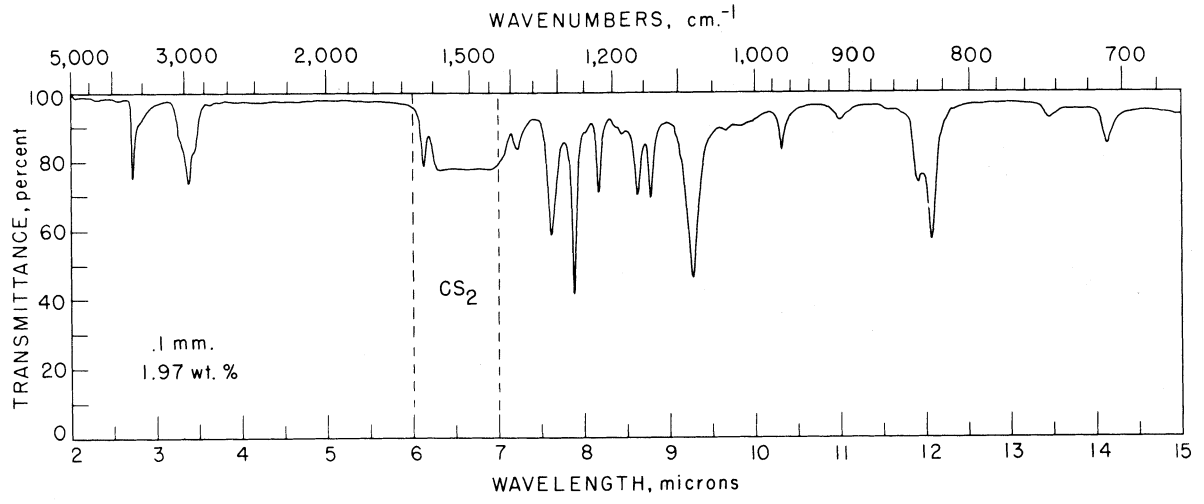


B. p. 233° (54)



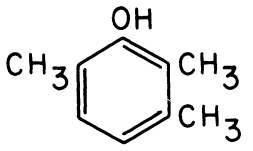
λ max, mμ (cyclohexane)	log ε
282.4	3.29
277.8	3.23
273.4	3.23

24

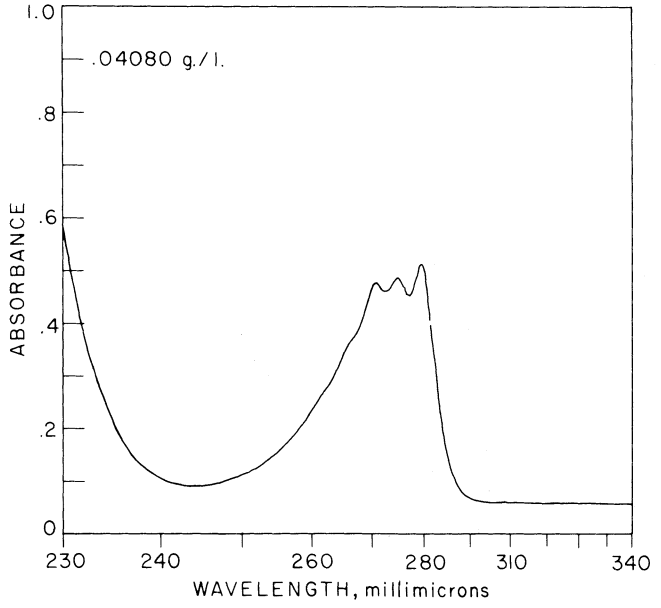


λ^{CS_2}: 14.12 (m), 13.45 (w), 12.05 (s), 11.90 (m), 11.00 (w), 10.30 (m), 9.27 (s), 8.77 (m), 8.62 (m), 8.45 (w), 8.37 (w), 8.17 (m), 8.02 (w), 7.88 (s), 7.62 (s), 7.22 (w).

2, 3, 6 - TRIMETHYLPHENOL

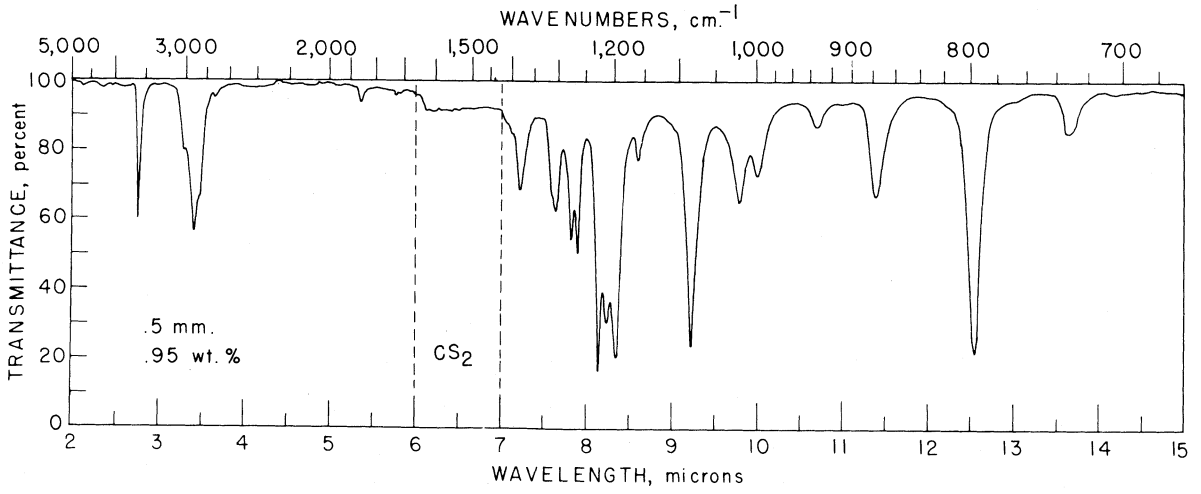


B. p. 100°/14 mm. (54)
[est. 220°]



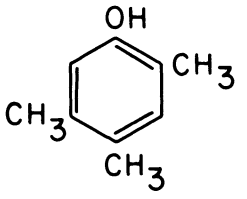
λ max, mμ (cyclohexane)	log ε
279.7	3.23
275.0	3.21
270.8	3.20
266.5	3.09

25

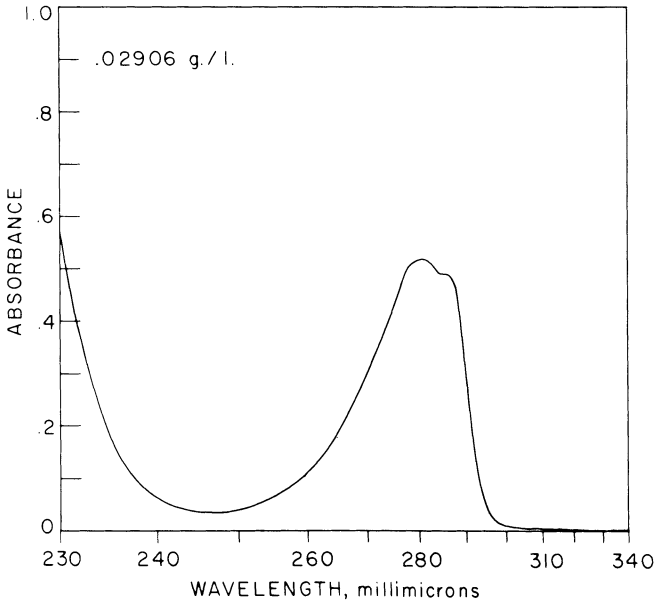


λ^{CS_2}: 13.68 (w), 12.55 (s), 11.40 (m), 10.72 (w), 10.02 (m), 9.82 (m), 9.25 (s), 8.62 (w), 8.38 (s), 8.26 (m), 8.17 (s), 7.93 (m), 7.85 (m), 7.67 (m), 7.25 (m), 7.15 (w), 7.10 (w).

2, 4, 5 - TRIMETHYLPHENOL

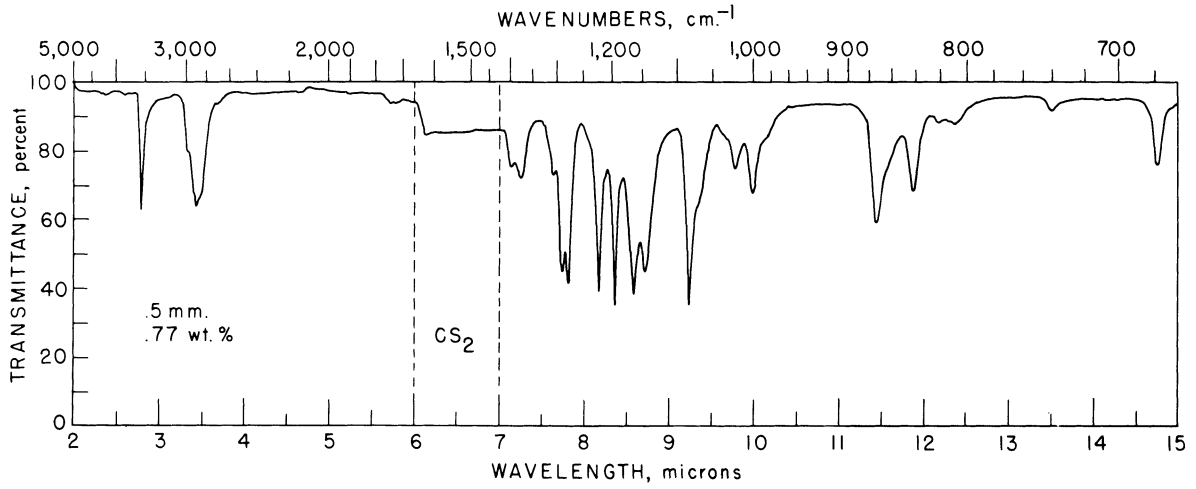


B. p. 232° (54)



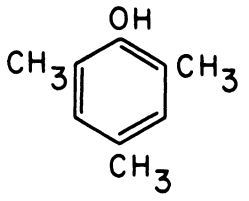
λ max, mμ (cyclohexane)	log ε
285.0	3.36
280.0	3.38

26

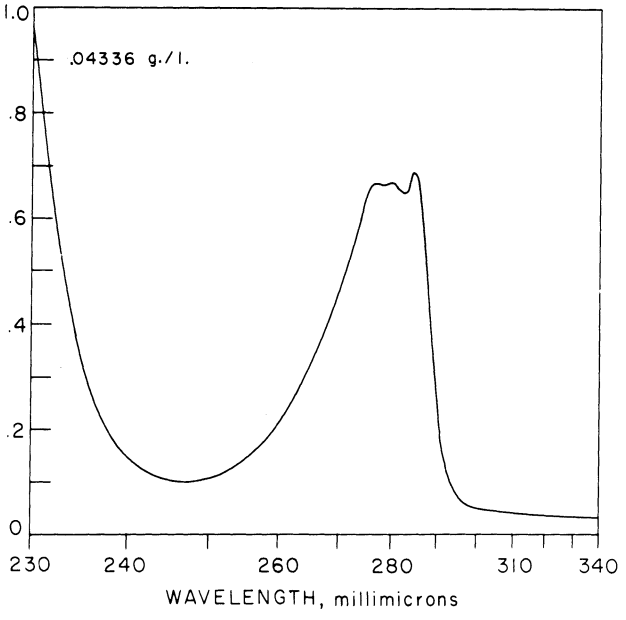


λ^{CS_2}: 14.78 (m), 13.54 (w), 12.42 (w), 12.22 (w), 11.90 (m), 11.47 (s), 10.20 (w), 10.02 (m), 9.82 (w), 9.71 (w), 9.37 (w), 9.27 (s), 8.75 (m), 8.62 (s), 8.40 (s), 8.21 (s), 7.84 (s), 7.77 (s), 7.67 (w), 7.29 (w), 7.17 (w).

2, 4, 6 - TRIMETHYLPHENOL

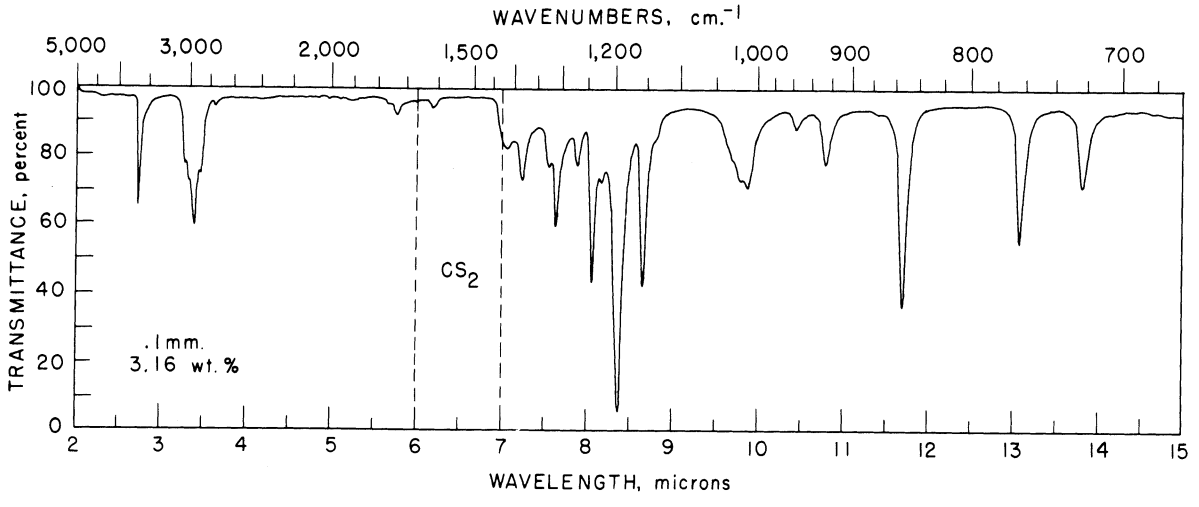


B. p. 222° (54)



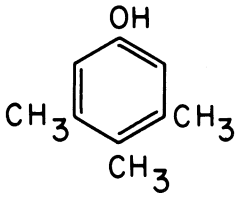
λ max, mμ (cyclohexane)	log ε
284.8	3.34
280.2	3.33
277.0	3.33

27

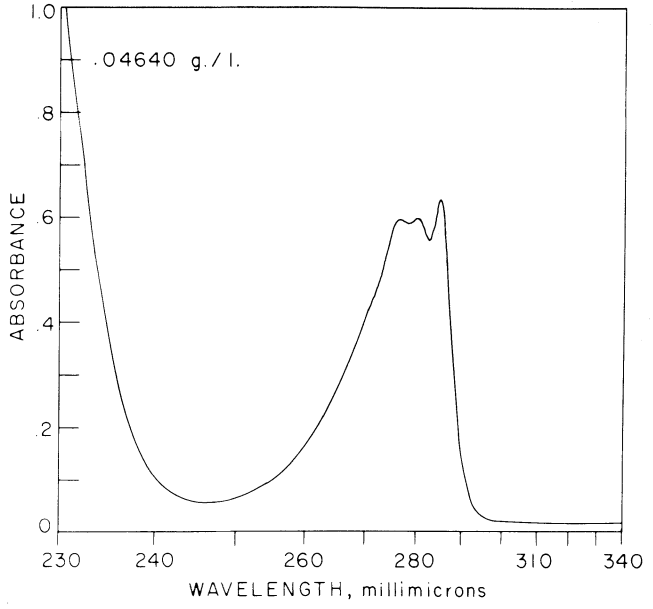


λ^{CS_2}: 13.84 (m), 13.09 (m), 11.71 (s), 10.82 (m), 10.45 (w), 9.88 (m), 9.80 (w), 9.70 (w), 9.65 (w), 8.80 (w), 8.65 (m), 8.38 (s), 8.18 (w), 8.06 (m), 7.90 (w), 7.64 (m), 7.56 (w), 7.24 (w), 7.05 (w).

3, 4, 5 - TRIMETHYLPHENOL

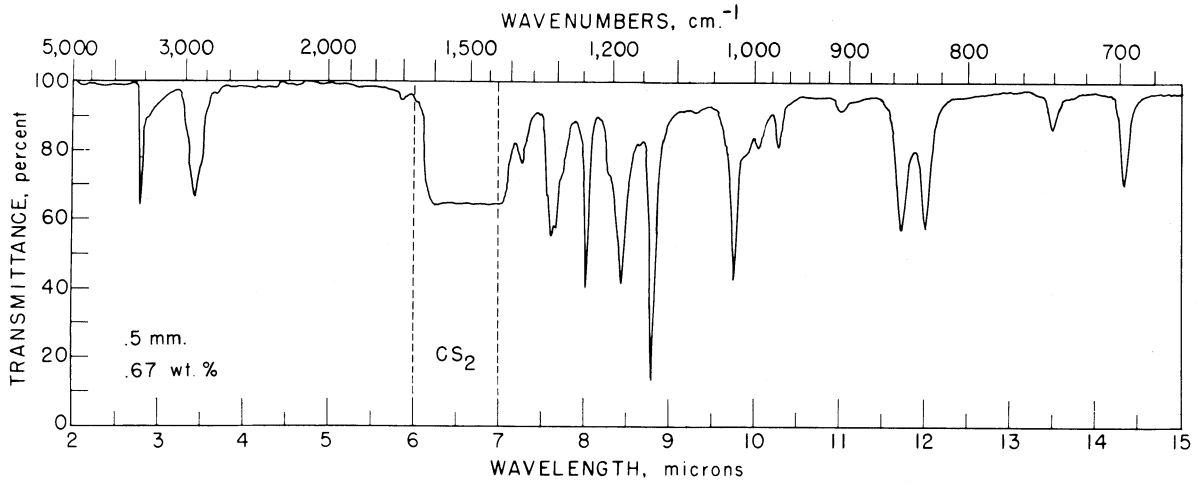


B. p. 248-249° (54)



λ max, mμ (cyclohexane)	log ε
284.7	3.32
280.2	3.31
276.0	3.31

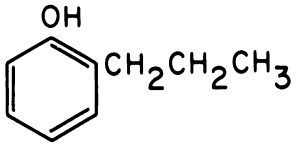
28



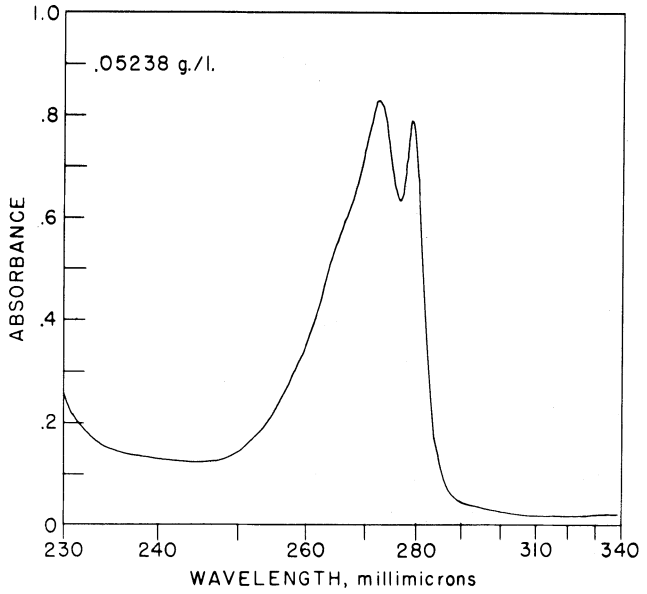
CS_2

λ : 14.33 (m), 13.49 (w), 12.00 (s), 11.72 (s), 11.02 (w), 10.28 (w), 10.05 (w), 9.89 (w), 9.75 (s), 9.30 (w), 8.80 (s), 8.65 (w), 8.44 (s), 8.30 (w), 8.02 (s), 7.73 (w), 7.67 (m), 7.62 (m), 7.57 (w), 7.27 (w).

2 - n - PROPYLPHENOL

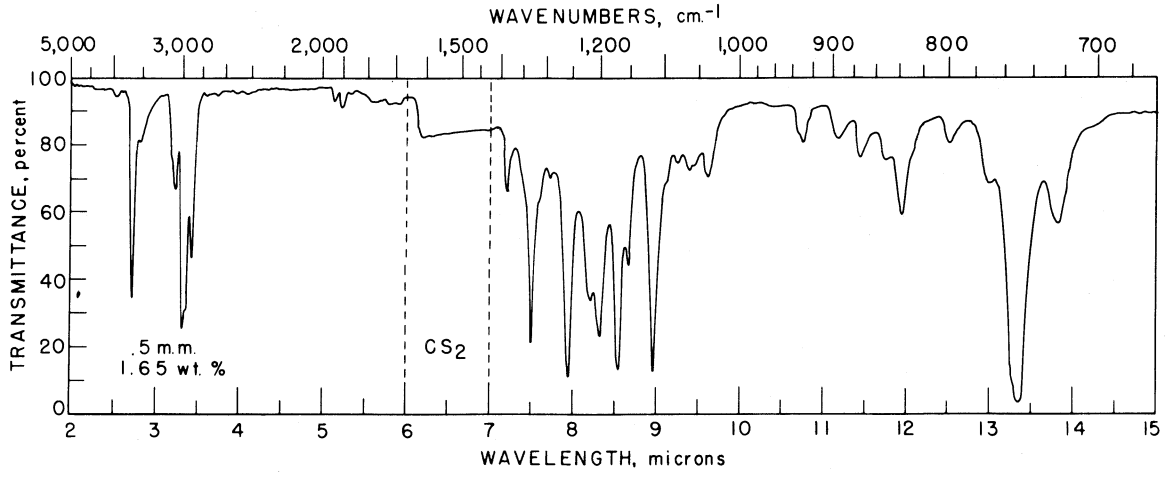


B. p. 220° (54)



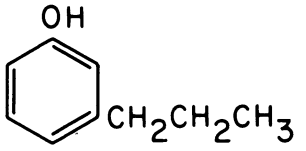
λ max, mμ (cyclohexane)	log ε
278.8	3.31
272.2	3.34

29

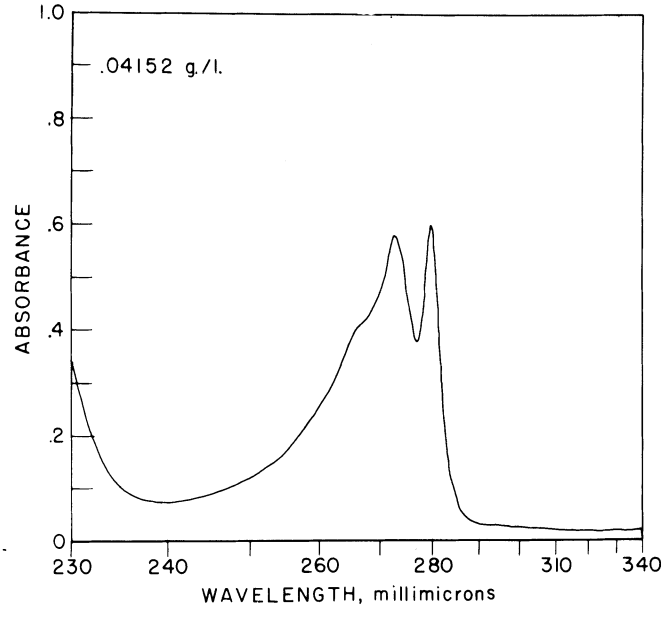


λ^{CS_2}: 13.82 (m), 13.35 (s), 13.01 (w), 12.53 (w), 11.95 (m), 11.76 (w), 11.47 (w), 11.20 (w), 10.77 (w), 10.72 (w), 9.64 (w), 9.47 (w), 9.42 (w), 9.27 (w), 9.14 (w), 8.99 (m), 8.69 (w), 8.57 (m), 8.35 (m), 8.23 (w), 7.97 (m), 7.74 (w), 7.63 (w), 7.54 (m), 7.24 (w).

3 - n - PROPYLPHENOL

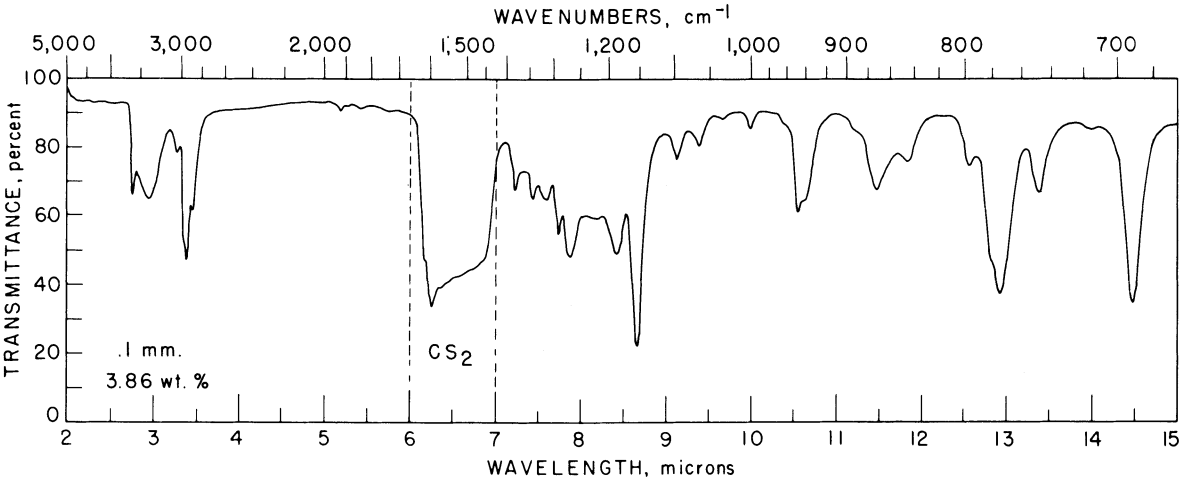


B. p. 228° (54)



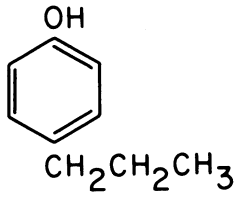
λ max, mμ (cyclohexane)	log ε
279.6	3.29
272.6	3.28
267.0	3.14
259.0	2.89

30

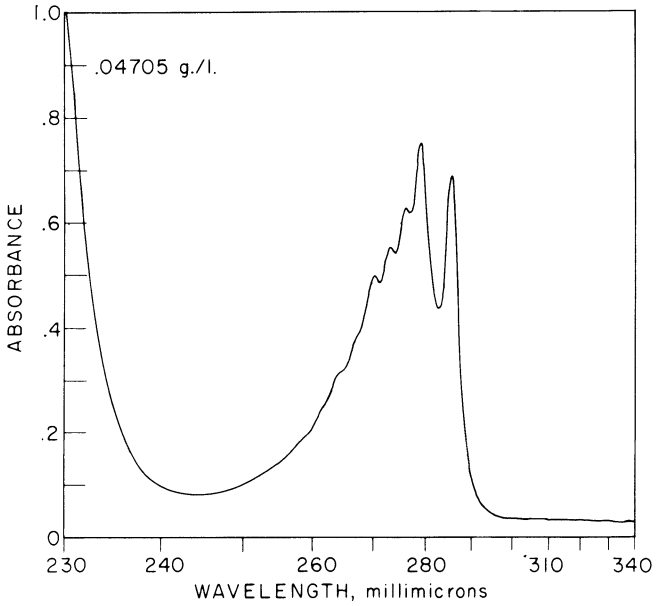


λ^{CS_2}: 14.48 (s), 13.98 (w), 13.37 (m), 12.92 (s), 12.56 (w), 11.85 (w), 11.48 (m), 11.22 (w), 10.64 (m), 10.56 (m), 10.00 (w), 9.66 (w), 9.41 (w), 9.14 (w), 8.68 (s), 8.45 (m), 7.90 (m), 7.76 (m). 7.63 (w), 7.47 (w), 7.26 (w).

4 - n - PROPYLPHENOL

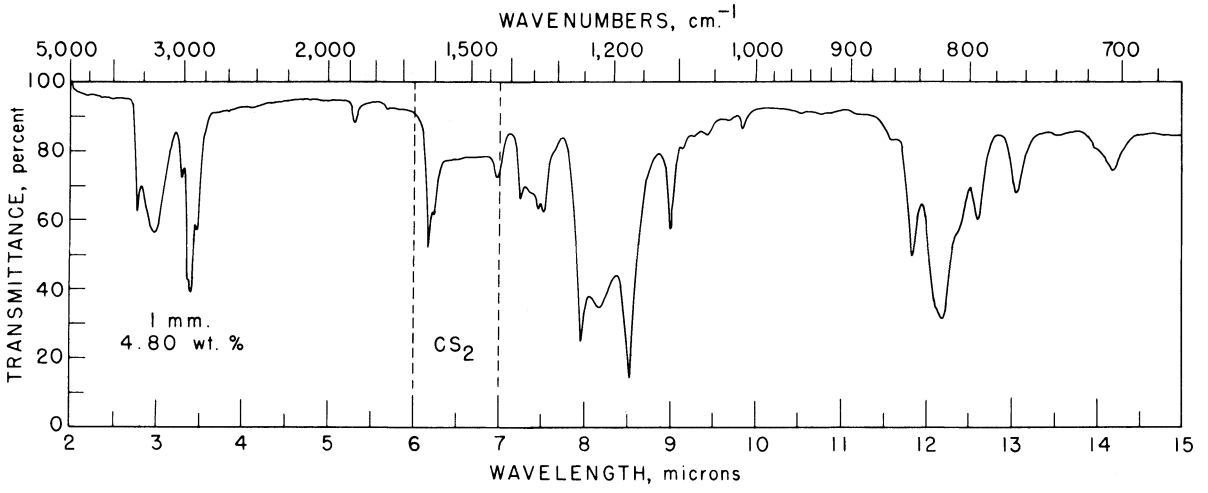


B. p. 232.6° (54)



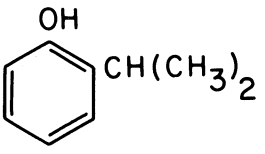
λ max, mμ (cyclohexane)	log ε
285.0	3.32
278.4	3.35
275.6	3.28
272.5	3.22
269.5	3.17
266.7	3.06
264.0	2.97
261.0	2.86
258.0	2.75

31

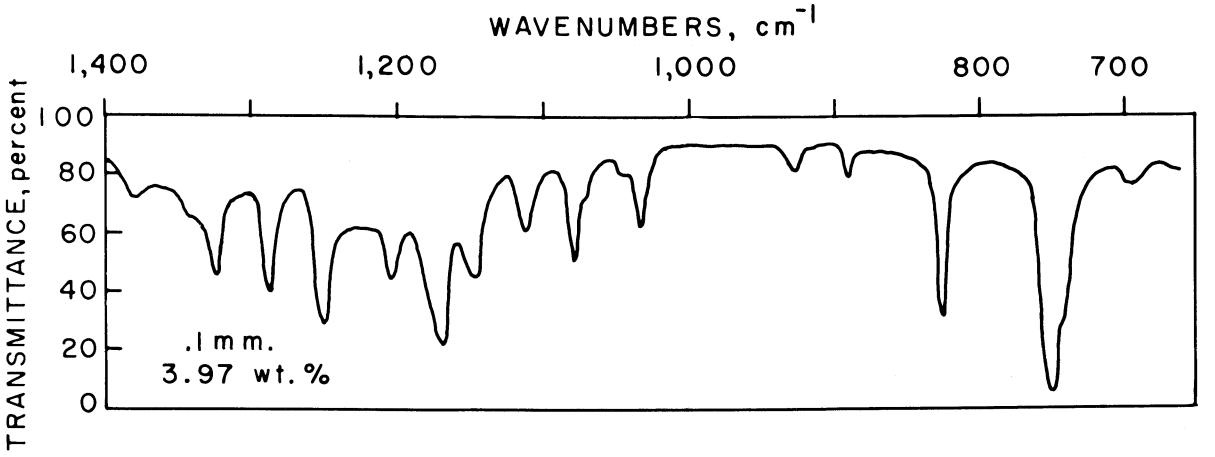


λ^{CS_2} : 14.20 (w), 13.58 (w), 13.07 (m), 12.62 (m), 12.40 (w), 12.20 (s), 11.85 (m), 11.62 (w), 9.86 (w), 9.68 (w), 9.45 (w), 9.28 (w), 9.16 (w), 9.02 (m), 8.56 (s), 8.19 (m), 7.98 (s), 7.54 (m), 7.48 (m), 7.38 (w), 7.27 (m).

2-ISOPROPYLPHENOL



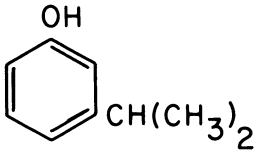
B.p. 214°/745 mm. (54)



λ^{CS_2}: 14.39 (w), 13.42 (w), 13.33 (s), 12.09 (m), 11.21 (w), 10.79 (w), 9.71 (m), 9.56 (w), 9.35 (w), 9.26 (m), 8.98 (m), 8.70 (m), 8.55 (s), 8.31 (m), 7.98 (m), 7.76 (m), 7.55 (m), 7.43 (w), 7.25 (w). (11)

32
33

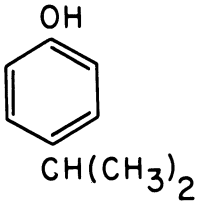
3-ISOPROPYLPHENOL



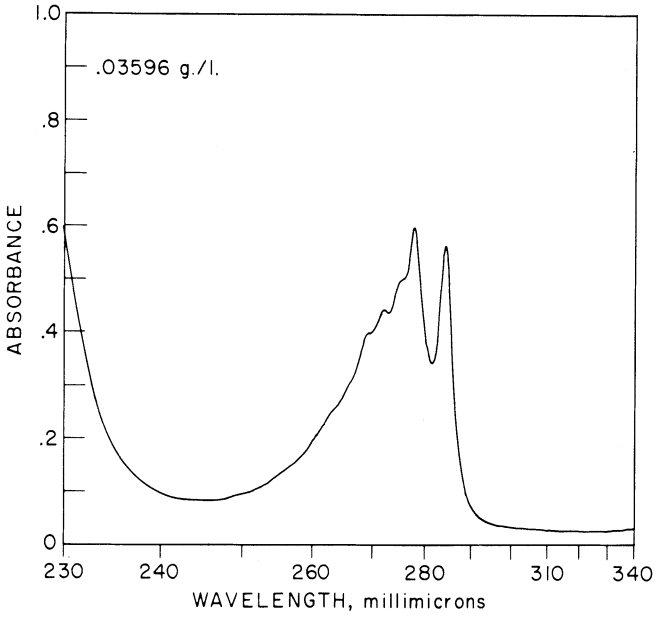
B.p. 228° (54)

Infrared bands, μ : 14.71 (s), 12.82 (s), 12.33 (w), 11.63 (s), 10.75 (s), 10.00 (w), 9.52 (w), 8.93 (w), 8.56 (m), 8.45 (s), 8.05 (s), 7.86 (s). (49)

4-ISOPROPYLPHENOL

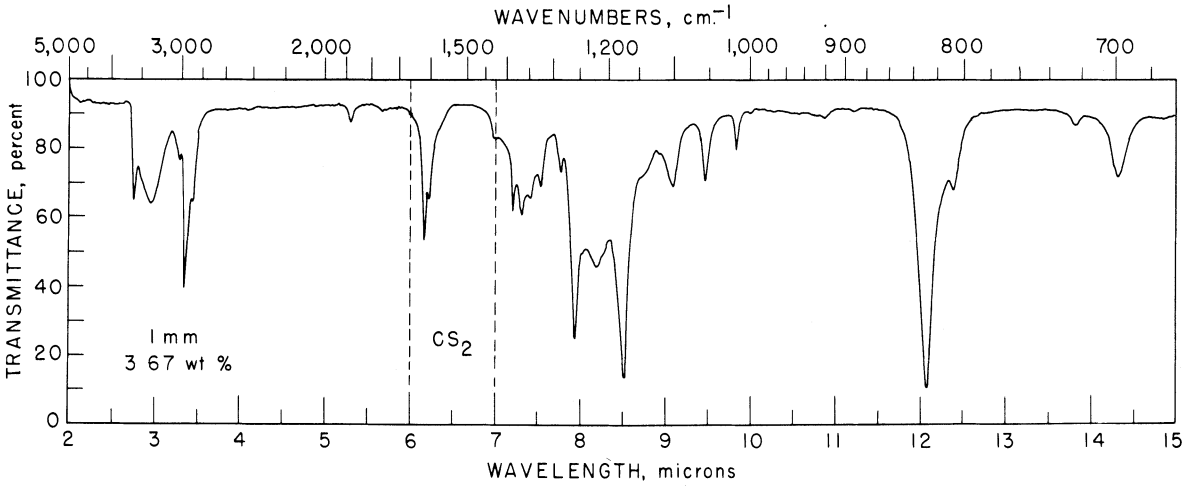


B. p. 228-229°/745 mm. (54)



λ max, mμ (cyclohexane)	log ε
284.2	3.32
277.6	3.35
275.2	3.27
271.9	3.22
269.2	3.17
266.0	3.05
263.2	2.97

34



λ^{CS_2}: 14.34 (m), 13.83 (w), 12.40 (w), 12.08 (s), 9.85 (w), 9.49 (m), 9.10 (m), 8.97 (w), 8.78 (w), 8.53 (s), 8.21 (w), 8.03 (w), 7.96 (m), 7.79 (w), 7.55 (w), 7.43 (w), 7.33 (w), 7.22 (w).

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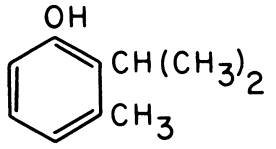
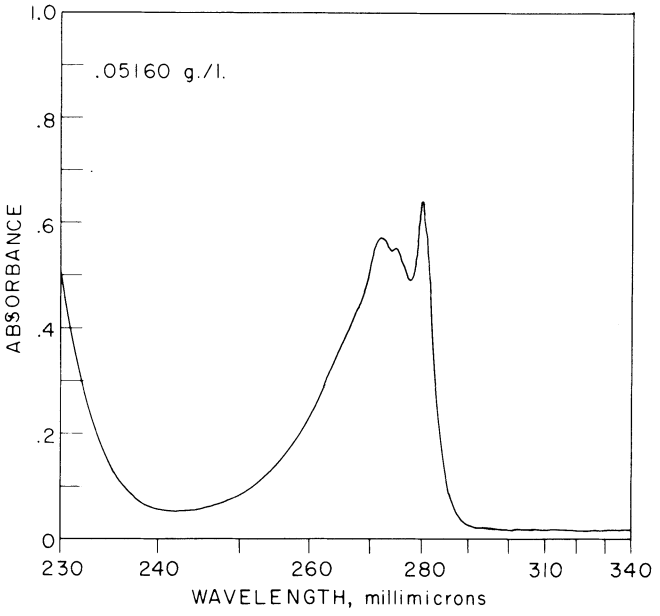
2-ISOPROPYL-3-METHYLPHENOL

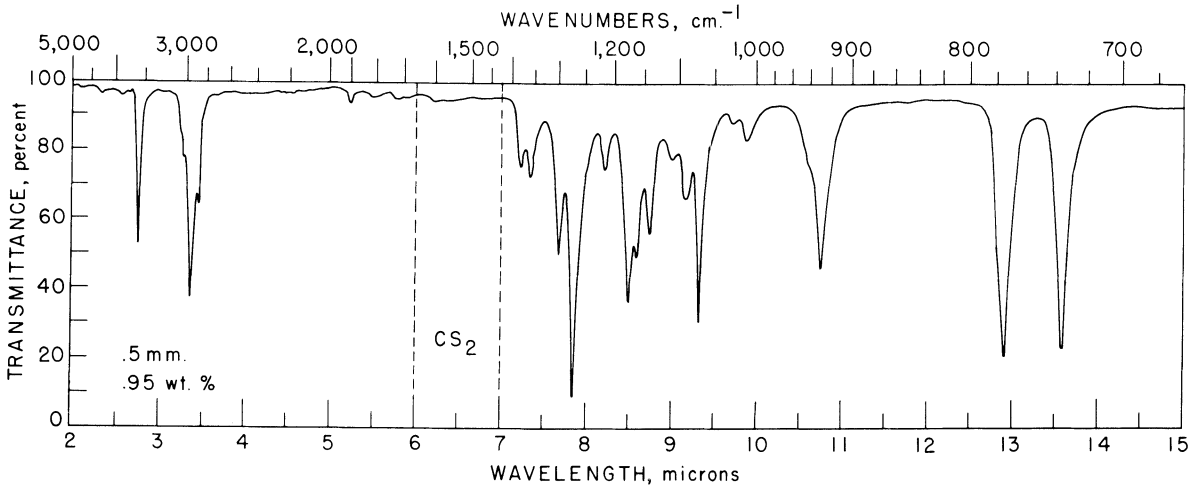


B. p. 228.5° (54)



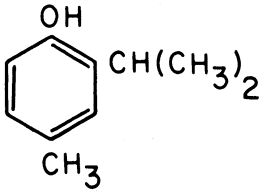
λ max, mμ (cyclohexane)	log ε
280.2	3.27
274.8	3.27
272.2	3.22

35

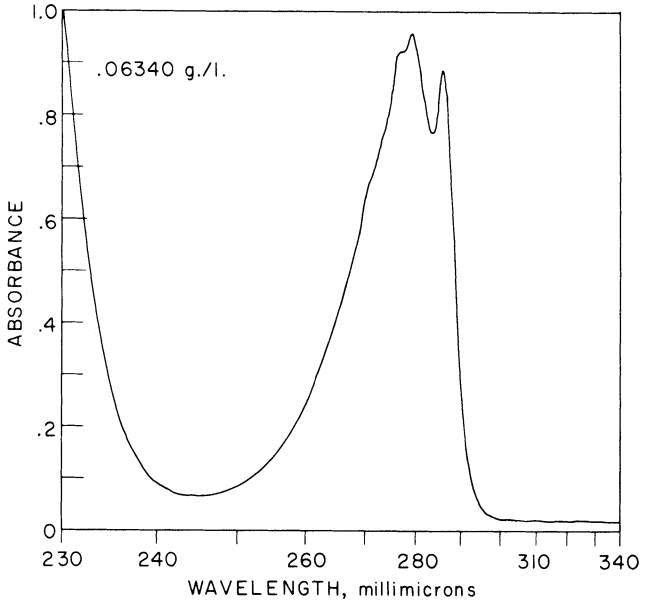


λ^{CS_2}: 13.58 (s), 12.92 (s), 10.77 (s), 10.65 (w), 9.90 (w), 9.74 (w), 9.35 (s), 9.19 (m), 9.02 (w), 8.77 (m), 8.62 (m), 8.53 (s), 8.24 (m), 7.88 (s), 7.72 (m), 7.37 (m), 7.25 (m).

2-ISOPROPYL-4-METHYLPHENOL

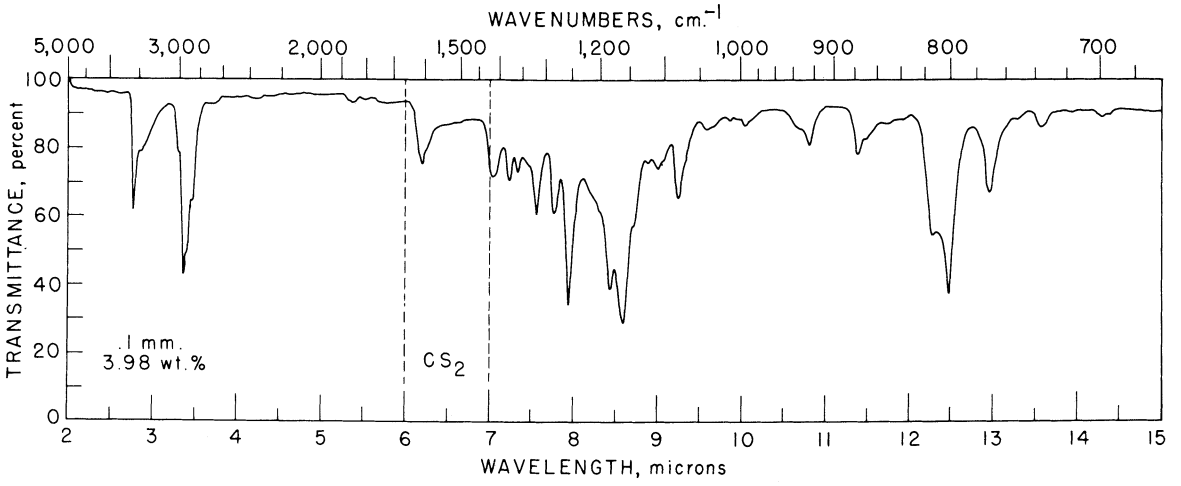


B. p. 228-229°/763 mm. (54)



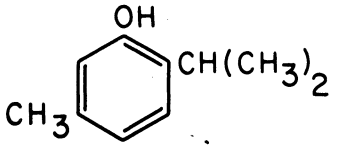
λ max, mμ (cyclohexane)	log ε
285.9	3.32
279.2	3.36
277.0	3.34
271.0	3.20

36

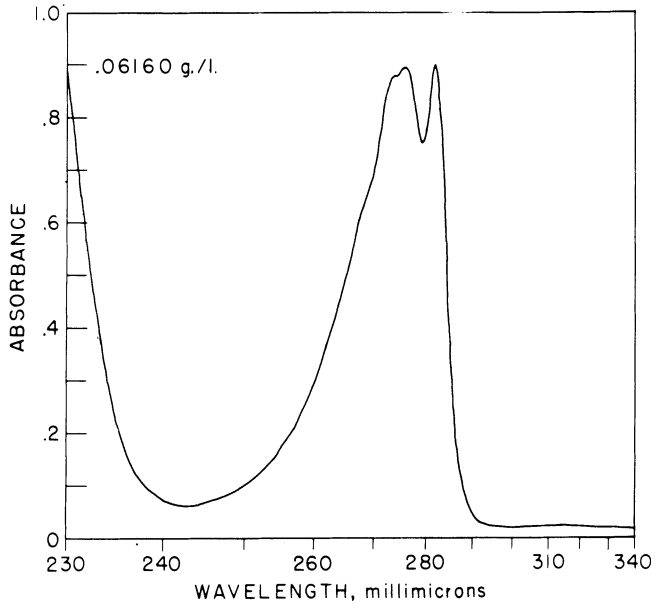


λ^{CS_2}: 14.27 (w), 13.57 (w), 13.27 (w), 12.94 (m), 12.47 (s), 12.27 (m), 11.90 (w), 11.76 (w), 11.50 (w), 11.38 (m), 10.81 (m), 10.67 (w), 10.07 (w), 9.87 (w), 9.60 (w), 9.34 (w), 9.25 (m), 9.07 (w), 9.00 (w), 8.88 (w), 8.72 (w), 8.60 (s), 8.44 (m), 8.32 (w), 8.18 (w), 7.95 (s), 7.77 (m), 7.57 (m), 7.47 (w), 7.34 (w), 7.24 (w), 7.05 (w).

2-ISOPROPYL-5-METHYLPHENOL

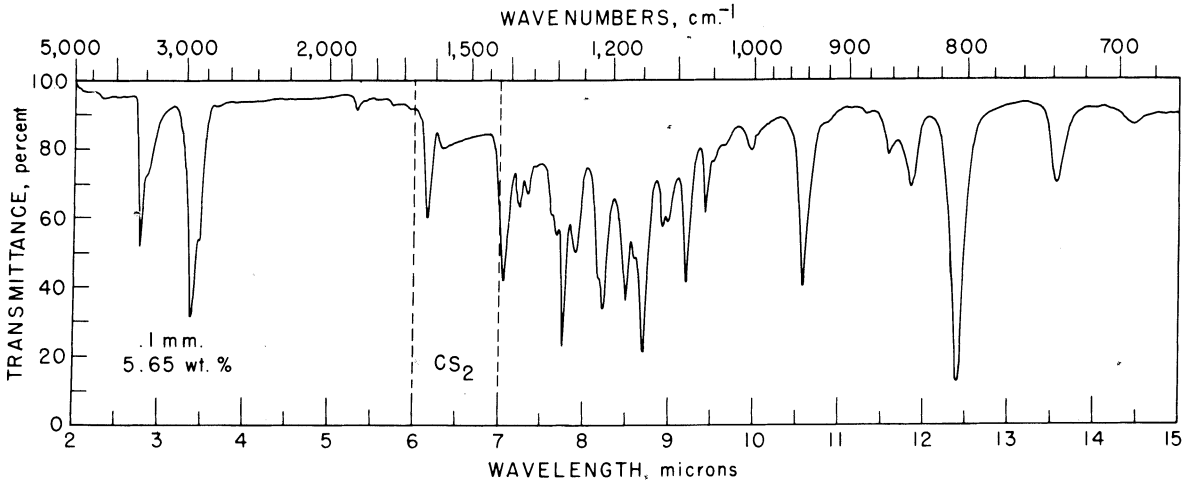


B. p. 233.5° (54)



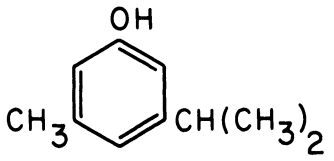
λ max, mμ (cyclohexane)	log ε
281.8	3.34
276.0	3.34
273.8	3.33

37

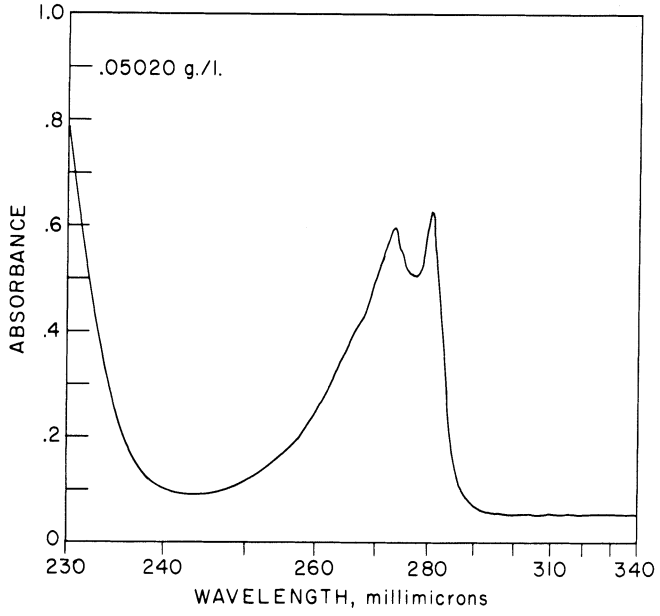


λ^{CS_2}: 14.47 (w), 13.57 (m), 12.40 (s), 11.85 (m), 11.57 (w), 11.32 (w), 10.85 (w), 10.57 (s), 9.97 (w), 9.65 (w), 9.52 (w), 9.44 (m), 9.21 (m), 9.00 (w), 8.93 (m), 8.70 (s), 8.60 (w), 8.50 (m), 8.23 (m), 8.18 (w), 7.90 (m), 7.75 (s), 7.68 (w), 7.62 (w), 7.35 (w), 7.24 (w), 7.06 (m).

3-ISOPROPYL-5-METHYLPHENOL

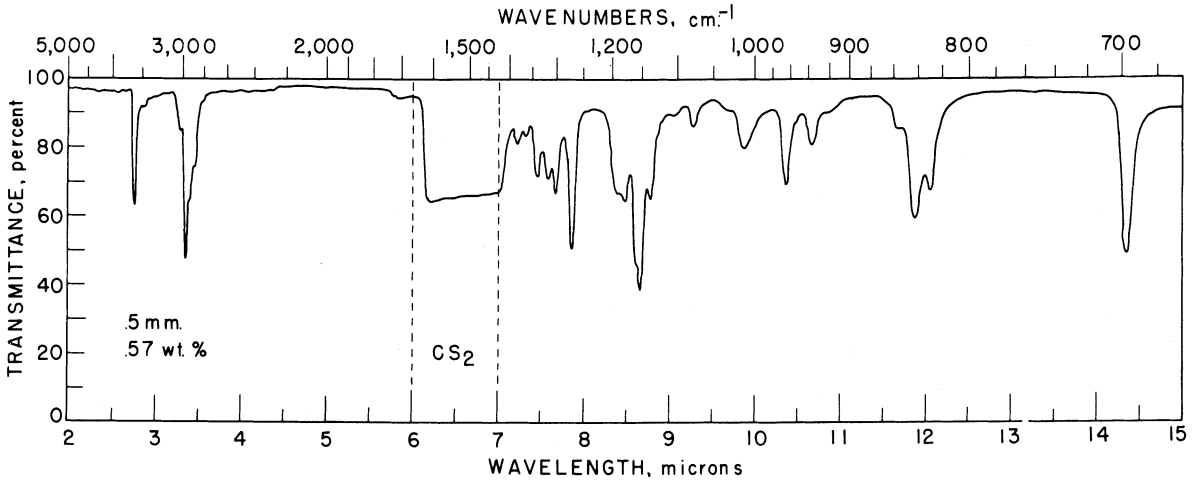


B. p. 241° (54)



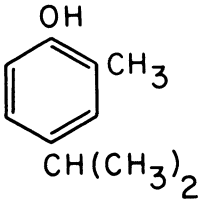
λ max, mμ (cyclohexane)	log ε
280.5	3.28
273.0	3.25

38

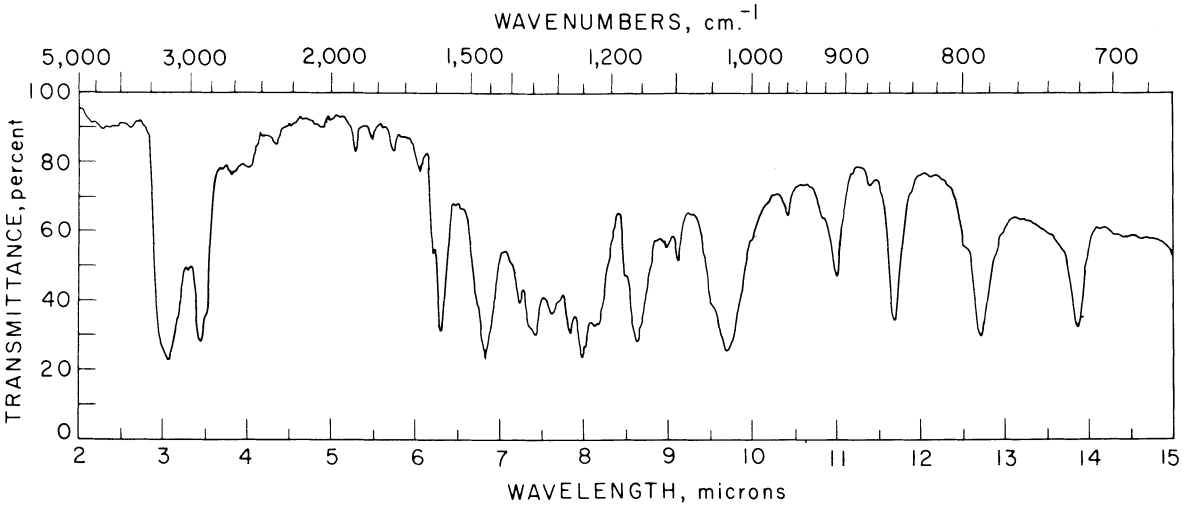


λ^{CS_2}: 14.35 (s), 12.06 (m), 11.88 (m), 11.70 (w), 10.67 (m), 10.37 (m), 9.90 (m), 9.30 (w), 9.07 (w), 8.80 (m), 8.69 (s), 8.64 (w), 8.50 (m), 8.42 (w), 7.88 (s), 7.70 (m), 7.61 (m), 7.48 (m), 7.35 (w), 7.25 (w).

4-ISOPROPYL-2-METHYLPHENOL



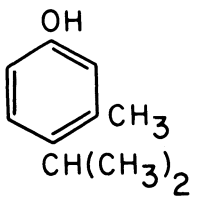
B.p. 230-234° (54)



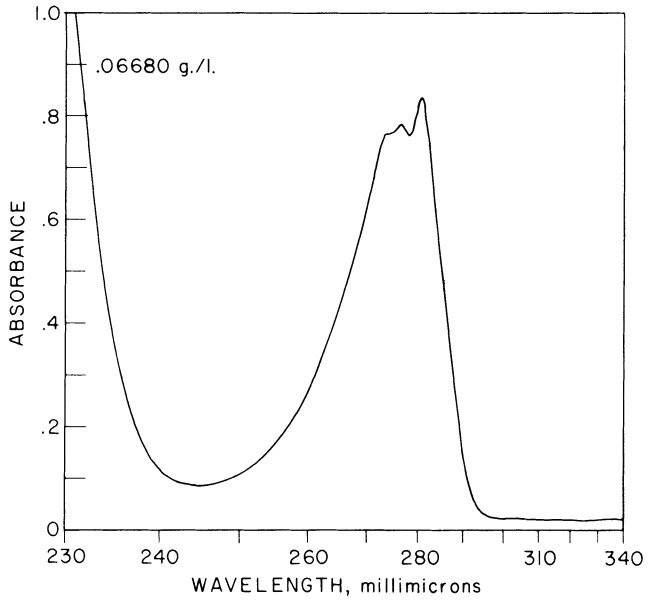
39

λ_{max}^{melt}: 13.87 (s), 12.72 (s), 12.54 (w), 11.70 (s), 11.39 (w), 11.00 (m), 10.84 (w), 10.42 (w), 9.70 (s), 9.54 (w), 9.12 (w), 9.00 (w), 8.64 (s), 8.48 (w), 8.17 (w), 7.98 (m), 7.84 (m), 7.62 (w), 7.43 (m), 7.36 (w), 7.23 (w). (99)

4 - ISOPROPYL - 3 - METHYLPHENOL

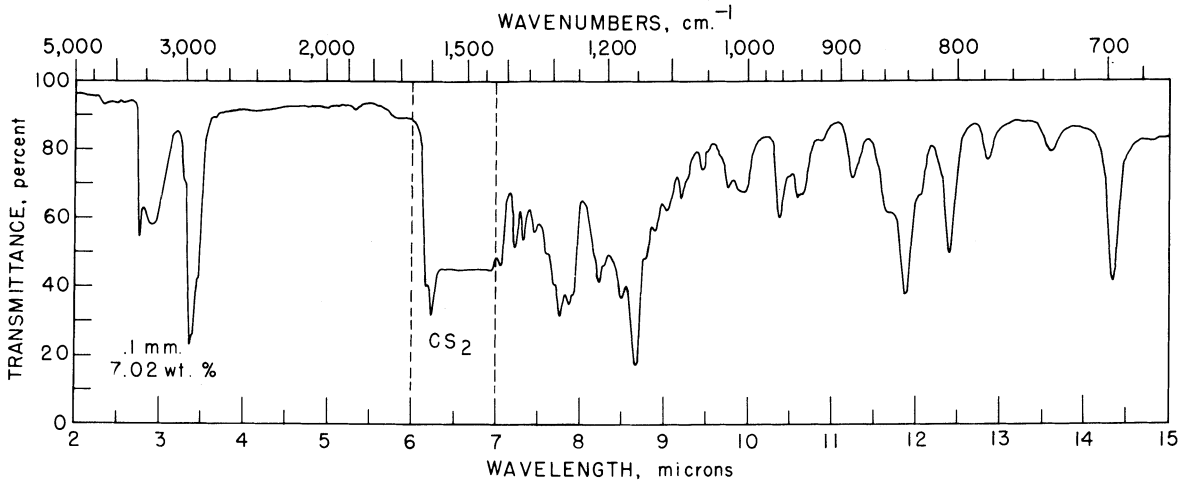


B. p. 238° (54)



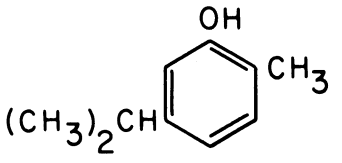
λ max, mμ (cyclohexane)	log ε
280.7	3.28
276.4	3.25
273.5	3.24

40

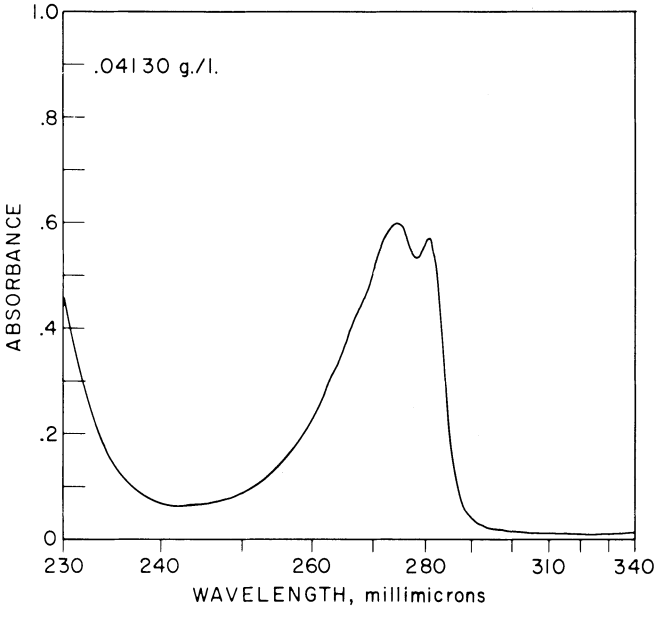


λ^{CS_2}: 14.35 (s), 13.60 (m), 12.85 (m), 12.40 (s), 12.05 (w), 11.87 (s), 11.67 (w), 11.24 (m), 10.87 (w), 10.65 (m), 10.58 (m), 10.37 (m), 9.90 (w), 9.77 (w), 9.47 (w), 9.21 (w), 9.05 (w), 8.90 (w), 8.79 (w), 8.67 (s), 8.50 (m), 8.30 (w), 8.22 (m), 7.92 (w), 7.87 (m), 7.76 (m), 7.70 (w), 7.60 (w), 7.48 (w), 7.34 (w), 7.24 (w), 7.07 (w).

5-ISOPROPYL-2-METHYLPHENOL

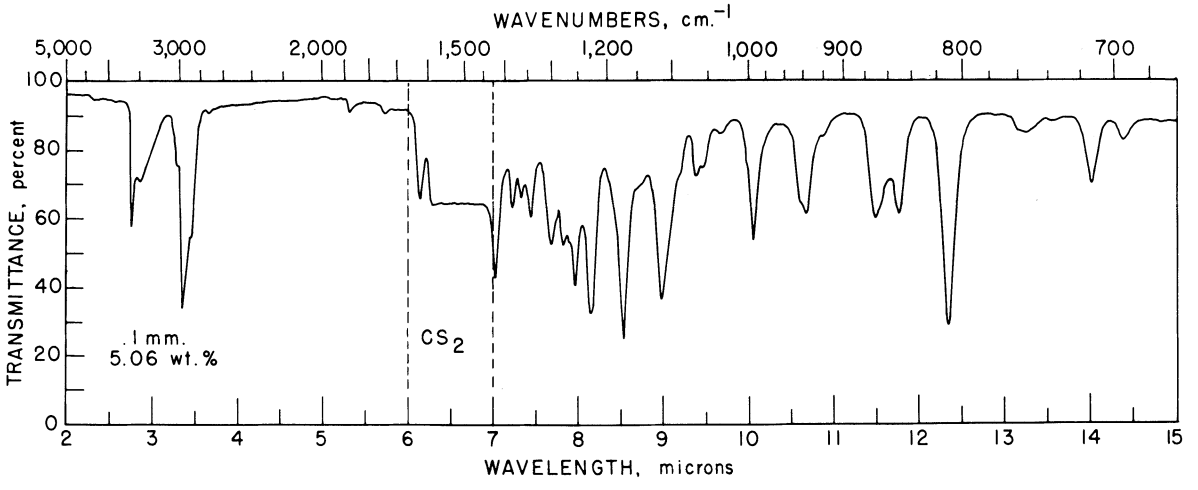


B. p. 236.8-237.4 (54)



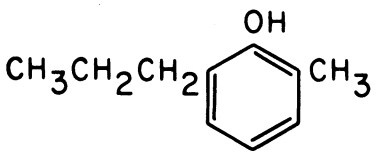
λ max, mμ (cyclohexane)	log ε
280.8	3.33
274.5	3.31

41

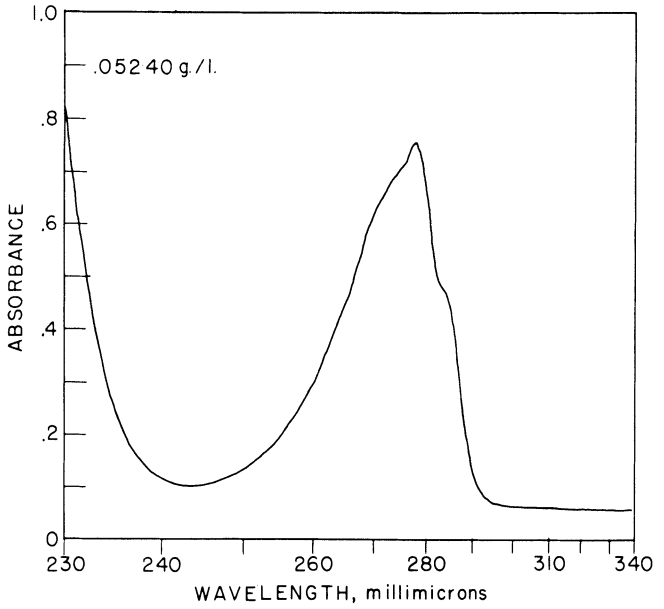


λ^{CS_2}: 14.40 (w), 14.02 (m), 13.58 (w), 13.22 (w), 12.34 (s), 11.75 (m), 11.49 (m), 10.85 (w), 10.67 (m), 10.62 (m), 10.06 (m), 9.68 (w), 9.47 (w), 9.39 (w), 8.98 (s), 8.75 (w), 8.54 (s), 8.15 (s), 7.97 (m), 7.92 (w), 7.82 (w), 7.68 (m), 7.44 (w), 7.34 (w), 7.23 (w), 7.04 (m).

2-METHYL-6-n-PROPYLPHENOL

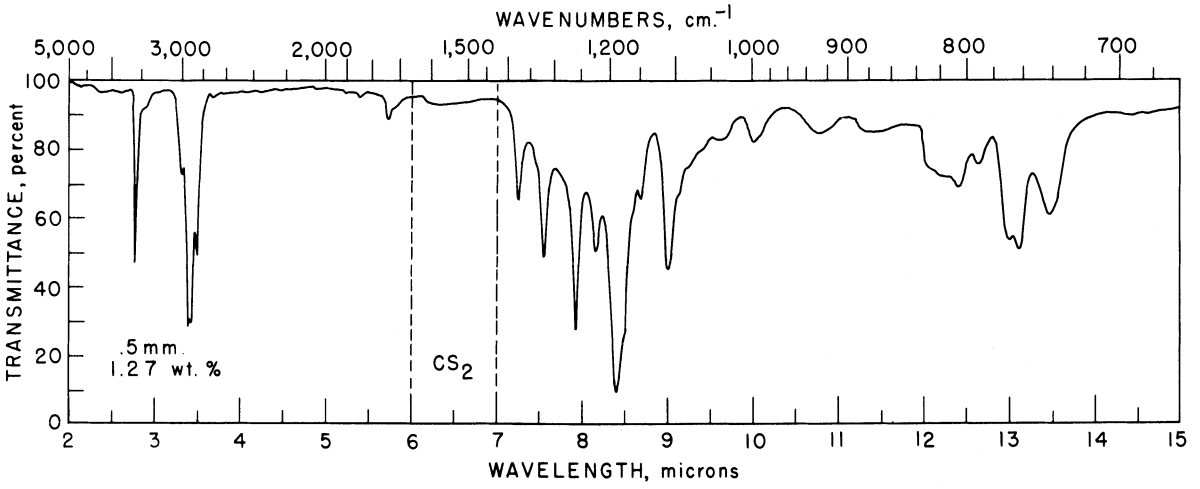


B. p. 105-107/12 mm. (54)
[est. 233°]



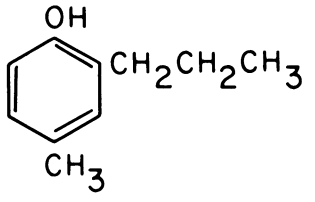
λ max, mμ (cyclohexane)	log ε
284.0	3.13
277.9	3.33

42

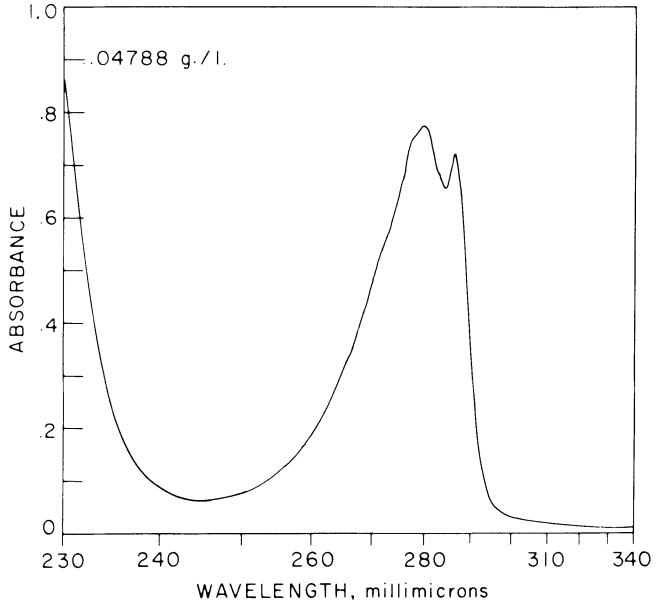


λ^{CS_2}: 14.35 (w), 13.49 (m), 13.12 (m), 13.00 (m), 12.65 (w), 12.42 (w), 12.32 (w), 12.22 (w), 12.07 (w), 11.44 (w), 10.83 (w), 10.02 (w), 9.67 (w), 9.40 (w), 9.25 (w), 9.15 (w), 9.02 (s), 8.70 (w), 8.61 (w), 8.50 (w), 8.42 (s), 8.17 (w), 7.94 (s), 7.57 (m), 7.26 (m).

4-METHYL-2-n-PROPYLPHENOL

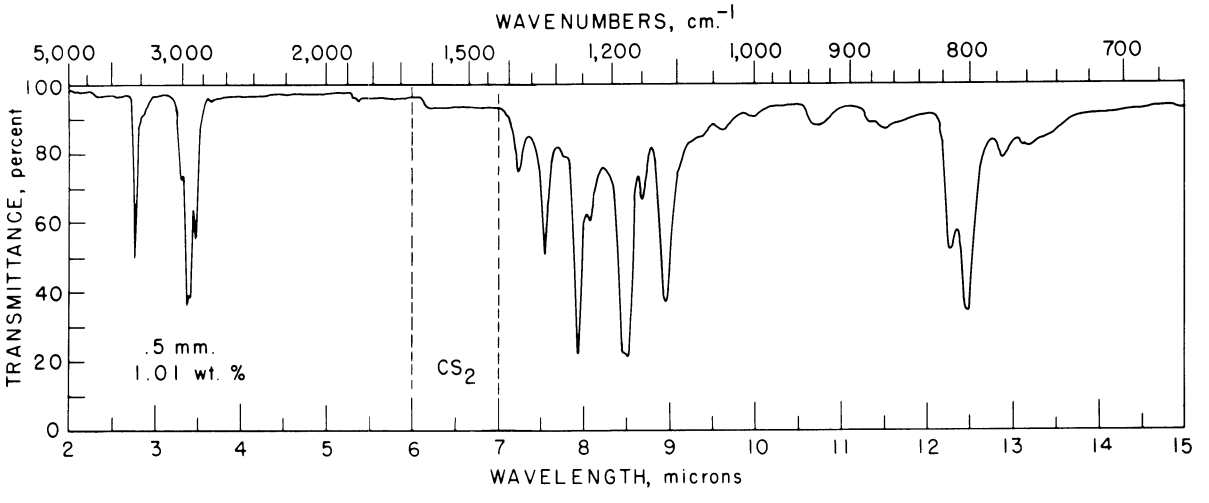


B. p. 121-123°/18 mm. (54)
[est. 241°]



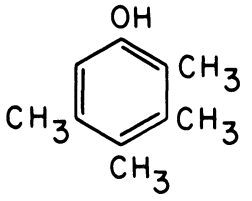
λ max, mμ (cyclohexane)	log ε
286.4	3.35
280.0	3.38
277.5	3.37
272.0	3.23

43

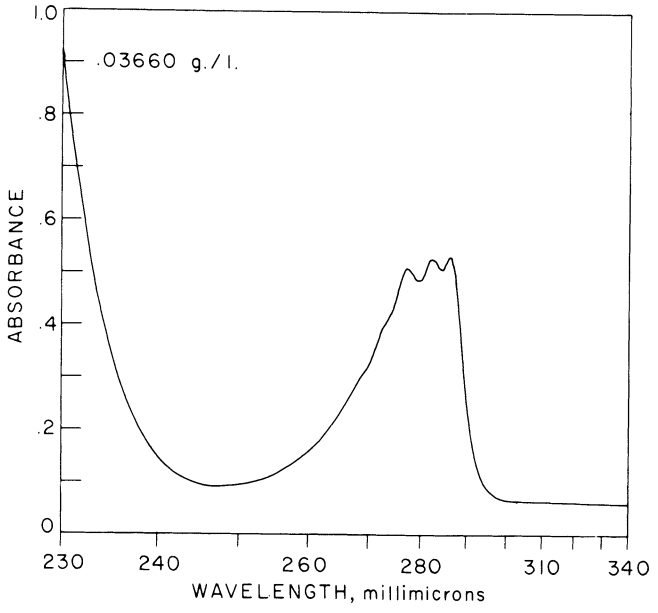


$\lambda_{max}^{CS_2}$: 13.45 (w), 13.23 (w), 13.13 (w), 12.90 (w), 12.48 (s), 12.28 (m), 11.52 (w), 11.34 (w), 10.78 (w), 10.00 (w), 9.65 (w), 9.40 (w), 9.28 (w), 9.16 (w), 8.97 (s), 8.70 (m), 8.54 (s), 8.48 (w), 8.10 (w), 7.96 (s), 7.80 (w), 7.57 (m), 7.26 (m).

2, 3, 4, 5 - TETRAMETHYLPHENOL

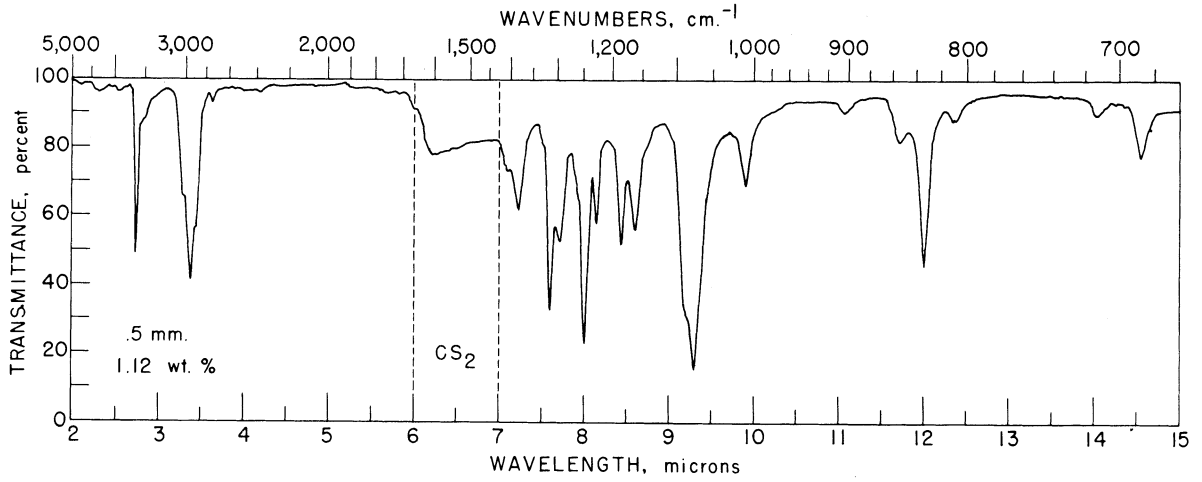


B. p. 260° (54)



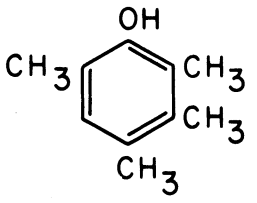
λ max, mμ (cyclohexane)	log ε
286.2	3.34
282.4	3.33
277.2	3.32
272.8	3.20
268.0	3.05

44

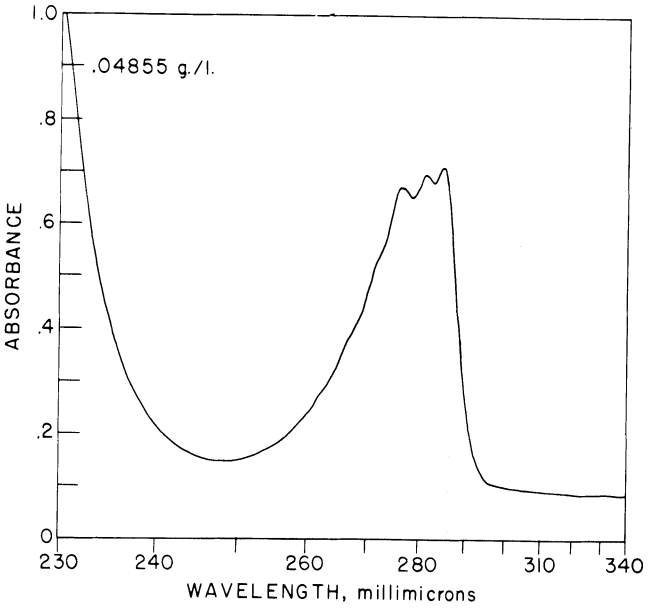


λ^{CS_2}: 14.54 (m), 14.02 (w), 12.35 (w), 12.00 (s), 11.70 (w), 11.07 (w), 9.91 (m), 9.30 (s), 9.22 (w), 8.60 (m), 8.44 (m), 8.15 (m), 8.02 (s), 7.72 (m), 7.61 (s), 7.24 (m), 7.10 (w).

2, 3, 4, 6 - TETRAMETHYLPHENOL

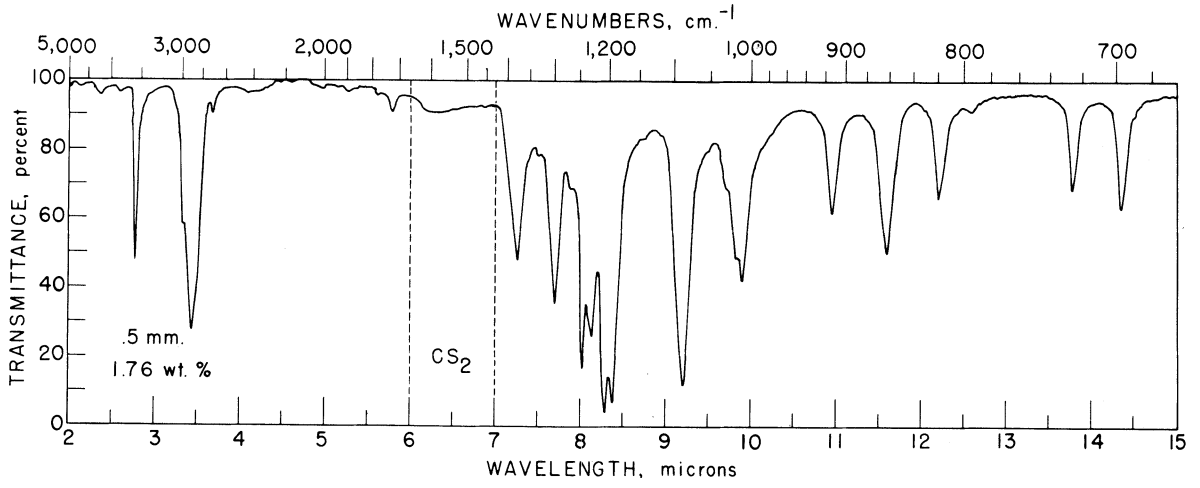


B. p. 250° (54)



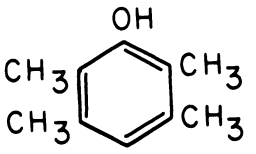
λ max, mμ (cyclohexane)	log ε
285.0	3.34
281.2	3.33
276.3	3.32

45

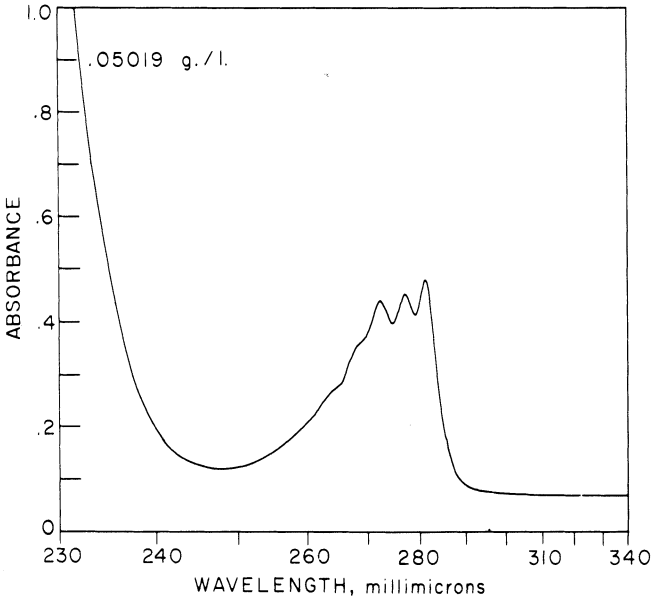


λ^{CS_2}: 14.34 (m), 13.76 (m), 12.57 (w), 12.20 (m), 11.57 (s), 10.94 (m), 9.90 (m), 9.82 (w), 9.70(w), 9.20(s), 8.74 (w), 8.37 (s), 8.29 (s), 8.14 (m), 8.02 (m), 7.88 (w), 7.70 (m), 7.50 (w), 7.26 (m).

2, 3, 5, 6 - TETRAMETHYLPHENOL

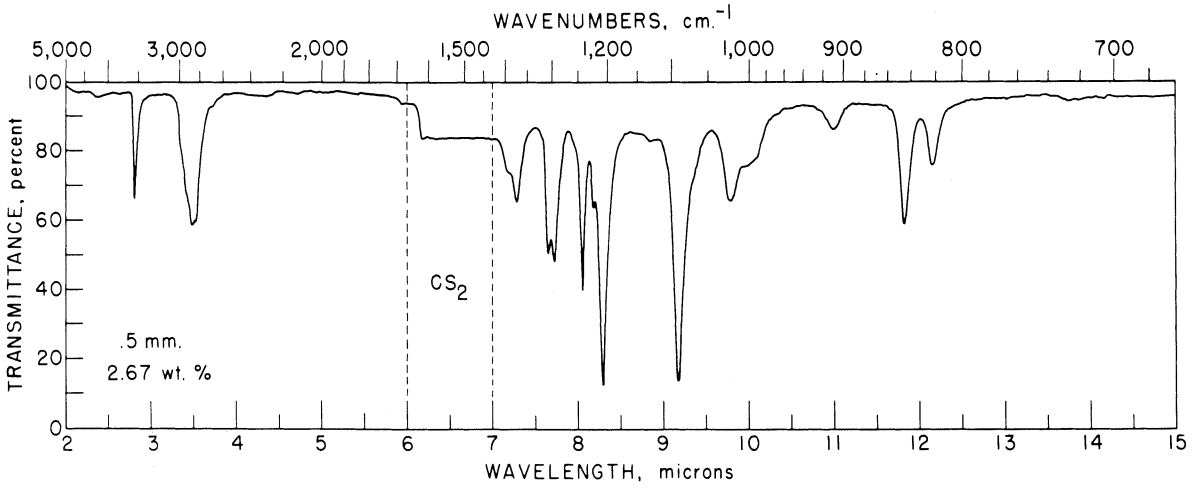


B. p. 247-248° (54)



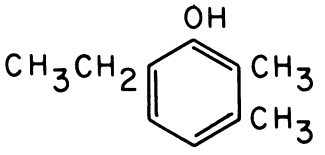
λ max, mμ (cyclohexane)	log ε
281.2	3.17
277.0	3.14
272.2	3.13
268.4	3.04
263.8	2.92

46

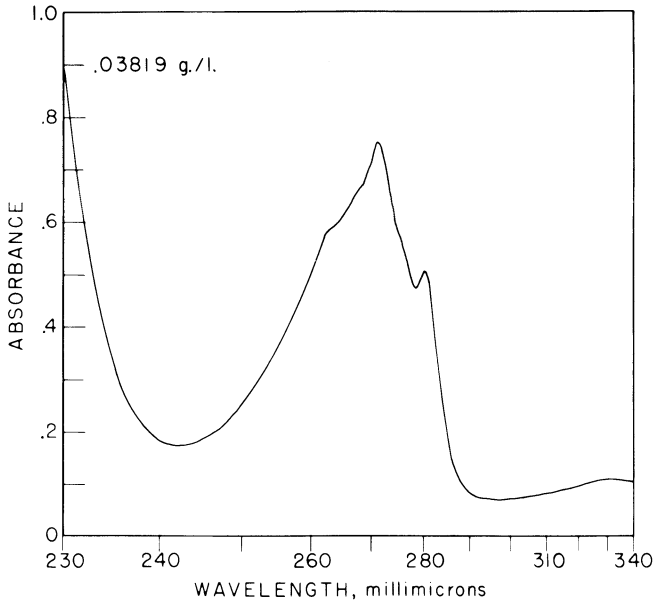


λ^{CS_2}: 12.15 (m), 11.82 (m), 11.00 (w), 10.08 (w), 9.78 (m), 9.17 (s), 8.82 (w), 8.28 (s), 8.17 (w), 8.04 (m), 7.72 (m), 7.64 (m), 7.27 (m), 7.17 (m).

2, 3 - DIMETHYL - 6 - ETHYLPHENOL

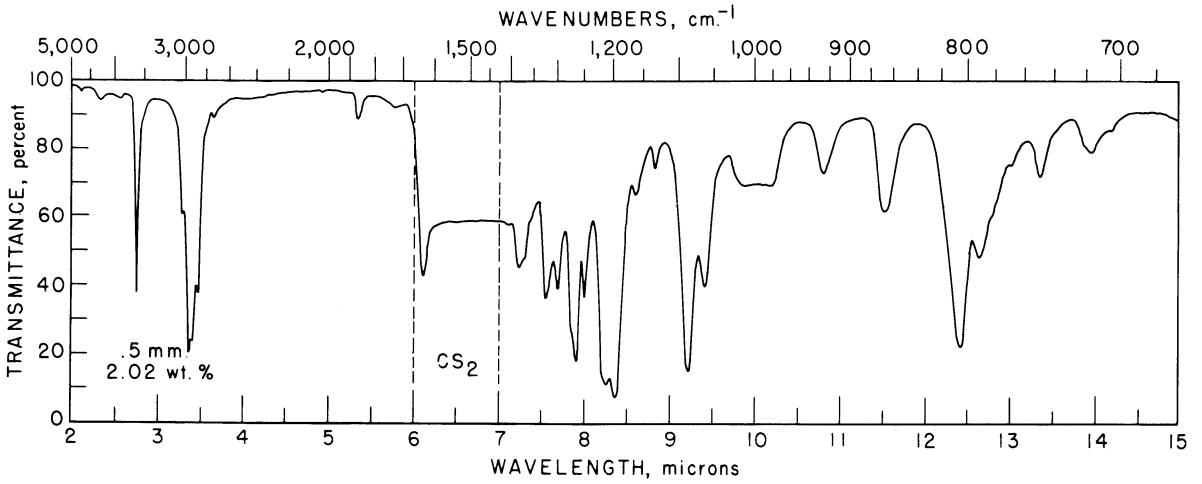


B. p. 166°/100 mm. (54)
[est. 240°]



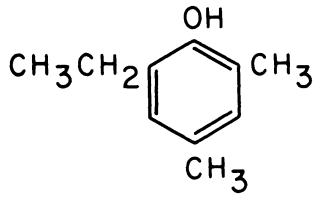
λ max, mμ (cyclohexane)	log ε
335.0	2.63
280.2	3.30
270.9	3.47
267.0	3.41
263.0	3.36

47

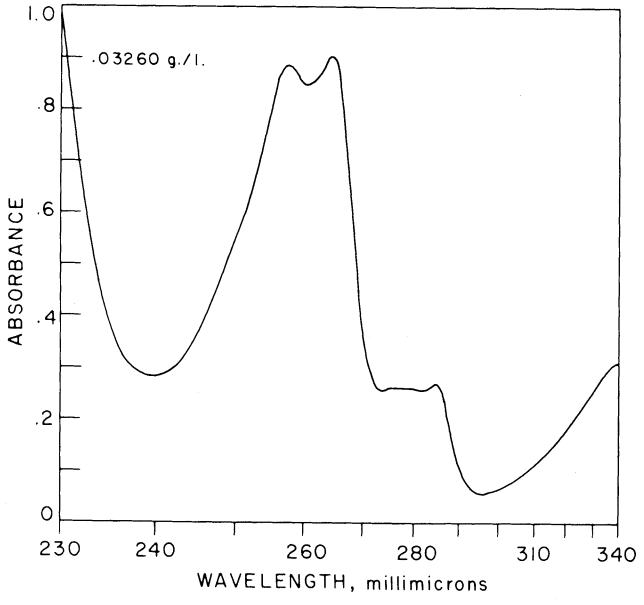


λ^{CS_2}: 14.20 (w), 13.97 (w), 13.38 (m), 13.04 (w), 12.81 (w), 12.65 (m), 12.44 (s), 11.55 (m), 10.84 (m), 10.24 (w), 9.95 (w), 9.44 (m), 9.25 (s), 8.85 (w), 8.63 (w), 8.38 (s), 8.28 (s), 8.03 (m), 7.93 (s), 7.88 (w), 7.72 (m), 7.57 (m), 7.40 (w), 7.32 (w), 7.26 (w), 7.13 (w).

2, 4 - DIMETHYL - 6 - ETHYLPHENOL

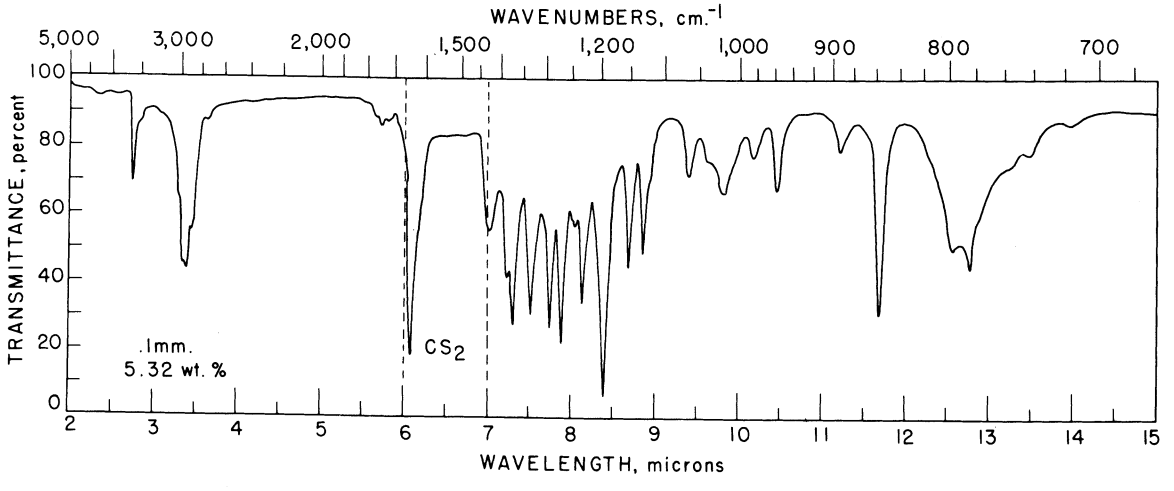


B. p. 227-228° (54)



λ max, mμ (cyclohexane)	log ε
345.0	3.17
284.5	3.08
276.0	3.07
264.5	3.62
257.4	3.61

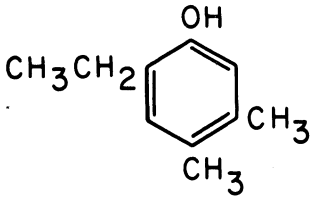
48



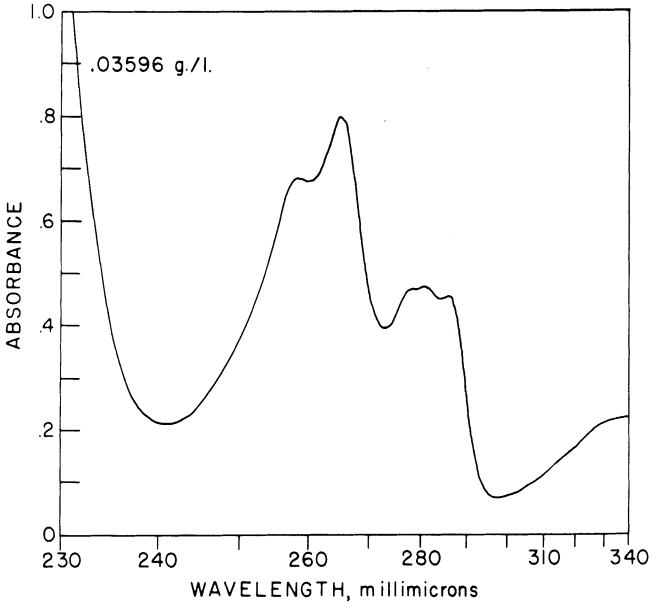
CS_2

λ : 13.98 (w), 13.48 (w), 13.28 (w), 12.76 (m), 12.56 (m), 11.68 (s), 11.22 (w), 10.46 (m), 10.18 (w), 9.86 (m), 9.65 (w), 9.40 (m), 8.86 (m), 8.68 (m), 8.40 (s), 8.13 (m), 8.05 (w), 7.89 (m), 7.75 (m), 7.54 (m), 7.32 (m), 7.23 (w), 7.04 (w).

3, 4 - DIMETHYL - 6 - ETHYLPHENOL

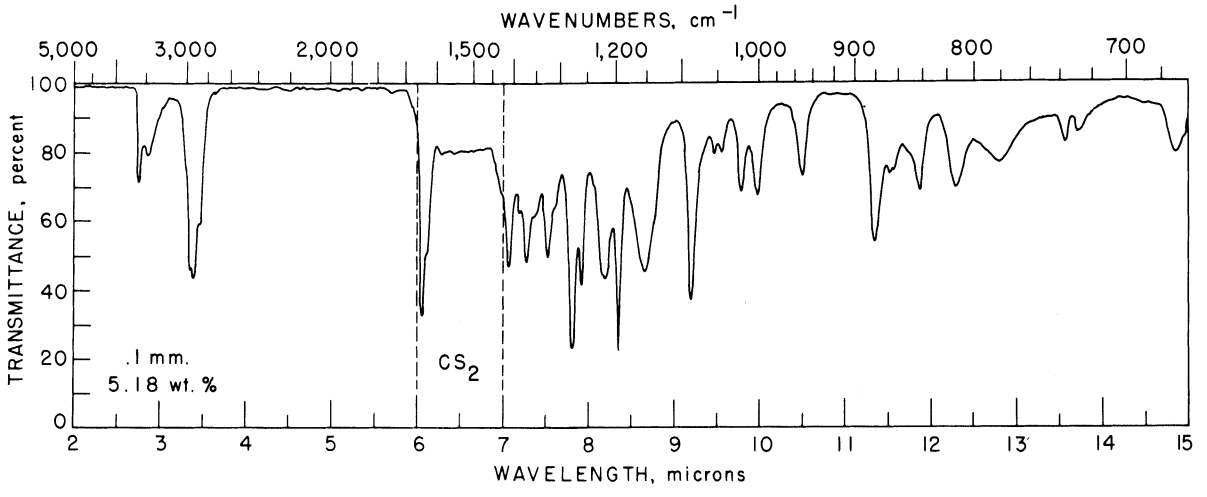


B. p. [est. 250°]



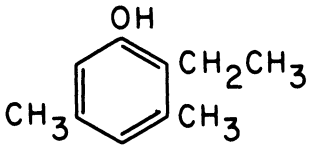
λ cyclohexane max, mμ	log ε
339.0	2.95
286.0	3.28
281.0	3.30
278.0	3.29
265.3	3.53
258.4	3.46

49

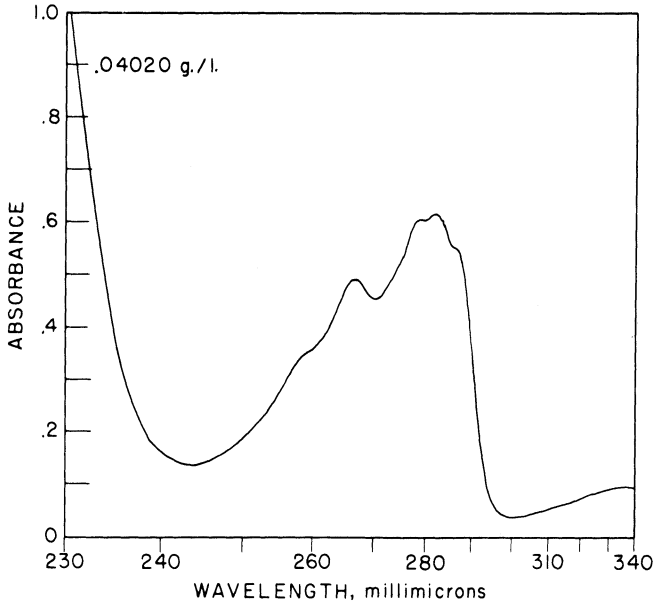


λ^{CS_2}: 14.87 (m), 13.72 (w), 13.57 (w), 12.82 (w), 12.30 (m), 11.87 (m), 11.57 (w), 11.52 (w), 11.35 (s), 10.51 (m), 9.99 (m), 9.80 (m), 9.57 (w), 9.49 (w), 9.22 (s), 8.79 (w), 8.67 (s), 8.37 (s), 8.22 (m), 7.94 (m), 7.84 (s), 7.62 (w), 7.55 (m), 7.38 (w), 7.30 (m), 7.22 (w), 7.09 (m).

3, 5 - DIMETHYL - 2 - ETHYLPHENOL

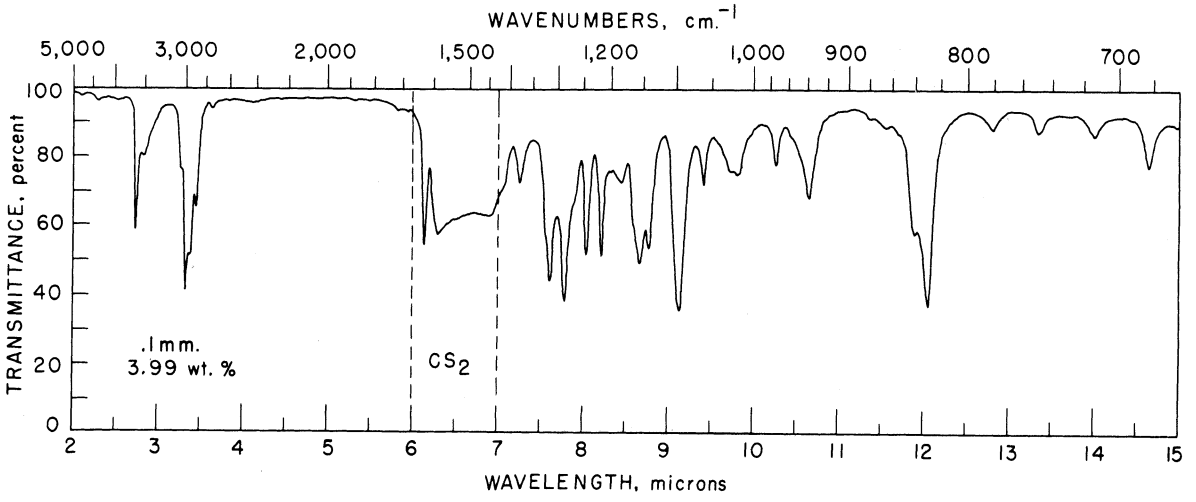


B. p. 90-93°/1 mm.
[est. 250°]



λ max, mμ (cyclohexane)	log ε
338.5	2.52
286.0	3.31
281.7	3.36
278.5	3.35
266.5	3.26
259.0	3.11

50



λ^{CS_2}: 14.97 (w), 14.63 (w), 14.00 (w), 13.32 (w), 12.79 (w), 12.05 (s), 11.88 (m), 11.67 (w), 11.54 (w), 11.35 (w), 10.65 (m), 10.25 (w), 9.80 (w), 9.72 (w), 9.40 (w), 9.12 (s), 8.77 (m), 8.67 (m), 8.59 (w), 8.45 (w), 8.21 (m), 8.03 (m), 7.89 (w), 7.78 (m), 7.60 (m), 7.56 (w), 7.25 (w).

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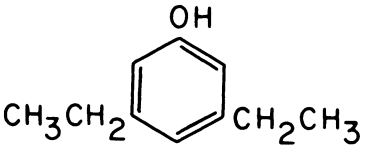
3, 5 - DIETHYLPHENOL



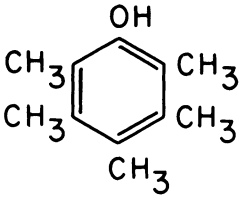
B.p. 248° (54)

Infrared bands, μ : 14.29 (s), 11.70 (s), 11.29 (w), 10.73 (s), 10.35 (w), 10.08 (m), 9.82 (m), 9.43 (m), 8.65 (s). (49)

51

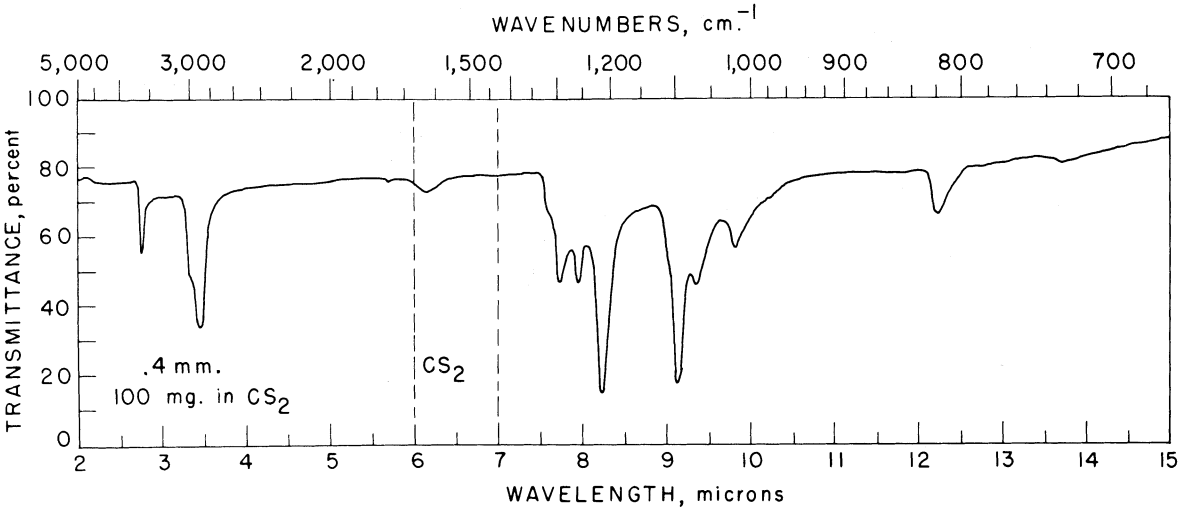
52

PENTAMETHYLPHENOL



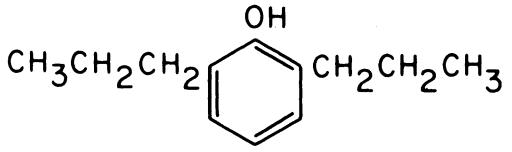
B.p. 267° (43)

$\lambda_{max,\ m\mu}^{alcohol}$: 280.7 (3.20) (12)

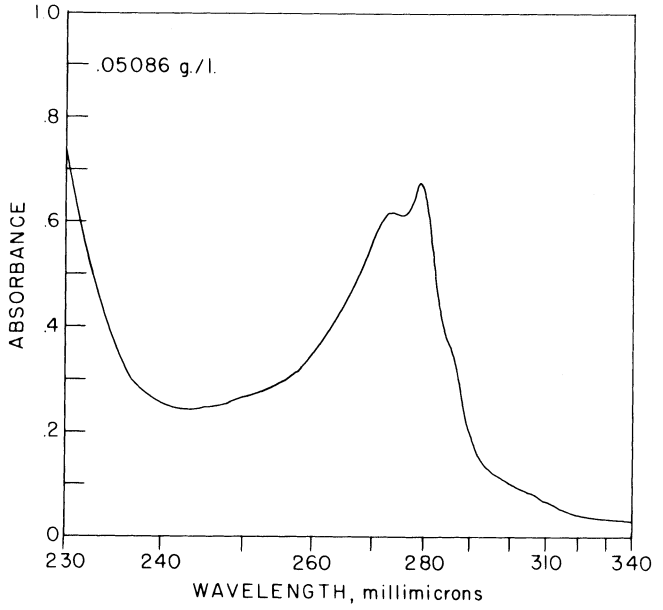


λ^{CS_2}: 13.60 (w), 12.34 (m), 10.25 (w), 9.83 (m), 9.36 (m), 9.14 (s), 8.64 (w), 8.24 (s), 7.96 (m), 7.74 (m), 7.62 (w). (99)

2, 6 - DI - n - PROPYLPHENOL

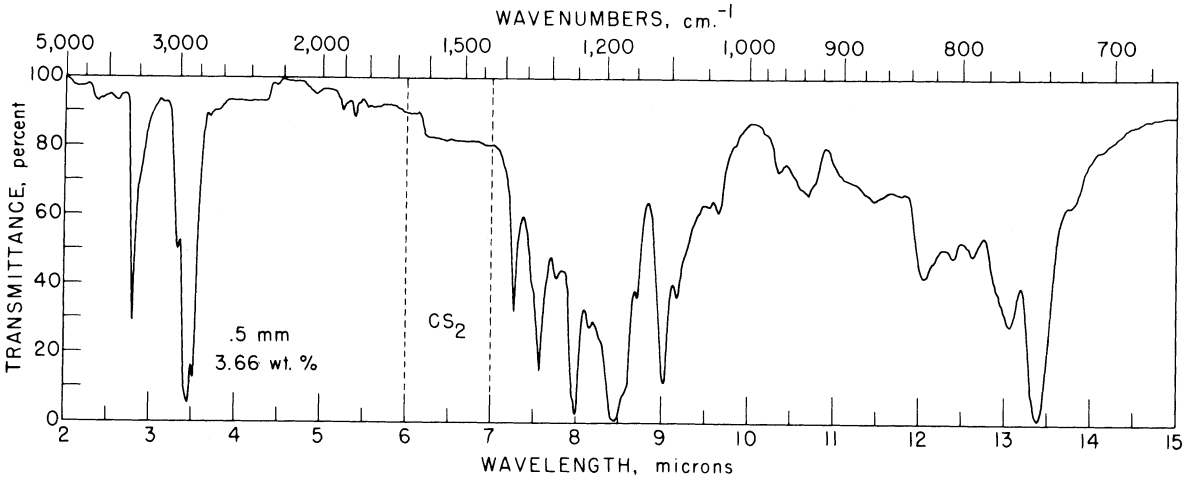


B. p. 256°/764 mm. (54)



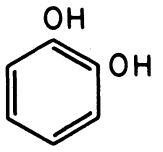
λ max, mμ (cyclohexane)	log ε
285.0	3.09
278.7	3.36
273.0	3.33

53

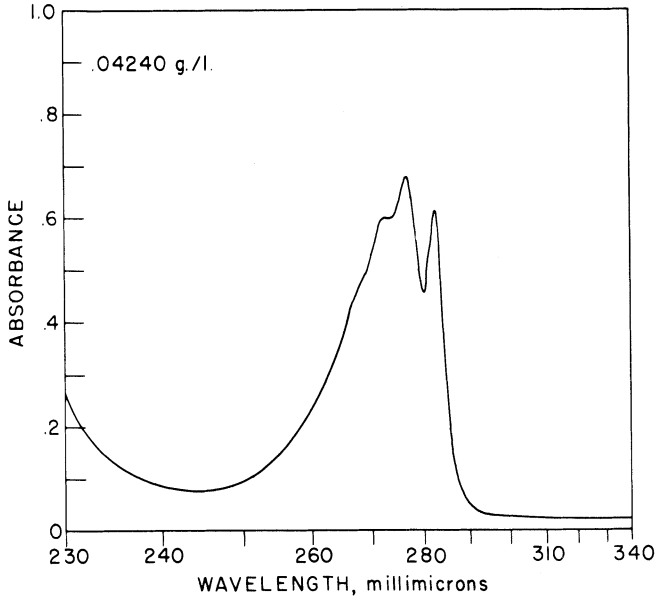


λ^{CS_2}: 13.75 (w), 13.40 (s), 13.07 (m), 12.65 (w), 12.40 (w), 12.17 (w), 12.05 (w), 11.77 (w), 11.47 (w), 10.78 (w), 10.70 (w), 10.60 (w), 10.35 (w), 10.18 (w), 9.84 (w), 9.65 (w), 9.17 (w), 9.02 (s), 8.71 (w), 8.57 (w), 8.45 (s), 8.27 (w), 8.15 (w), 7.99 (s), 7.75 (w), 7.57 (m), 7.49 (w), 7.27 (m).

CATECHOL

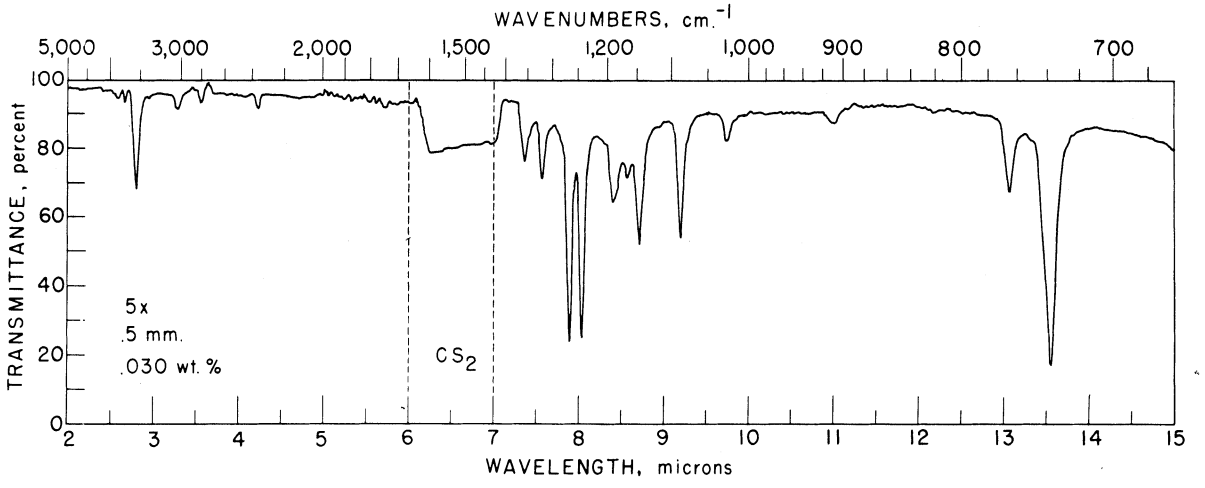


B. p. 245° (54)



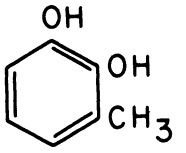
λ max, mμ (cyclohexane)	log ε
282.4	3.20
276.6	3.25
273.0	3.19

54

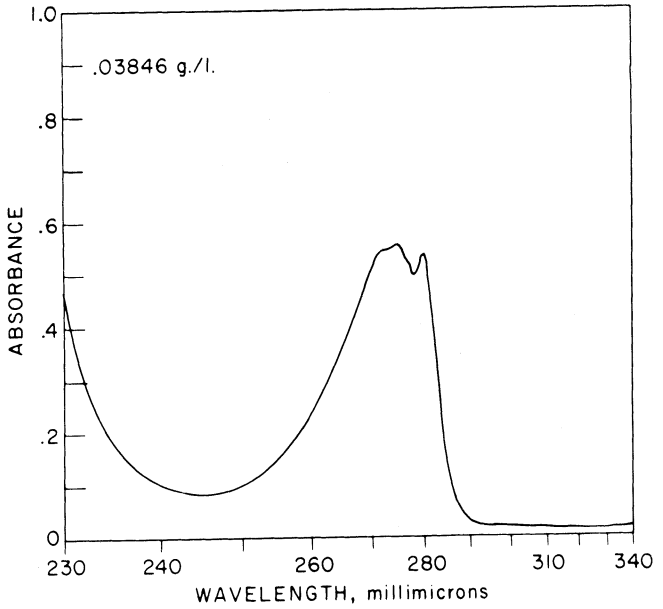


λ^{CS_2}: 14.96 (w), 13.52 (s), 13.04 (m), 10.98 (w), 9.73 (w), 9.19 (m), 8.71 (m), 8.56 (w), 8.90 (m), 8.40 (w), 8.03 (s), 7.88 (s), 7.57 (m), 7.37 (m).

3-METHYLCATECHOL

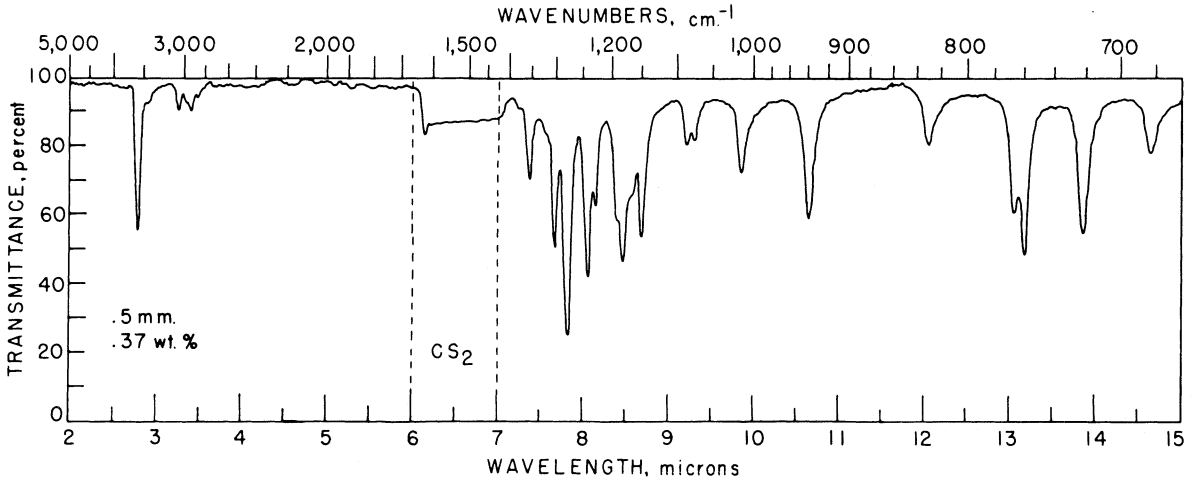


B. p. 248° (12)



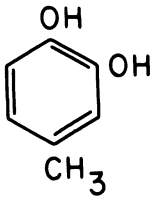
λ max, mμ (cyclohexane)	log ε
280.2	3.24
275.0	3.26
272.0	3.25

55

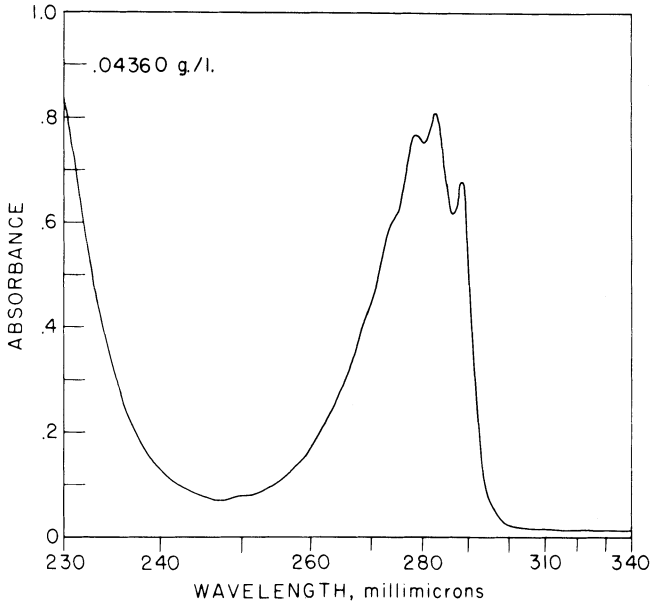


λ^{CS_2} : 14.65 (m), 14.02 (w), 13.85 (s), 13.17 (s), 13.05 (m), 12.05 (m), 10.65 (s), 9.87 (m), 9.33 (m), 9.24 (m), 8.70 (m), 8.60 (w), 8.49 (s), 8.43 (w), 8.16 (w), 8.08 (s), 7.84 (s), 7.69 (m), 7.40 (m), 7.27 (w).

4-METHYLCATECHOL

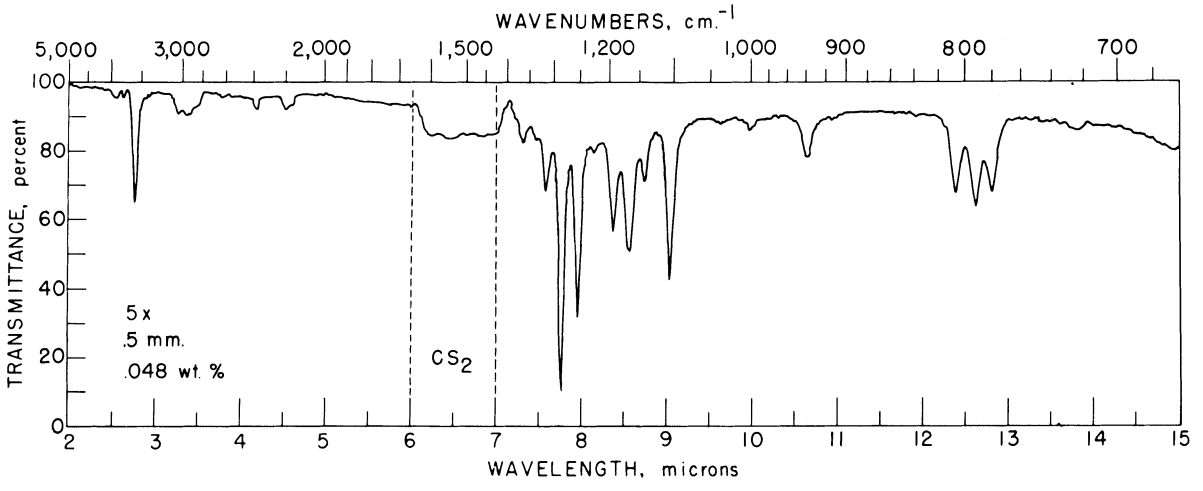


B. p. 258° (12)



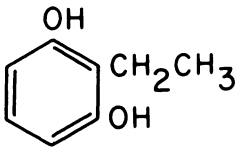
λ max, mμ (cyclohexane)	log ε
288.5	3.34
282.5	3.43
278.4	3.40
274.0	3.30

56

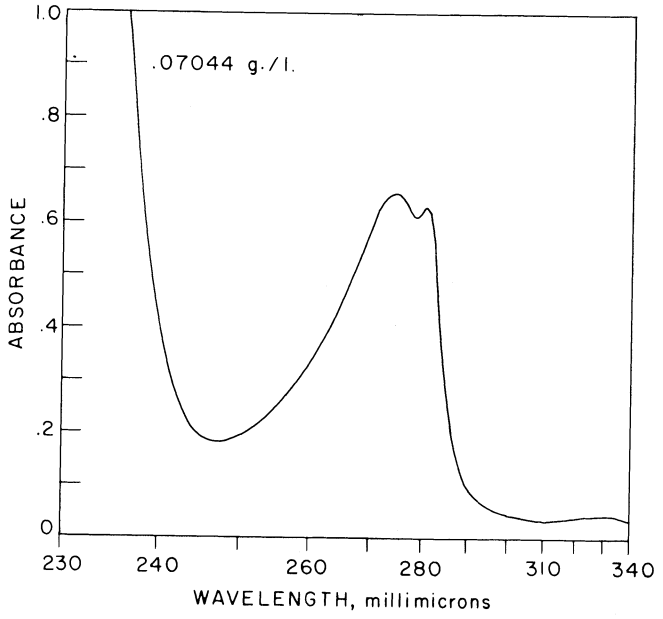


λ^{CS_2}: 13.80 (w), 12.80 (m), 12.62 (m), 12.38 (m), 10.65 (m), 9.04 (s), 8.75 (m), 8.57 (s), 8.38 (m), 8.15 (w), 7.97 (s), 7.77 (s), 7.59 (m), 7.48 (w), 7.32 (w), 7.25 (w).

2-ETHYLRESORCINOL

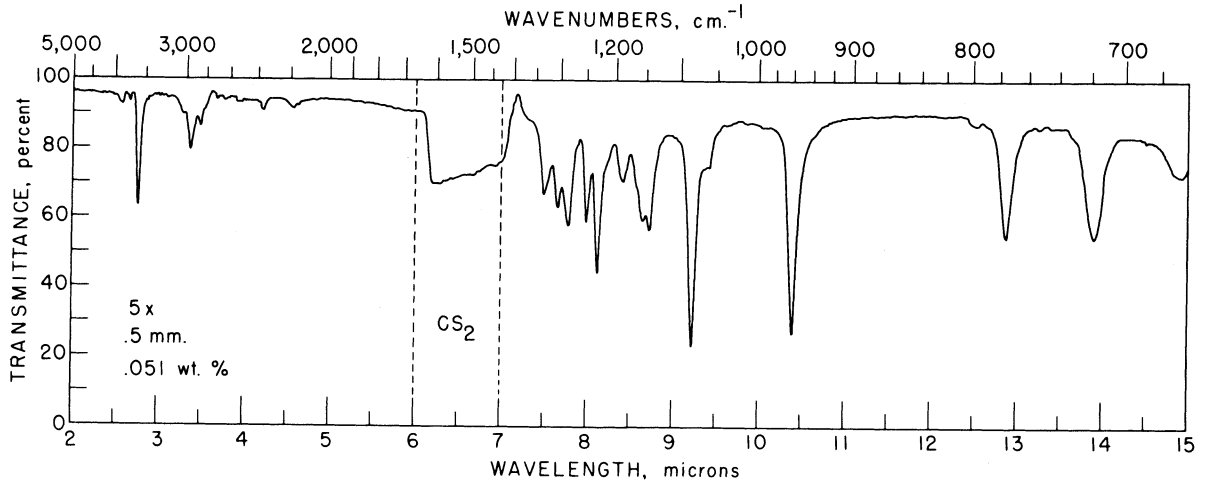


B. p. [est. 265°]



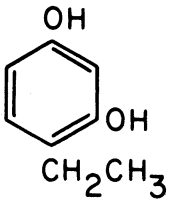
λ EtOH max, mμ	log ε
280.5	3.10
274.5	3.11

57

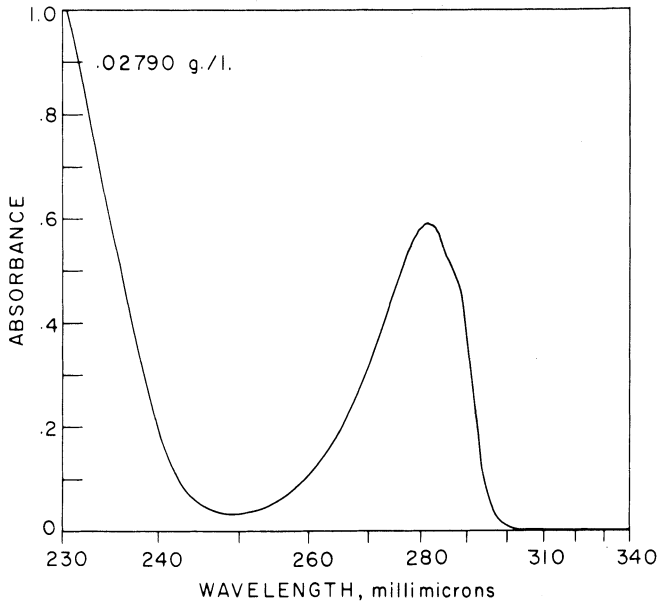


λ^{CS_2}: 14.92 (w), 13.92 (s), 12.88 (s), 10.40 (s), 9.42 (w), 9.23 (s), 8.73 (m), 8.65 (w), 8.42 (m), 8.13 (m), 7.99 (m), 7.78 (m), 7.65 (m), 7.50 (m), 7.30 (w).

4-ETHYLRESORCINOL

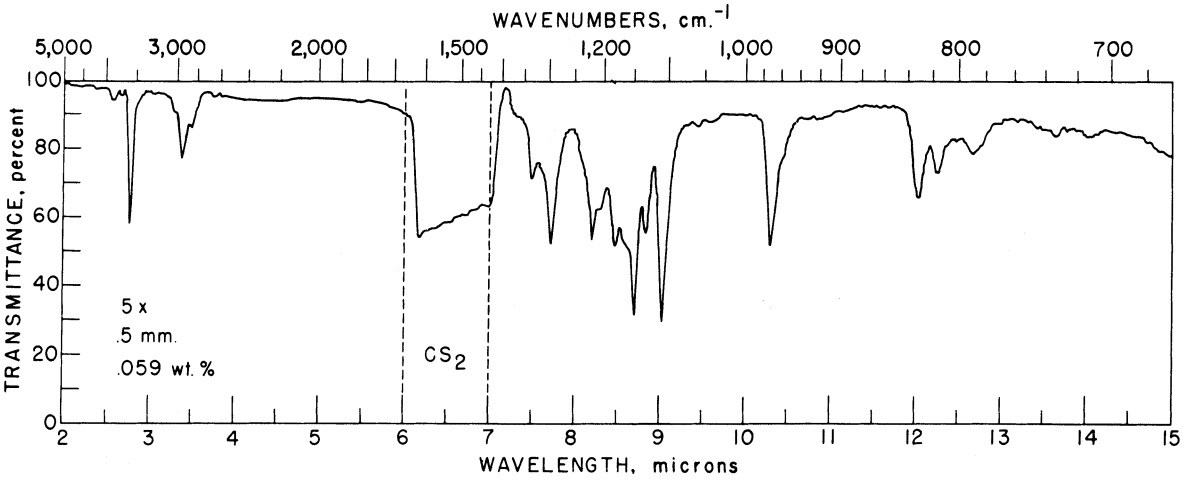


B. p. 131°/15 mm. (12)
[est. 270°]



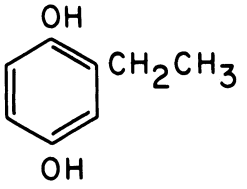
λ max, mμ (EtOH)	log ε
287.0	2.99
281.5	3.07

58

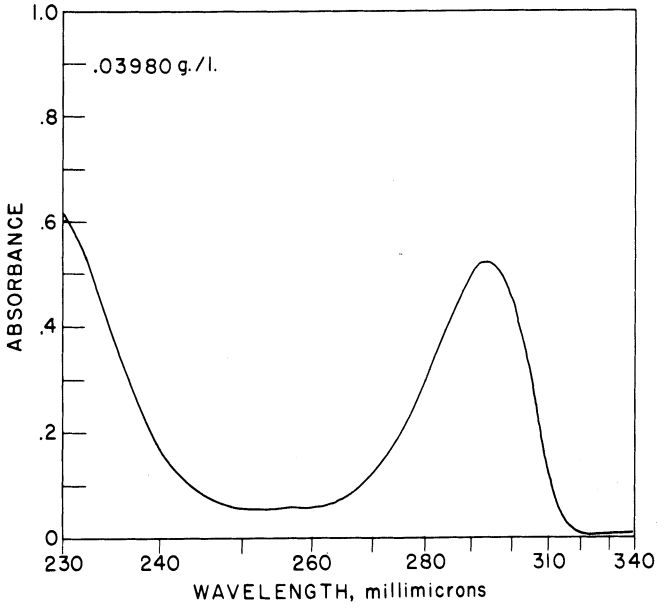


λ^{CS_2}: 14.05 (w), 13.62 (w), 12.64 (m), 12.44 (w), 12.24 (m), 12.02 (m), 11.77 (w), 10.30 (s), 9.43 (w), 9.04 (s), 8.84 (m), 8.71 (s), 8.48 (m), 8.30 (w), 8.22 (m), 7.72 (m), 7.50 (w), 7.30 (w).

2-ETHYLHYDROQUINONE

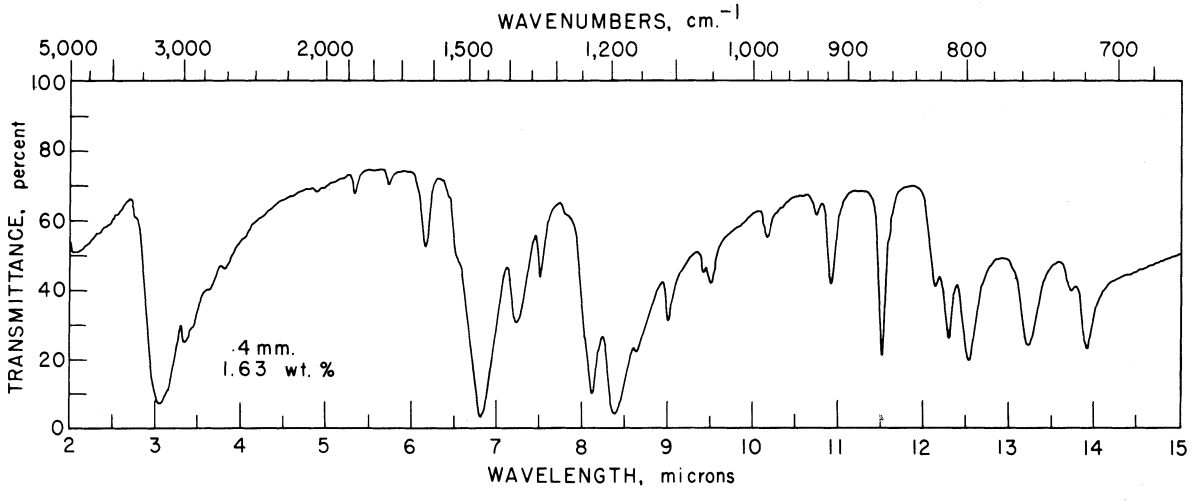


B.p. [est. 285°]



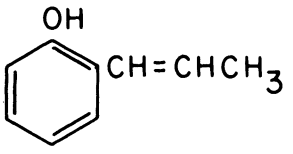
λ max, mμ (EtOH)	log ε
293.8	3.21

59

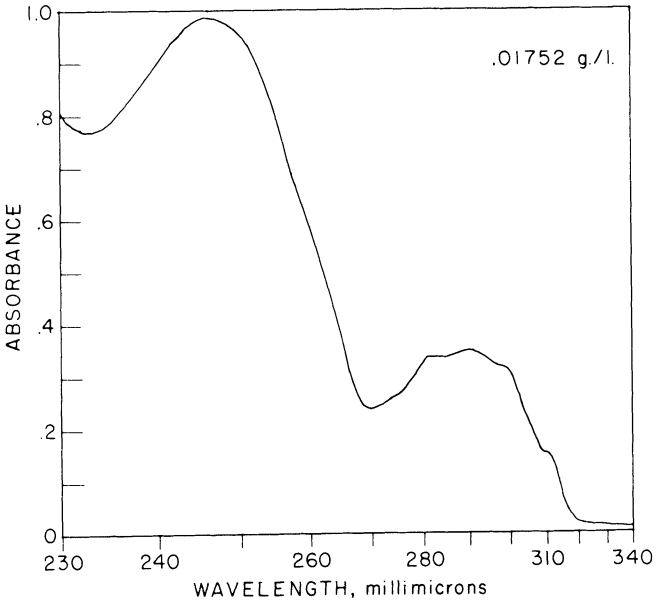


λ^{KBr}: 13.91 (s), 13.72 (w), 13.22 (s), 12.52 (s), 12.28 (m), 12.13 (w), 11.50 (s), 10.91 (m), 10.74 (w), 10.15 (w), 9.51 (w), 9.41 (w), 9.00 (m), 8.64 (w), 8.37 (s), 8.12 (s), 7.80 (w), 7.52 (m), 7.22 (m).

2-(PROPEN-1-YL) PHENOL

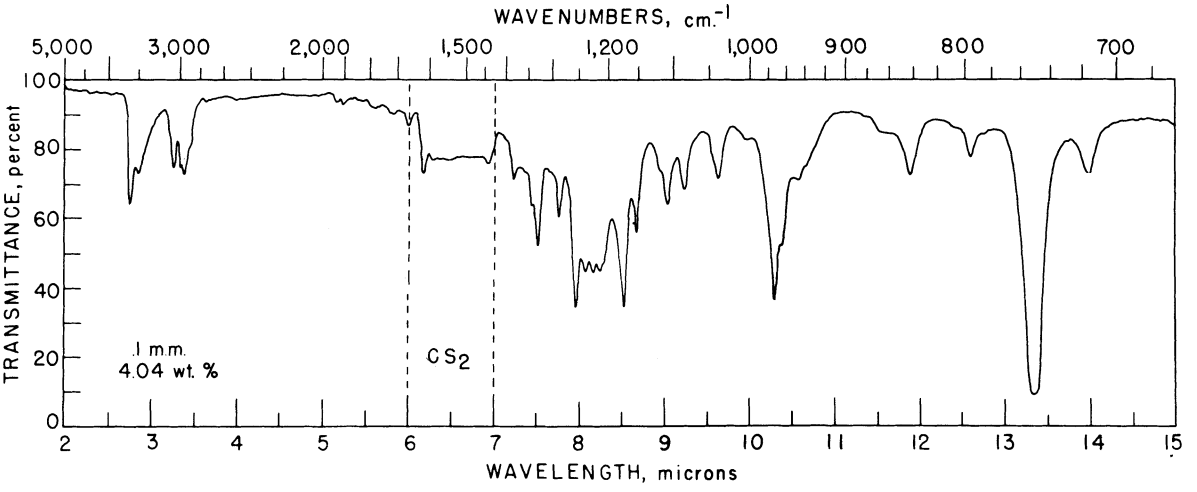


B.p. 230-231° (43)



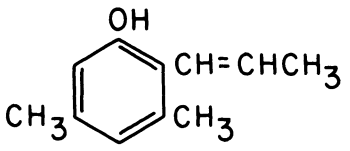
λ max, mμ (cyclohexane)	log ε
311.0	3.04
300.0	3.37
290.0	3.42
281.7	3.40
246.5	3.88

60



λ^{CS_2}: 14.00 (w), 13.36 (s), 12.75 (w), 12.60 (w), 11.90 (w), 11.60 (w), 10.69 (w), 10.60 (w), 10.40 (w), 10.30 (m), 9.65 (w), 9.25 (w), 9.05 (w), 8.98 (w), 8.70 (w), 8.55 (m), 8.32 (w), 8.26 (w), 8.18 (w), 8.09 (w), 7.99 (m), 7.79 (w), 7.54 (w), 7.49 (w), 7.26 (w).

3, 5 - DIMETHYL - 2 - (PROPEN - 1 - YL) PHENOL



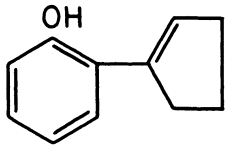
B.p. [est. 260°]

$\lambda_{max}^{EtOH-0.1\% HOAc}$, mμ : 297 (3.42), 254 (4.00), 220 (4.38).

λ_{min}: 279 (3.24), 239 (3.87). (6)

61

2 - (CYCLOPENTEN - 1 - YL) PHENOL



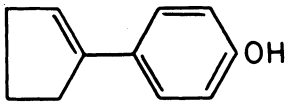
B.p. [est. 272°]

$\lambda_{max}^{EtOH-0.1\% HOAc}$, mμ : 304 (3.50 infl.), 295 (3.59), 253 (3.88), 227.5 (3.87).

λ_{min}: 274 (3.31), 237 (3.77). (6)

62

4 - (CYCLOPENTEN - 1 - YL) PHENOL



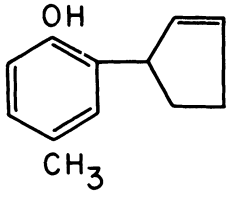
B.p. [est. 293°]

$\lambda_{max}^{EtOH-0.1\% HOAc}$, mμ : 290 (3.43 infl.), 262.5 (4.27).

λ_{min}: 227.5 (3.36). (6)

63

2 - (CYCLOPENTEN - 2 - YL) - 4 - METHYLPHENOL



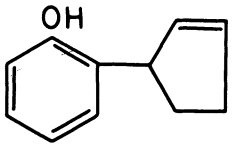
B.p. 105-108°/1.3 mm. (5)
[est. 284°]

$\lambda_{max}^{EtOH-0.1\% HOAc}$, mμ: 281.0 (3.39), 221.0 (3.82).

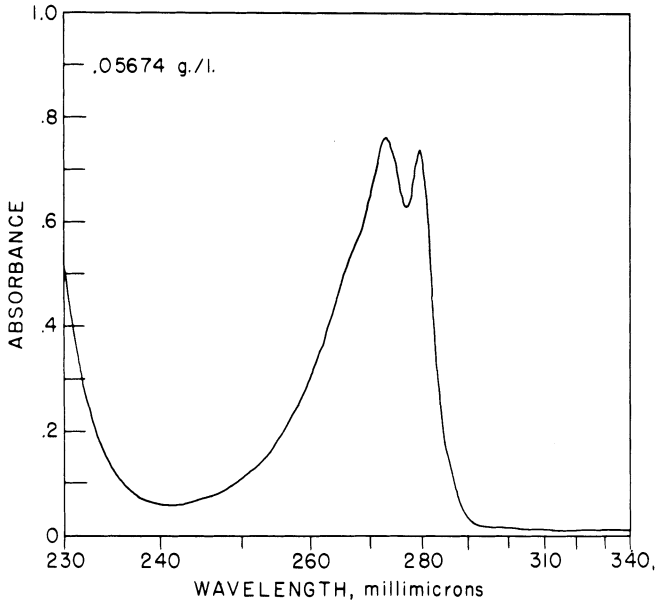
64

λ_{min}: 247.5 (2.16), 217.5 (3.81). (5)

2-(CYCLOPENTEN-2-YL) PHENOL

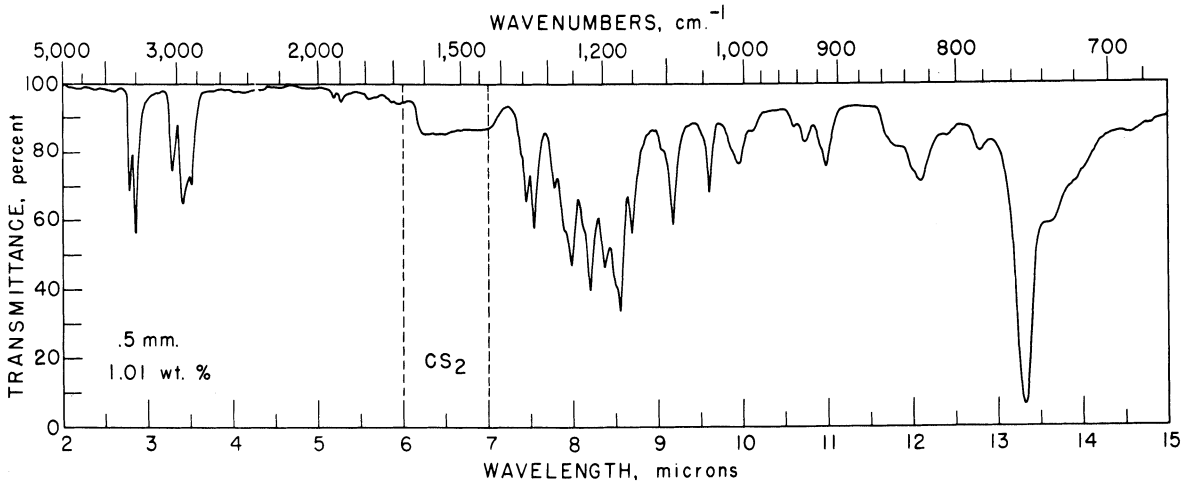


B.p. 133-135°/12 mm. (8)
[est. 270°]



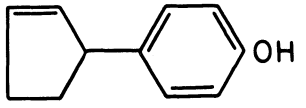
λ cyclohexane max, mμ	log ε
279.5	3.32
272.9	3.33
267.0	3.19

65

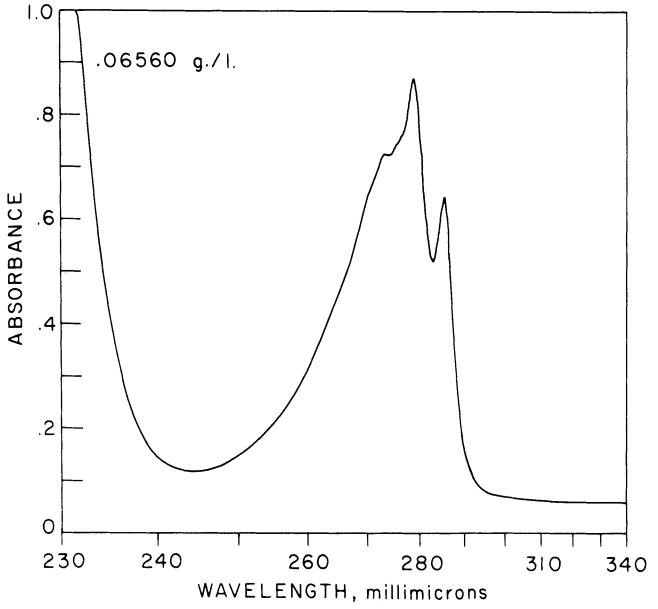


λ^{CS_2}: 13.63 (w), 13.34 (s), 12.80 (w), 12.40 (w), 12.10 (m), 11.80 (w), 10.97 (m), 10.74 (w), 10.60 (w), 10.12 (w), 9.94 (m), 9.61 (m), 9.17 (m), 9.06 (w), 8.70 (w), 8.57 (m), 8.50 (w), 8.39 (w), 8.22 (m), 7.99 (m), 7.90 (w), 7.78 (w), 7.55 (m), 7.45 (w), 7.40 (w).

4-(CYCLOPENTEN-2-YL)PHENOL

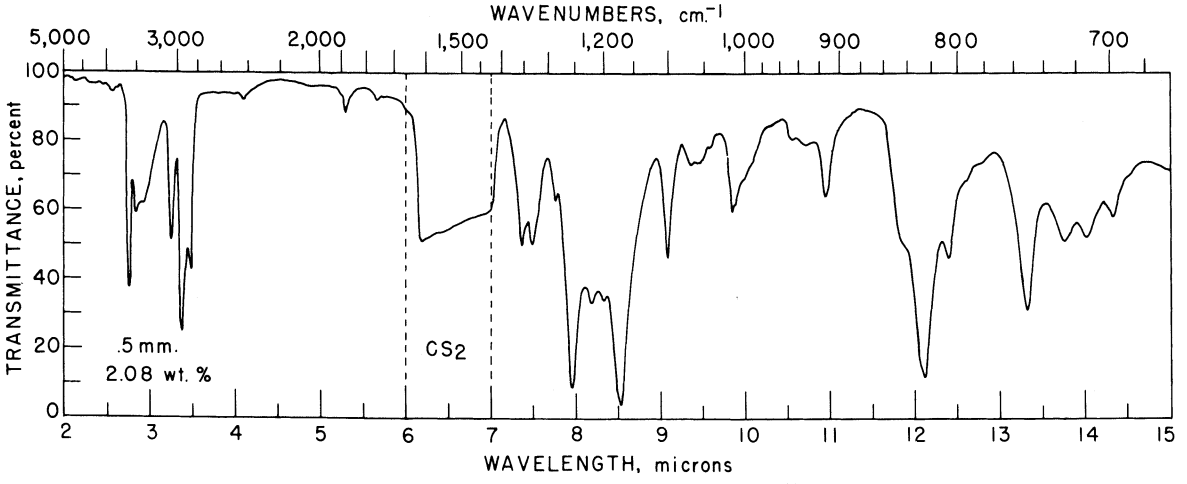


B.p. 114-117°/1.5 mm. (5)
[est. 293°]



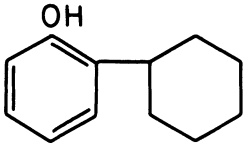
λ cyclohexane max, mμ	log ε
285.3	3.21
278.7	3.33
276.0	3.27
273.0	3.25
270.4	3.21

66

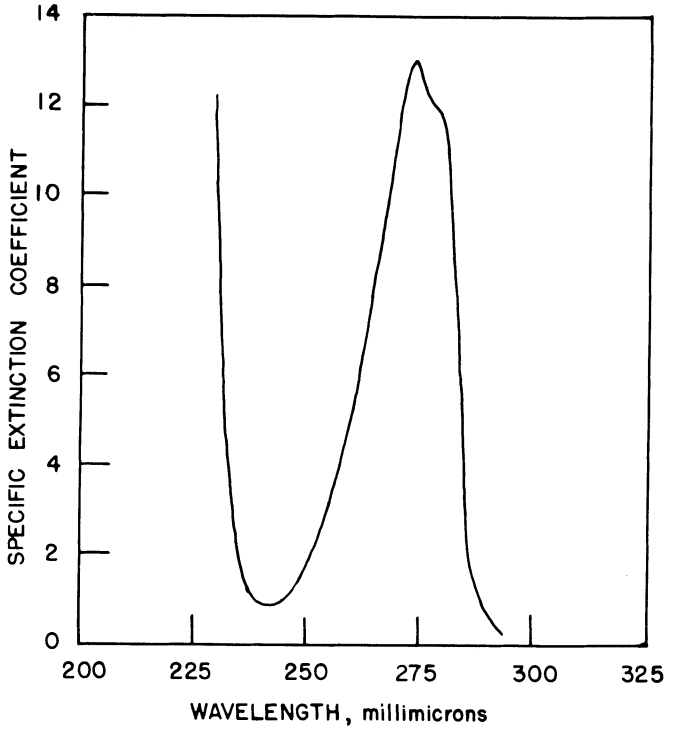


λ^{CS_2}: 14.32 (w), 14.02 (w), 13.75 (w), 13.32 (s), 12.40 (w), 12.12 (s), 11.85 (w), 10.94 (m), 10.72 (w), 10.55 (w), 10.00 (w), 9.85 (m), 9.60 (w), 9.37 (w), 9.09 (m), 8.55 (s), 8.34 (w), 8.20 (w), 7.97 (s), 7.78 (w), 7.51 (m), 7.38 (m).

2-CYCLOHEXYLPHENOL



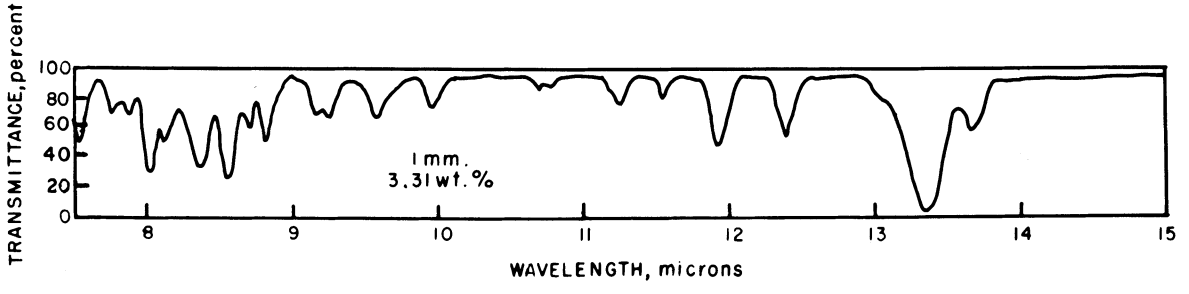
B.p. 282.5-283.5° (69)



λ alcohol max, mμ	log ε
279	3.32
274	3.36

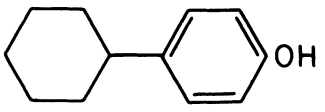
(85)

67

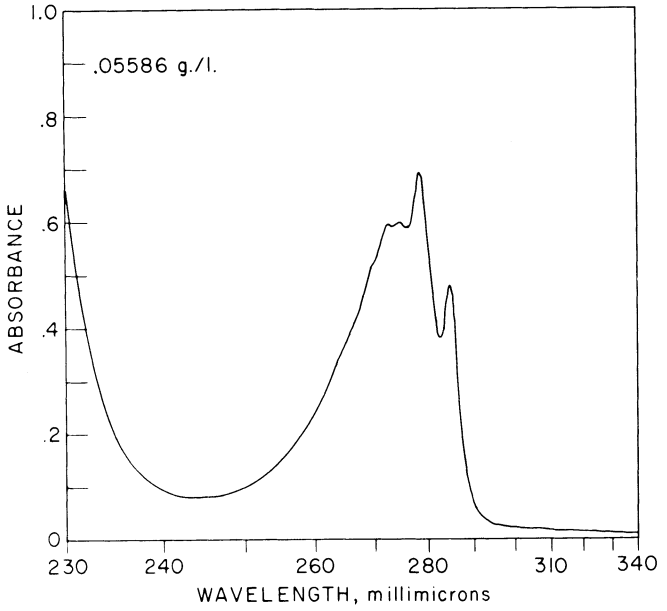


λ^{CS_2}: 13.63 (m), 13.32 (s), 13.00 (w), 12.39 (m), 11.90 (m), 11.55 (w), 11.28 (w), 10.77 (w), 10.70 (w), 9.95 (w), 9.53 (w), 9.22 (w), 9.14 (w), 8.80 (m), 8.69 (w), 8.54 (m), 8.33 (m), 8.12 (w), 8.00 (m), 7.87 (w), 7.75 (w), 7.54 (m). (118)

4-CYCLOHEXYLPHENOL

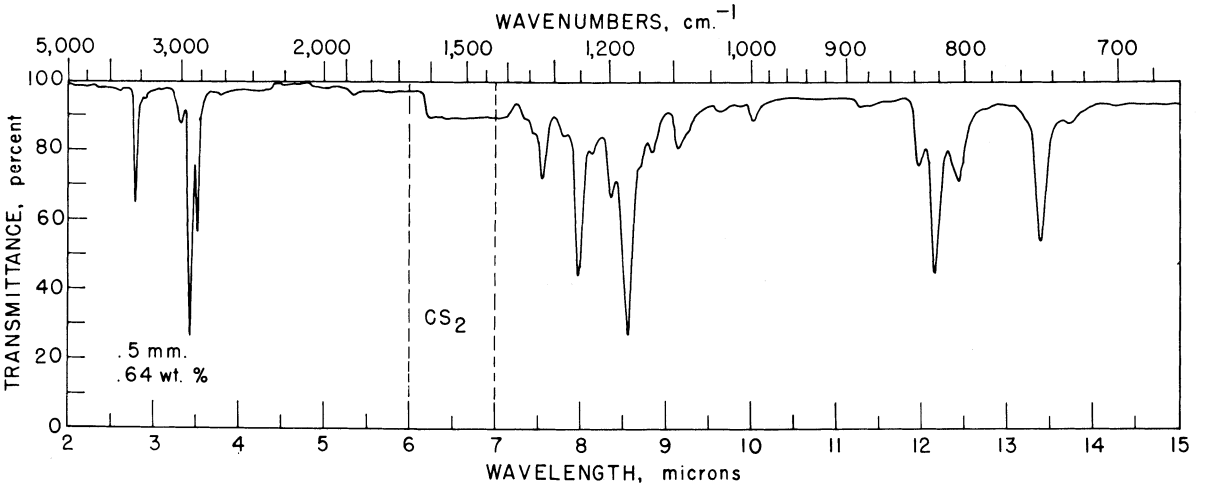


B.p. 293.5-295.5°/752 mm. (69)



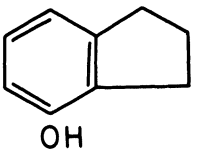
λ cyclohexane max, mμ	log ε
284.5	3.18
278.2	3.34
274.5	3.28
272.3	3.27
269.3	3.21
264.0	3.04

68

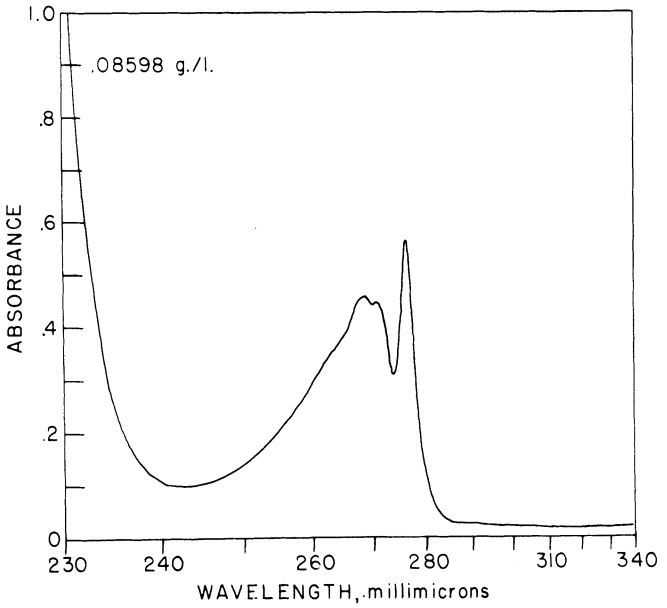


λ^{CS_2}: 13.72 (w), 13.37 (s), 13.19 (w), 12.42 (m), 12.14 (s), 11.95 (m), 11.27 (w), 10.00 (w), 9.62 (w), 9.25 (w), 9.15 (m), 8.84 (w), 8.70 (w), 8.56 (s), 8.35 (m), 8.13 (w), 7.97 (s), 7.82 (w), 7.55 (m), 7.45 (w), 7.35 (w).

4 - I N D A N O L

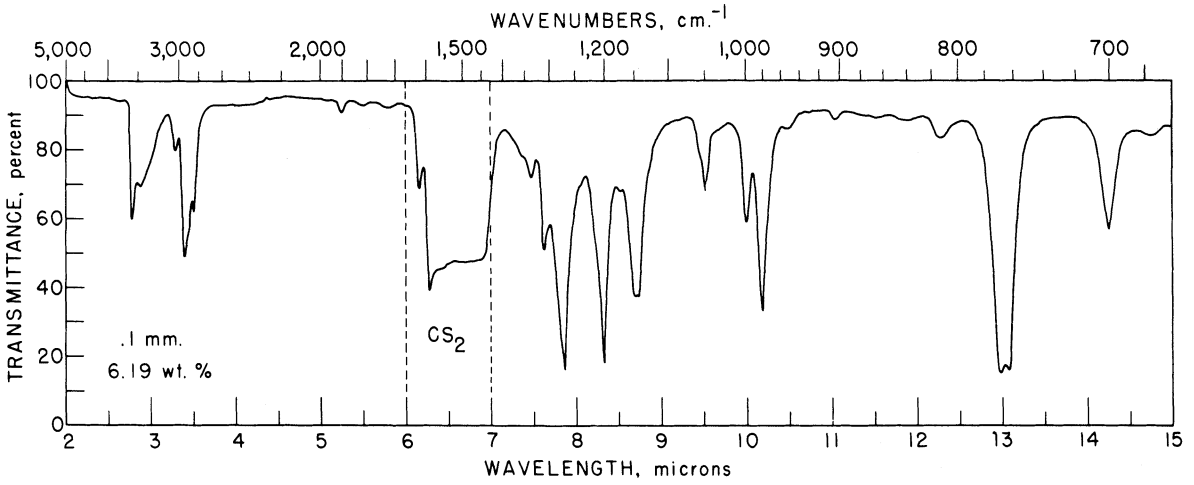


B.p. 245°/764 mm. (54)



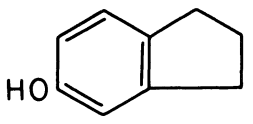
λ cyclohexane max, mμ	log ε
276.3	2.96
271.0	2.86
268.7	2.87

69

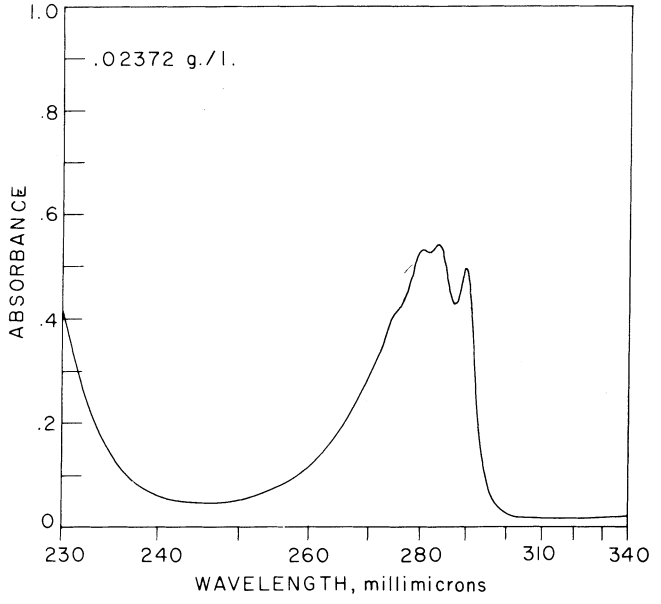


λ^{CS_2}: 14.75 (w), 14.25 (m), 13.07 (s), 12.98 (s), 12.28 (w), 11.05 (w), 10.50 (w), 10.18 (s), 10.00 (m), 9.65 (w), 9.51 (m), 8.70 (s), 8.52 (w), 8.32 (s), 8.05 (w), 7.85 (s), 7.62 (w), 7.47 (w).

5 - INDANOL

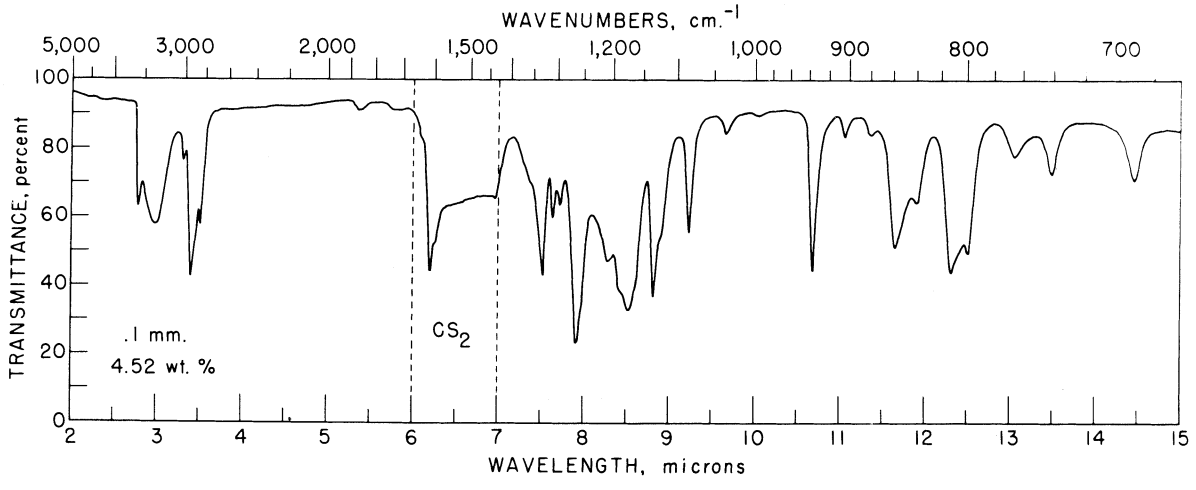


B.p. 255° (54)



λ cyclohexane max, mμ	log ε
289.5	3.45
283.3	3.48
280.0	3.47
275.0	3.36

70



λ^{CS_2}: 14.45 (m), 13.49 (m), 13.05 (w), 12.52 (s), 12.32 (s), 11.90 (m), 11.65 (s), 11.35 (w), 11.05 (w), 10.69 (s), 9.66 (w), 9.23 (m), 8.89 (w), 8.82 (s), 8.60 (w), 8.52 (s), 8.43 (w), 8.28 (w), 7.92 (s), 7.72 (w), 7.64 (w), 7.52 (m), 7.36 (w).

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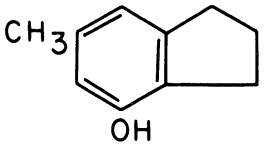
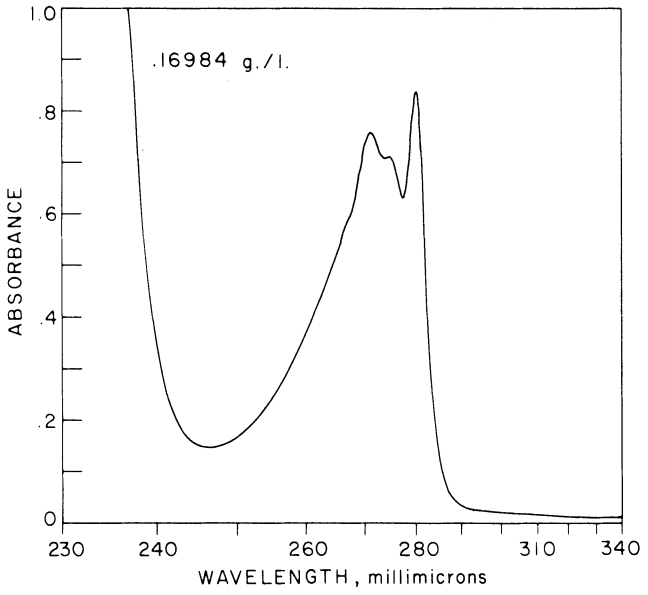
6-METHYL-4-INDANOL

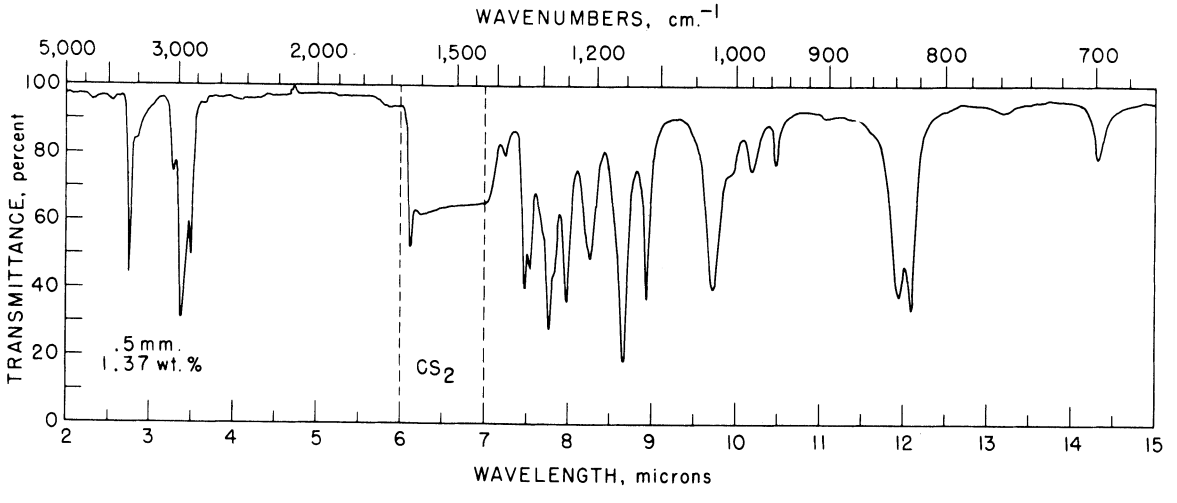


B.p. [est. 250°]



λ max, mμ (cyclohexane)	log ε
280.0	2.88
274.5	2.81
271.0	2.84

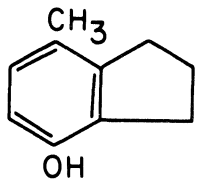
71



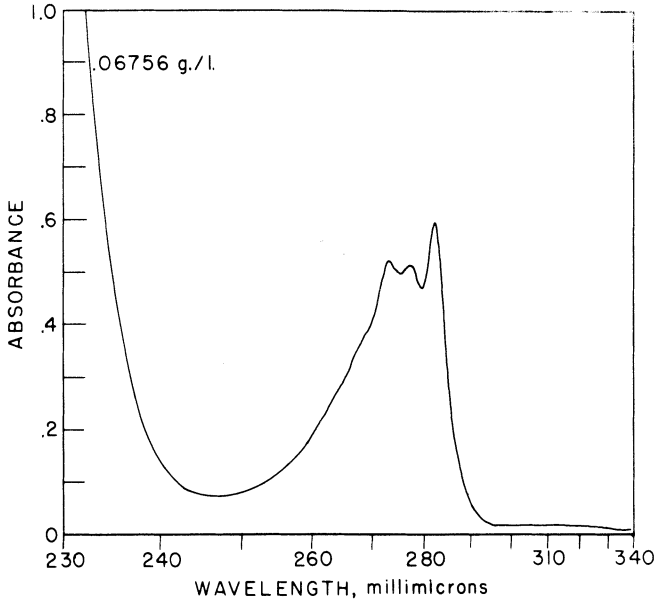
λ^{CS_2}: 14.33 (w), 12.10 (s), 11.95 (s), 10.48 (w), 10.20 (w), 9.73 (w), 8.94 (s), 8.67 (s), 8.27 (s), 7.99 (s), 7.78 (s), 7.55 (m), 7.49 (m), 7.25 (w).[1/]

1/ Spectra obtained from sample supplied by Coal Tar Research Association, Leeds, England.

7-METHYL-4-INDANOL

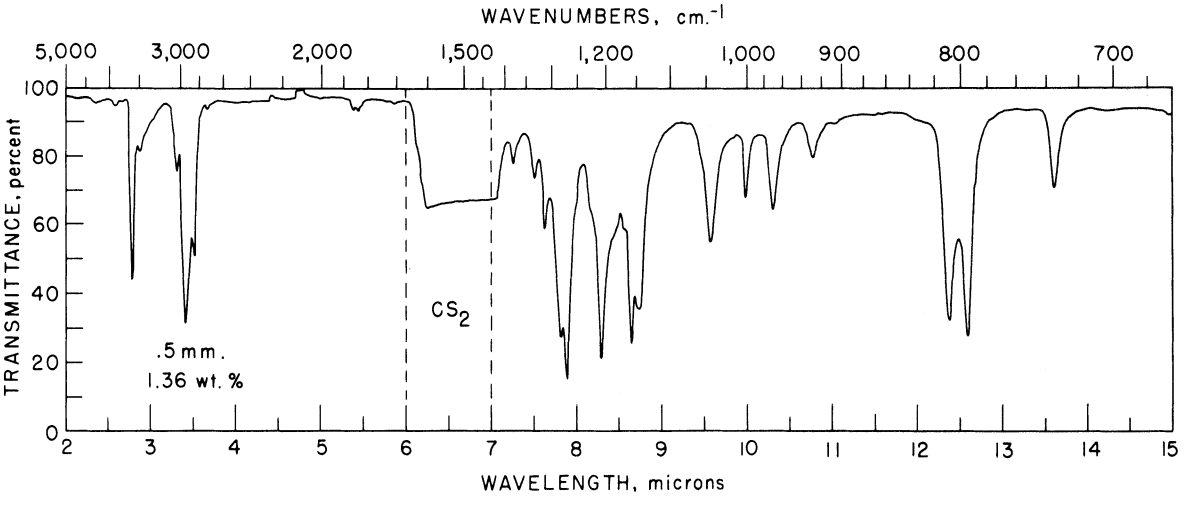


B.p. [est. 250°]



λ cyclohexane max, mμ	log ε
282.0	3.06
277.0	3.05
272.8	3.11

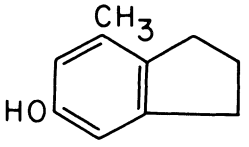
72



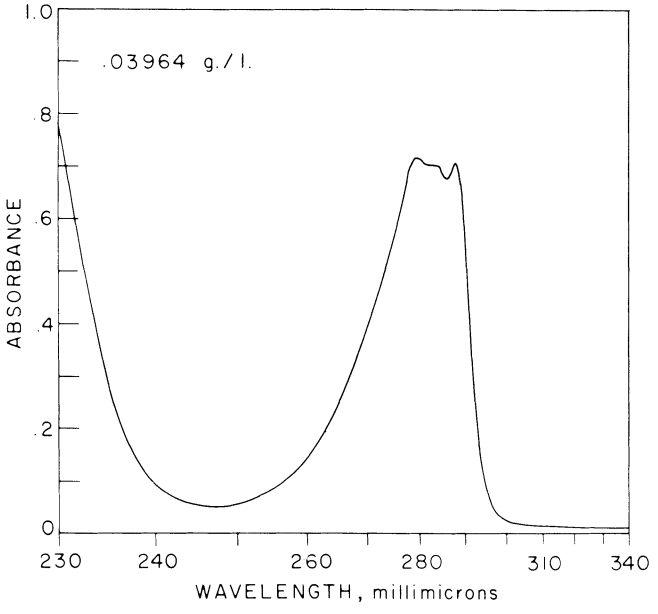
λ^{CS_2}: 13.62 (m), 12.59 (s), 12.37 (s), 10.78 (w), 10.30 (m), 9.98 (m), 9.57 (m), 8.73 (s), 8.64 (s), 8.56 (w), 8.29 (s), 7.88 (s), 7.82 (w), 7.62 (w), 7.50 (w), 7.26 (w).1/

1/ Spectra obtained from sample supplied by Coal Tar Research Association, Leeds, England.

7-METHYL-5-INDANOL

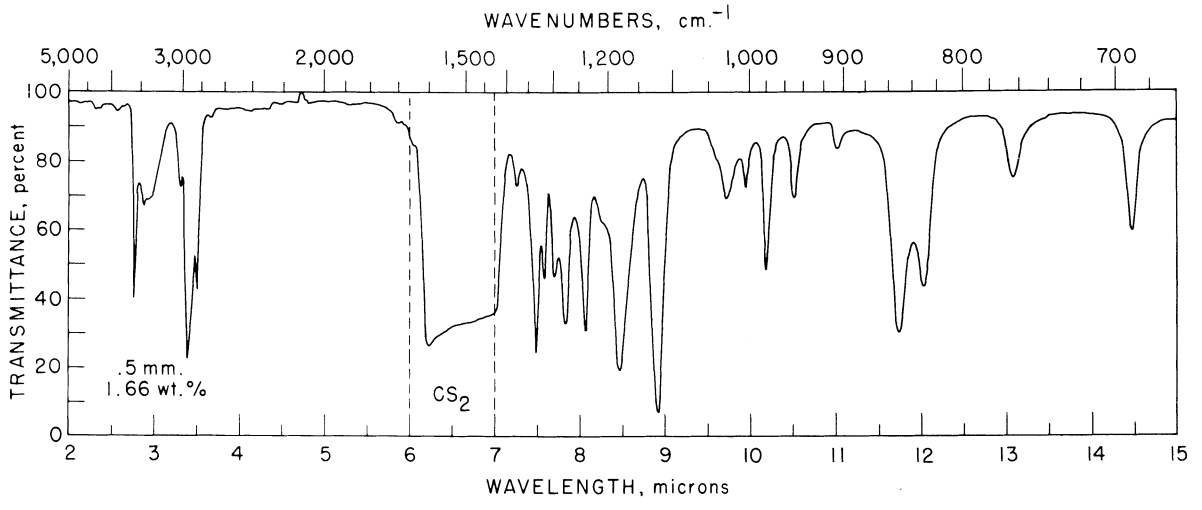


B.p. [est. 260°]



λ max, mμ cyclohexane	log ε
288.0	3.44
283.5	3.43
280.0	3.43

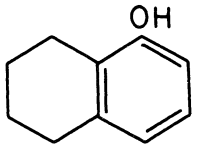
73



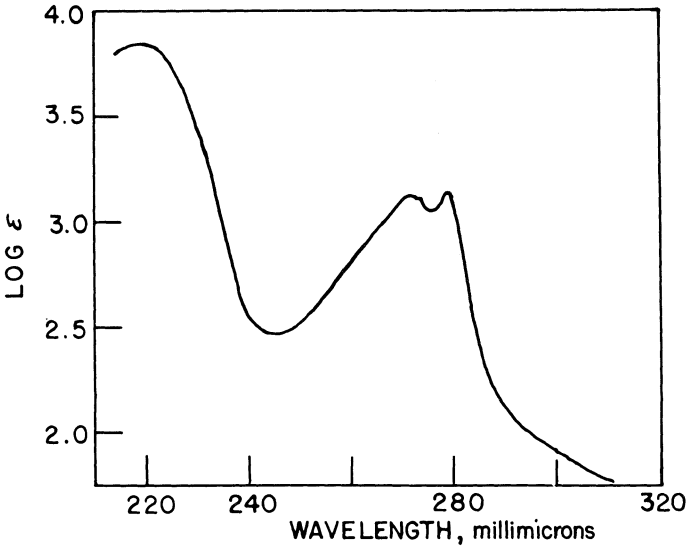
$\lambda_{max}^{CS_2}$: 14.48 (m), 13.10 (w), 12.04 (m), 11.75 (s), 11.03 (w), 10.53 (w), 10.20 (m), 9.96 (w), 9.73 (w), 8.93 (s), 8.47 (s), 8.27 (w), 8.07 (m), 7.84 (m), 7.71 (w), 7.59 (w), 7.50 (m), 7.26 (w). 1/

1/ Spectra obtained from sample supplied by Coal Tar Research Association, Leeds, England.

5, 6, 7, 8 - TETRAHYDRO - 1 - NAPHTHOL



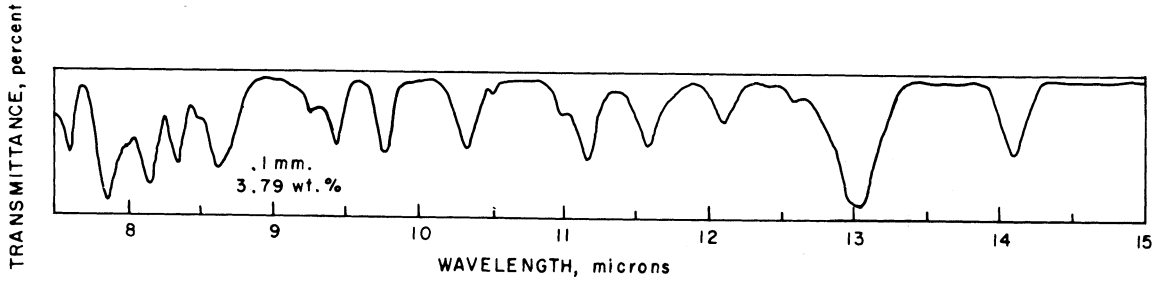
B.p. 264.5-265°/705 mm. (8)



λ max, mμ (cyclohexane)	log ε
279.0	3.14
274.5	3.09
271.5	3.11

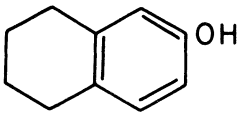
(37)

74

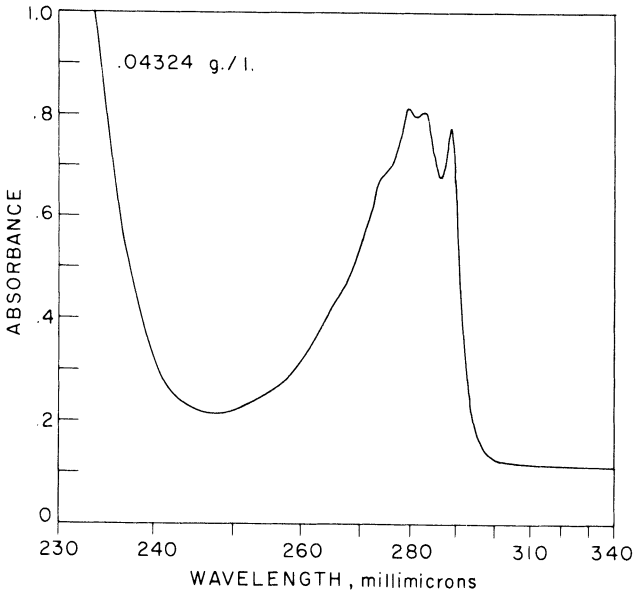


λ^{CS_2}: 14.09 (m), 13.04 (s), 12.60 (w), 12.12 (m), 11.57 (m), 11.15 (m), 11.00 (w), 10.48 (w), 10.30 (m), 9.70 (m), 9.38 (m), 9.22 (w), 8.69 (w), 8.58 (m), 8.45 (w), 8.30 (m), 8.12 (m), 7.97 (w), 7.85 (m), 7.60 (m). (118)

5, 6, 7, 8 - TETRAHYDRO - 2 - NAPHTHOL

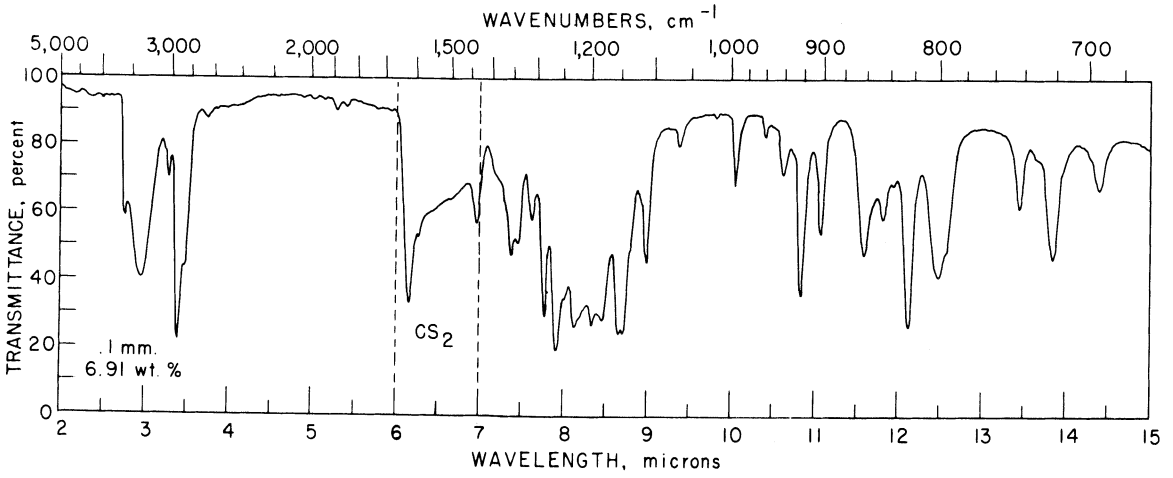


B.p. 275-276° (8)



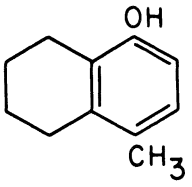
λ cyclohexane max, mμ	log ε
289.0	3.44
282.9	3.45
279.4	3.46
274.5	3.39

75



λ^{CS_2}: 14.41 (m), 13.85 (s), 13.65 (w), 13.45 (m), 12.57 (m), 12.47 (s), 12.12 (s), 11.94 (w), 11.82 (w), 11.59 (m), 11.07 (m), 10.84 (s), 10.63 (m), 10.41 (w), 10.06 (m), 9.82 (w), 9.39 (w), 8.99 (m) 8.80 (w), 8.72 (s), 8.67 (s), 8.47 (m), 8.35 (m), 8.18 (w), 8.14 (m), 8.02 (w), 7.92 (s), 7.78 (m), 7.64 (w), 7.47 (w), 7.38 (m), 7.32 (w), 7.20 (w).

4-METHYL-5,6,7,8-TETRAHYDRO-1-NAPHTHOL

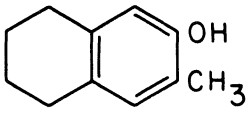


B.p. [est. 280°]

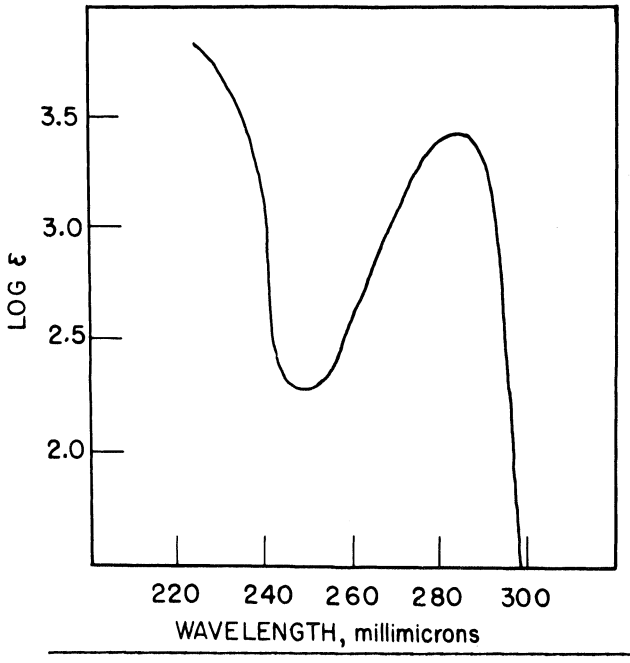
Infrared bands, μ : 12.40 (mineral oil). (29)

76

3-METHYL-5,6,7,8-TETRAHYDRO-2-NAPHTHOL



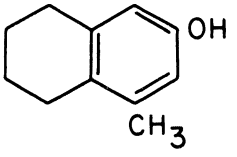
B.p. [est. 290°]



λ_{max} NaOH solution, mμ	log ε
285 (94)	3.42

77

4-METHYL-5,6,7,8-TETRAHYDRO-2-NAPHTHOL



B.p. [est. 290°]

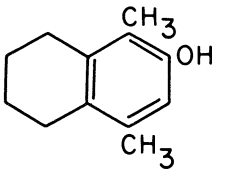
$\lambda_{max}^{alcohol}$, mμ: 281 (3.30).

λ_{min}: 251 (2.40).

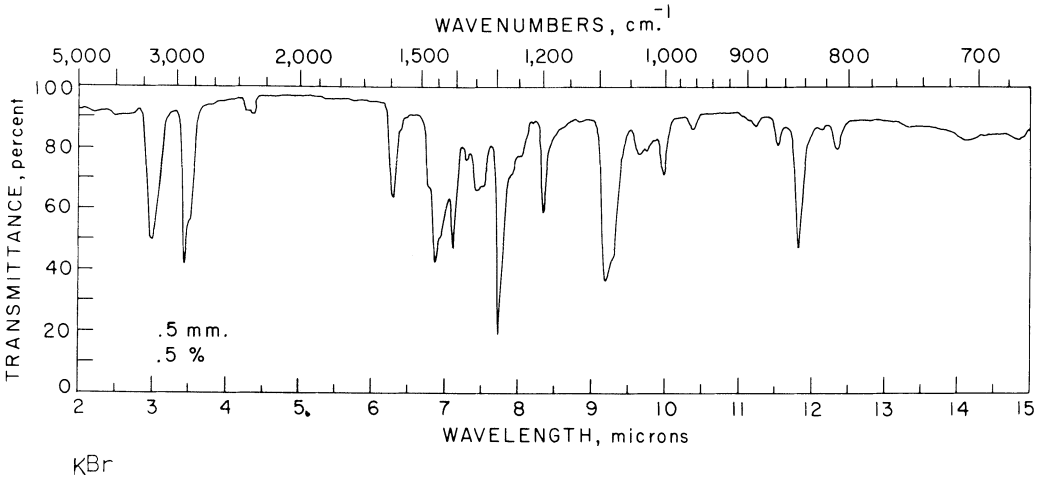
78

Infrared bands, μ: 11.76 (mineral oil). (29)

1, 4 - DIMETHYL - 5, 6, 7, 8 - TETRAHYDRO - 2 - NAPHTHOL



B.p. [est. 305°]



KBr

λ : 14.81 (w), 14.11 (w), 12.34 (w), 12.13 (w), 11.82 (s), 11.54 (w), 11.22 (w), 10.37 (w), 9.97 (m), 9.74 (w), 9.64 (w), 9.28 (m), 9.19 (s), 8.34 (m), 8.04 (w), 7.88 (w), 7.73 (s), 7.53 (w), 7.44 (w), 7.30 (w), 7.10 (m). (99)

79

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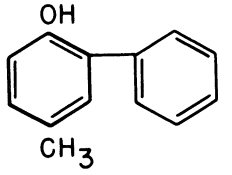
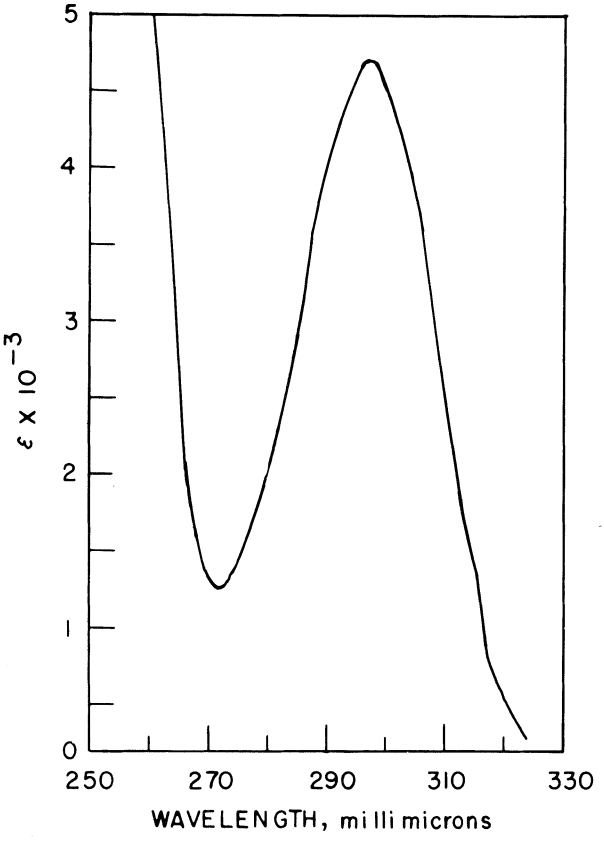
4 - METHYL - 2 - PHENYLPHENOL

80



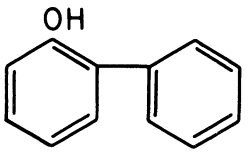
B.p. 101-105°/2 mm. (3)
[est. 280°]



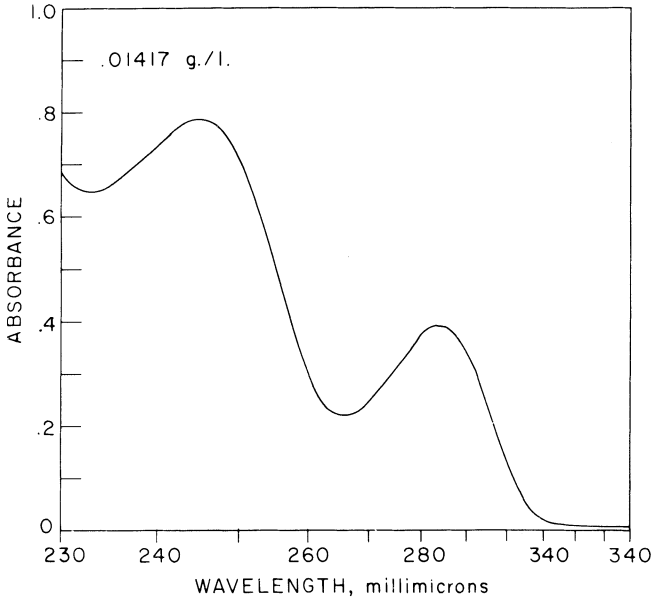
λ 95% alcohol max, mμ	log ε
296	3.67

(3)

2-PHENYLPHENOL

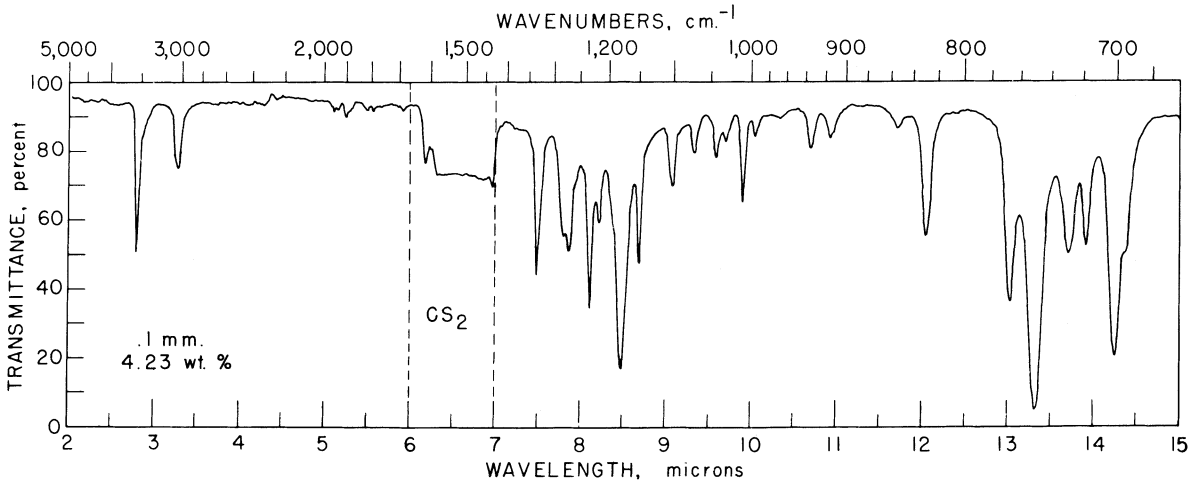


B.p. 275° (43)



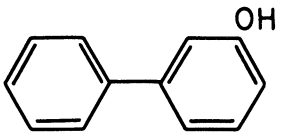
λ cyclohexane max, mμ	log ε
283.5	3.68
245.5	4.00

81

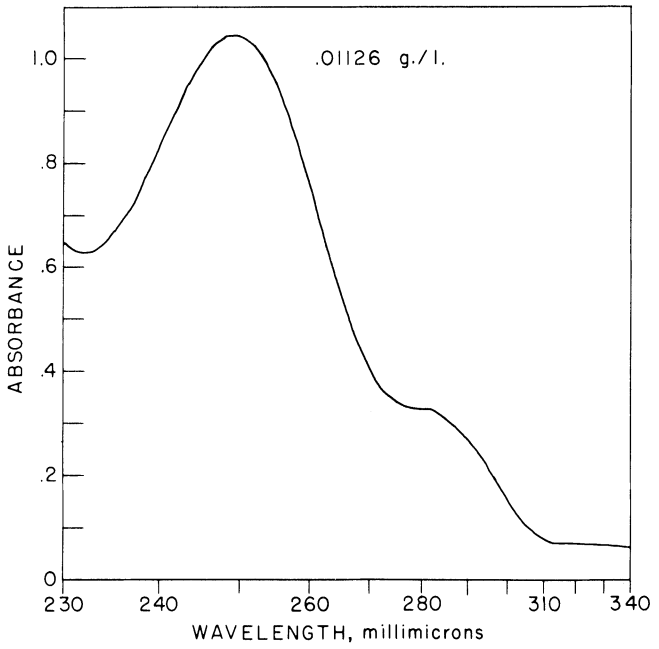


λ^{CS_2}: 14.37 (w), 14.24 (s), 13.91 (m), 13.70 (m), 13.32 (s), 13.02 (m), 12.04 (m), 11.69 (w), 10.92 (w), 10.68 (w), 10.32 (w), 10.04 (w), 9.89 (m), 9.70 (w), 9.58 (w), 9.33 (w), 9.07 (m), 8.68 (m), 8.49 (s), 8.22 (w), 8.11 (m), 7.87 (m), 7.80 (w), 7.49 (m).

3-PHENYLPHENOL

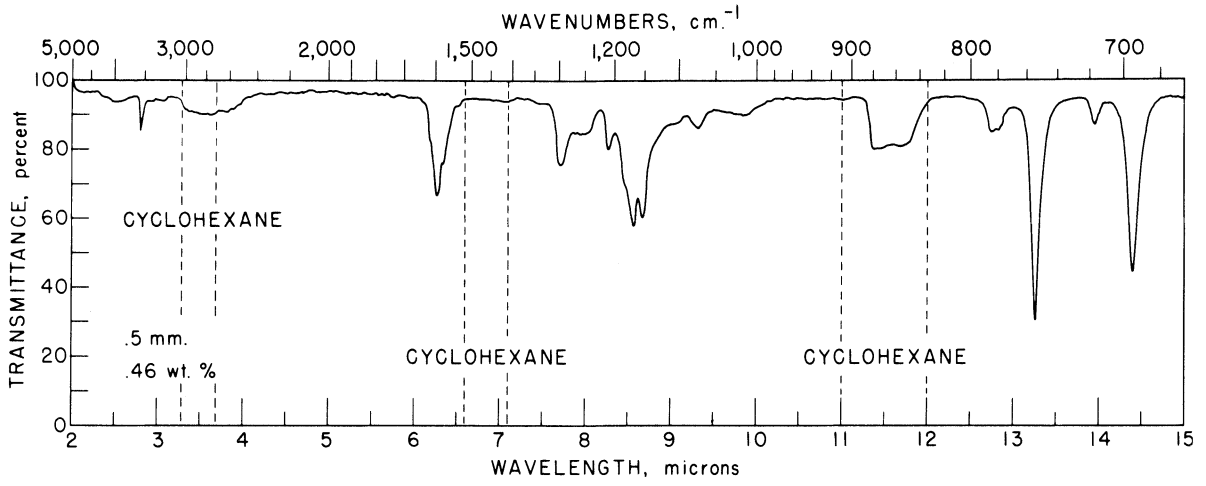


B.p. 325° (60)



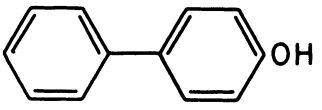
λ cyclohexane max, mμ	log ε
281.0	3.68
249.0	4.21

82

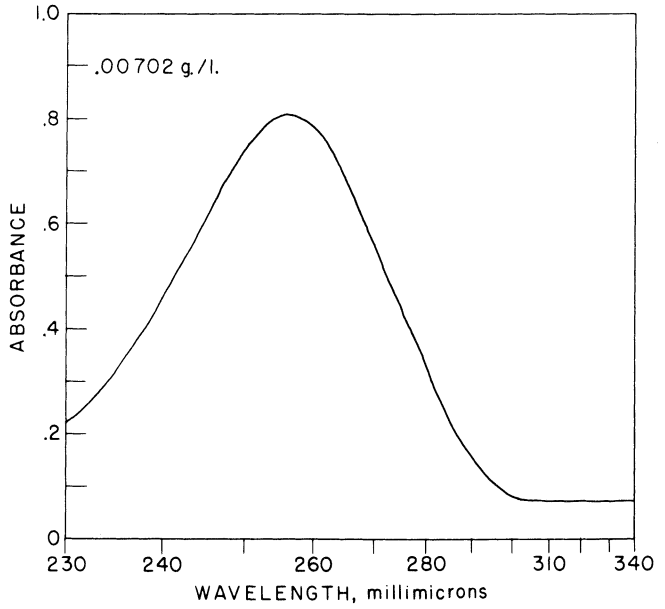


λ cyclohexane: 14.39 (s), 13.95 (w), 13.26 (s), 12.84 (w), 12.75 (w), 9.33 (w), 9.07 (w), 8.67 (m), 8.57 (m), 8.47 (w), 8.27 (w), 8.00 (w), 7.72 (m).

4 - PHENYLPHENOL

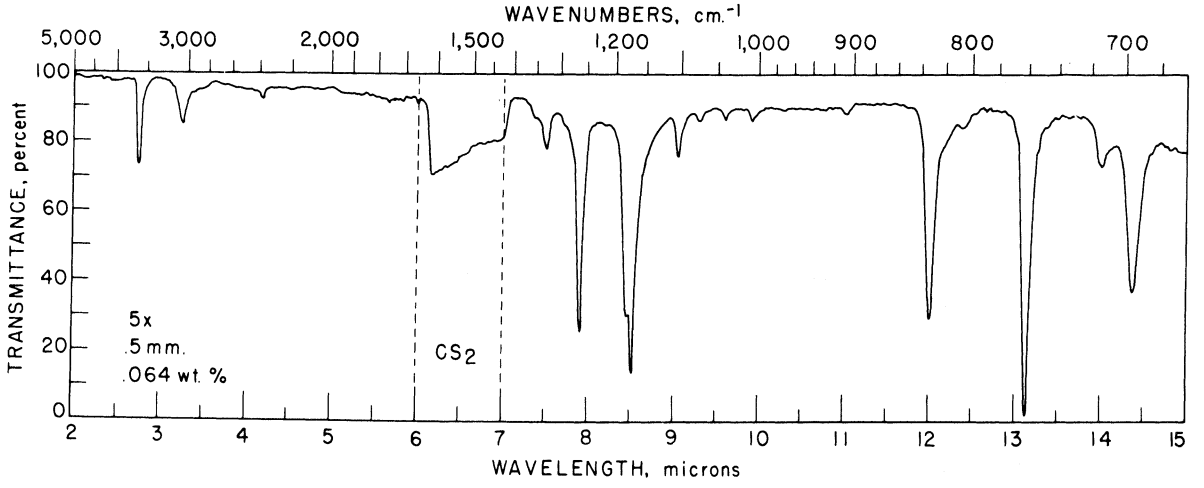


B.p. 319° (64)



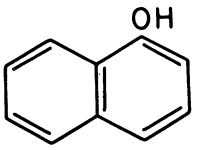
λ_{max}, mμ (cyclohexane)	log ε
256.5	4.31

83

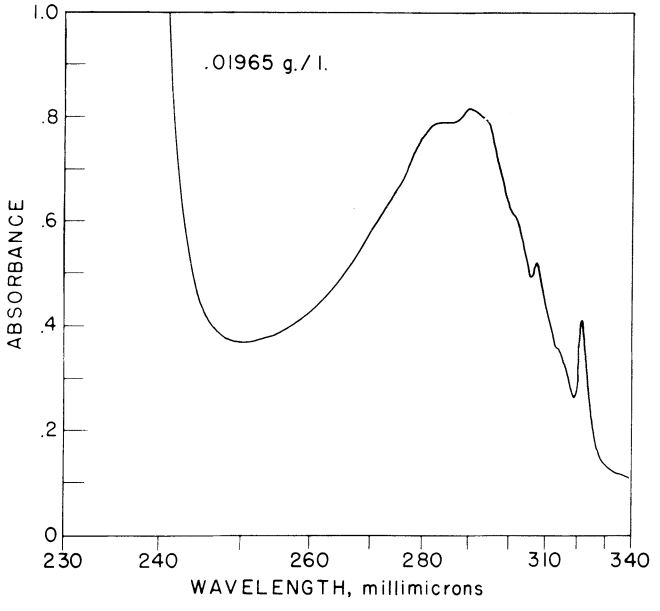


λ^{CS_2}: 14.38 (s), 14.00 (m), 13.14 (s), 12.40 (w), 12.01 (s), 9.93 (w), 9.62 (w), 9.32 (w), 9.07 (m), 8.54 (s), 8.48 (m), 8.22 (w), 7.94 (s), 7.85 (w), 7.53 (m), 7.40 (w).

1-NAPHTHOL

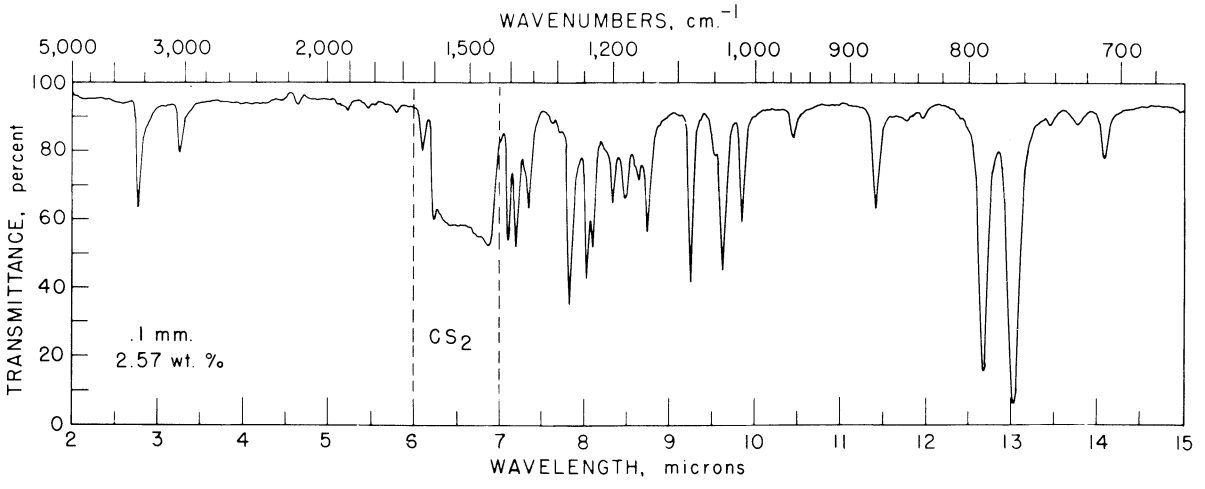


B.p. 288.01° (76)



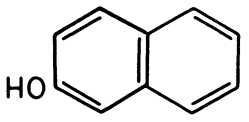
λ cyclohexane max, mμ	log ε
321.6	3.47
317.0	3.33
314.2	3.41
310.4	3.49
307.5	3.61
301.2	3.78
294.0	3.79
290.0	3.80
282.6	3.79

84

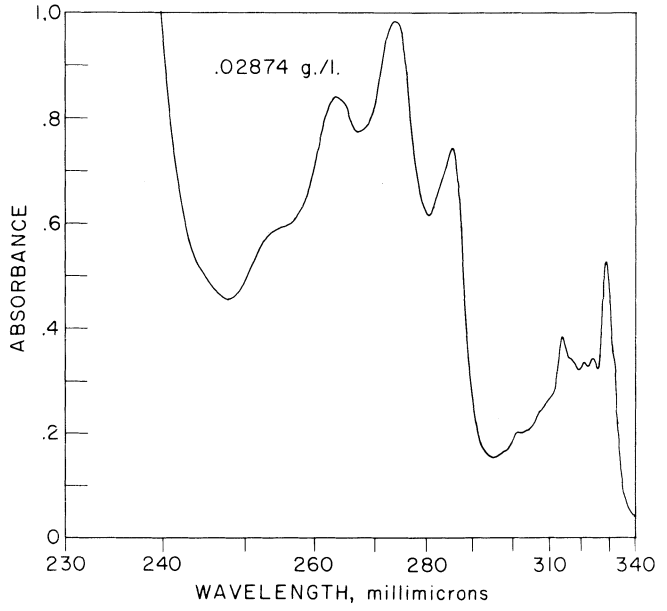


λ^{CS_2}: 14.08 (w), 13.77 (w), 13.44 (w), 13.02 (s), 12.66 (s), 11.95 (w), 11.75 (w), 11.39 (m), 10.44 (w), 9.84 (m), 9.62 (m), 9.52 (w), 9.24 (m), 8.73 (m), 8.64 (w), 8.59 (w), 8.48 (w), 8.33 (w), 8.10 (m), 8.02 (m), 7.83 (m), 7.71 (w), 7.62 (w), 7.35 (m), 7.20 (m), 7.10 (m).

2 - NAPHTHOL

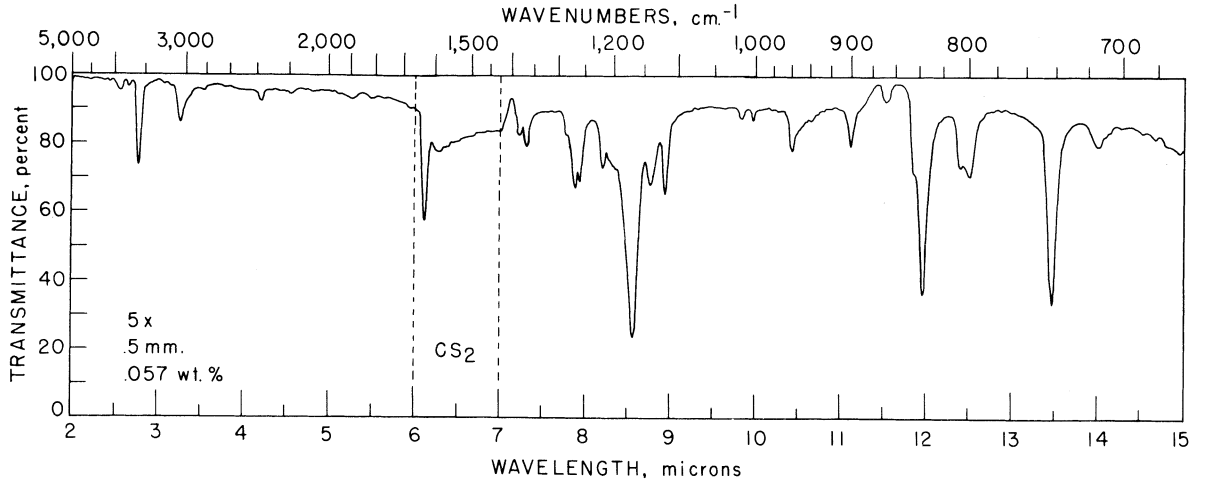


B.p. 294.85° (76)



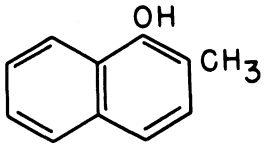
λ cyclohexane max, mμ	log ε
328.6	3.49
324.0	3.49
321.0	3.36
314.0	3.39
307.0	3.18
301.0	3.13
285.4	3.69
273.8	3.77
263.5	3.73
254.0	3.58

85

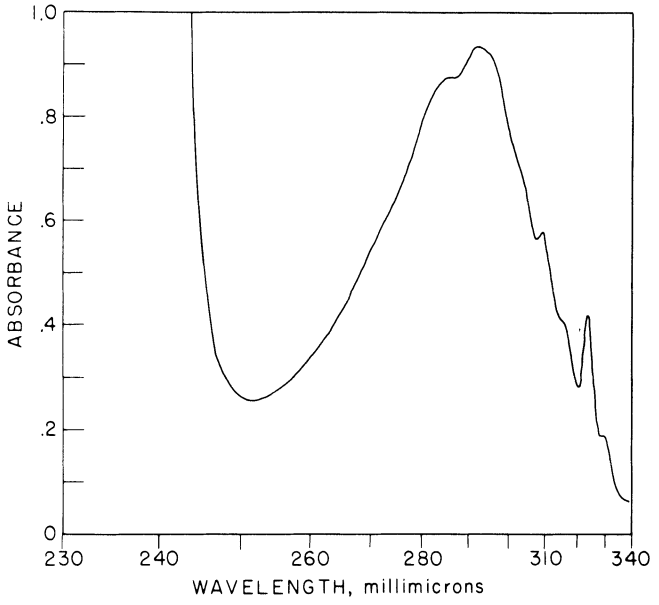


λ^{CS_2}: 14.00 (w), 13.46 (s), 12.50 (m), 12.38 (w), 11.95 (s), 11.85 (w), 11.52 (w), 11.10 (m), 10.42 (m), 9.83 (w), 8.94 (m), 8.77 (m), 8.57 (s), 8.35 (w), 8.20 (w), 7.95 (m), 7.88 (m), 7.78 (w), 7.32 (w), 7.23 (w).

2-METHYL-1-NAPHTHOL

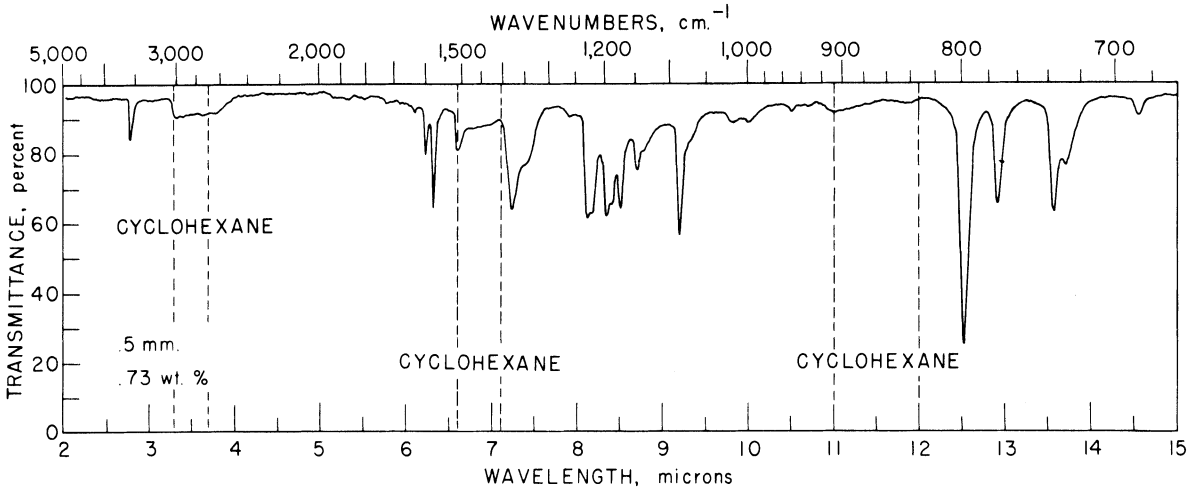


B.p. [est. 295°]



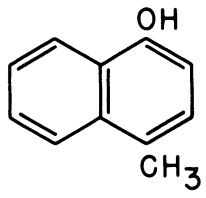
λ cyclohexane max, mμ
329.2
323.7
315.2
309.0
292.0
284.5

86

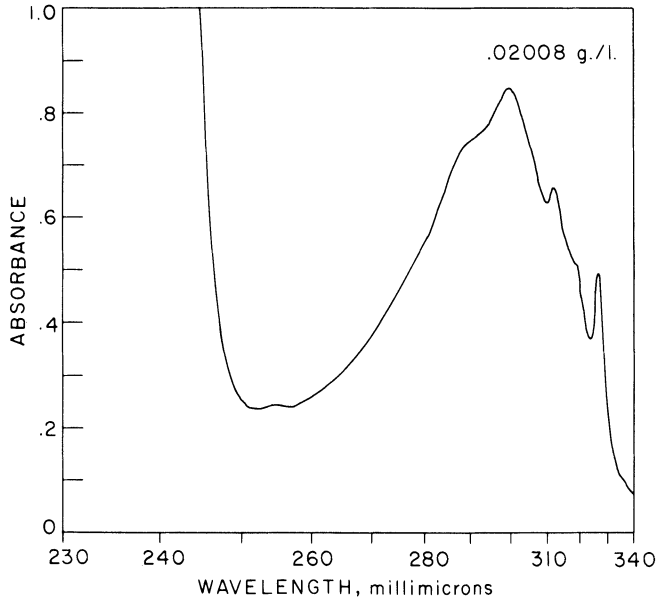


$\lambda^{\text{cyclohexane}}$: 14.55 (w), 13.71 (w), 13.56 (m), 12.92 (m), 12.52 (s), 10.52 (w), 9.84 (w), 9.21 (m), 8.79 (w), 8.71 (w), 8.51 (m), 8.42 (w), 8.35 (m), 8.17 (m), 8.12 (m), 7.92 (w), 7.42 (w), 7.24 (m).

4-METHYL-1-NAPHTHOL

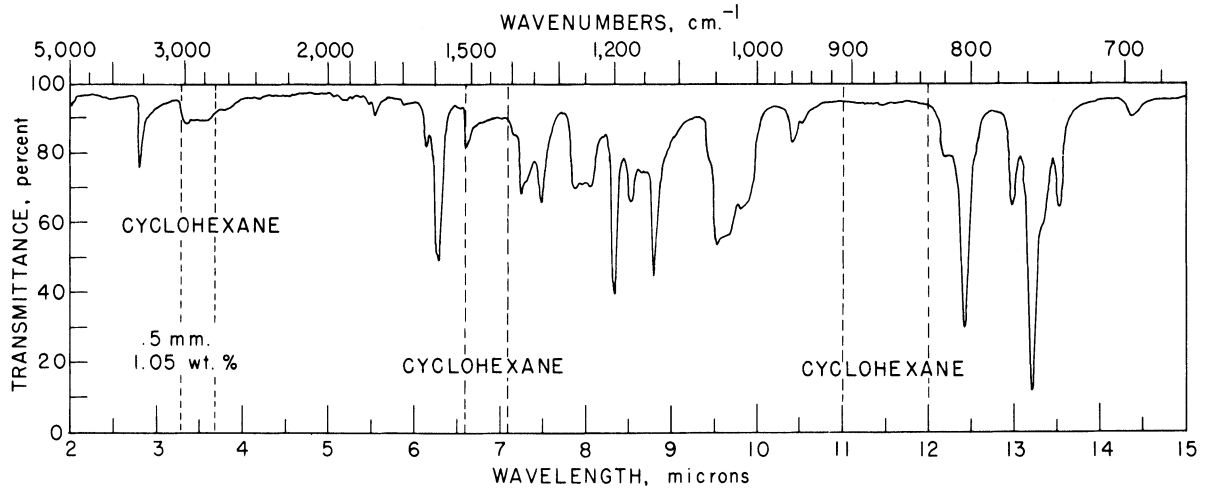


B.p. 177-179°/25 mm. (8)
[est. 298°]



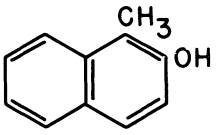
λ cyclohexane max, mμ	log ε
326.6	3.60
318.8	3.62
312.2	3.72
299.6	3.83
290.0	3.77

87

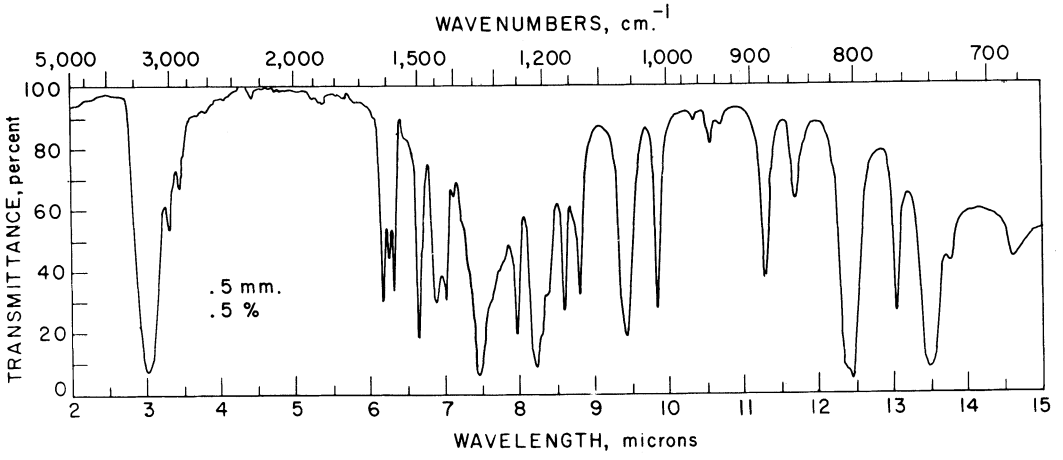


λ cyclohexane: 14.37 (w), 13.52 (m), 13.34 (w), 13.20 (s), 12.97 (m), 12.42 (s), 12.18 (w), 10.52 (w), 10.42 (w), 9.83 (m), 9.68 (m), 9.54 (m), 9.45 (w), 8.80 (m), 8.67 (w), 8.52 (w), 8.34 (m), 8.05 (m), 7.84 (m), 7.48 (m), 7.32 (w), 7.25 (w), 7.18 (w).

1-METHYL-2-NAPHTHOL



B.p. [est. 300°]

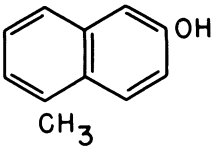


λ^{KBr}: 14.62 (w), 13.76 (w), 13.50 (s), 13.05 (m), 12.45 (s), 12.34 (s), 11.69 (m), 11.29 (m), 10.70 (w), 10.55 (w), 10.32 (w), 9.83 (m), 9.43 (s), 8.80 (m), 8.59 (m), 8.36 (w), 8.30 (w), 8.22 (s), 7.95 (m), 7.45 (s), 7.10 (w), 7.01 (w). (99)

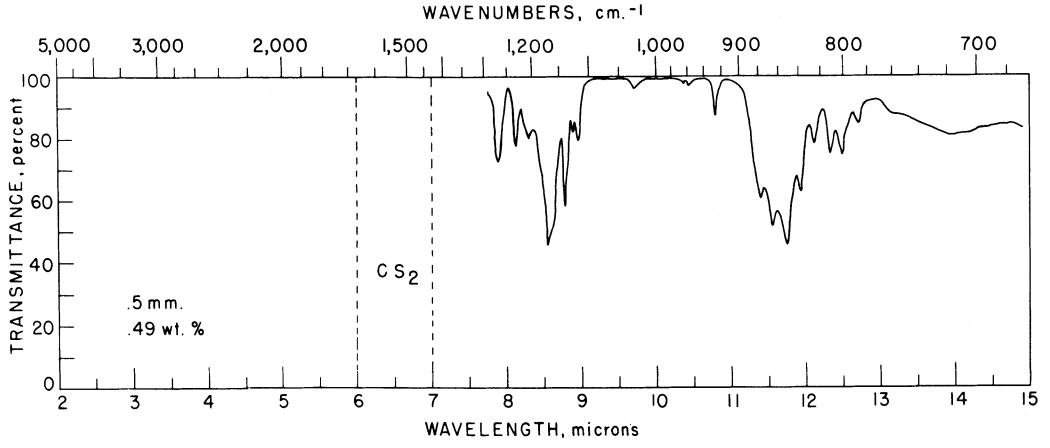
88

89

5-METHYL-2-NAPHTHOL



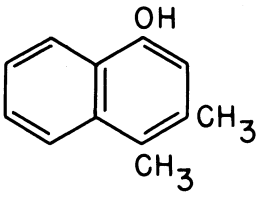
B.p. [est. 305°]



λ^{CS_2}: 12.71 (w), 12.50 (m), 12.33 (m), 12.12 (m), 11.93 (m), 11.75 (s), 11.55 (s), 11.38 (m), 10.79 (m), 10.44 (w), 10.36 (w), 9.71 (w), 8.96 (w), 8.89 (w), 8.79 (m), 8.55 (s), 8.29 (w), 8.12 (w), 7.87 (m).1/

1/ Spectrum supplied by W. W. Fowkes, Lignite Research Laboratory, U. S. Bureau of Mines, Grand Forks, N. D.

3, 4 - DIMETHYL - 1 - NAPHTHOL



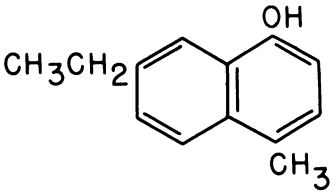
B.p. 205-210°/15 mm. (43)
[est. 315°]

$\lambda_{max}^{alcohol}$, mμ : 330 (3.73), 316 (3.85 sh), 306 (3.89), 242 (4.43). (25)

90

91

7 - ETHYL - 4 - METHYL - 1 - NAPHTHOL



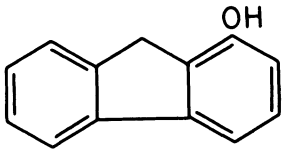
B.p. [est. 320°]

$\lambda_{max}^{alcohol}$, mμ : 331 (3.56), 316 (3.69 sh), 304 (3.76), 242 (4.57).

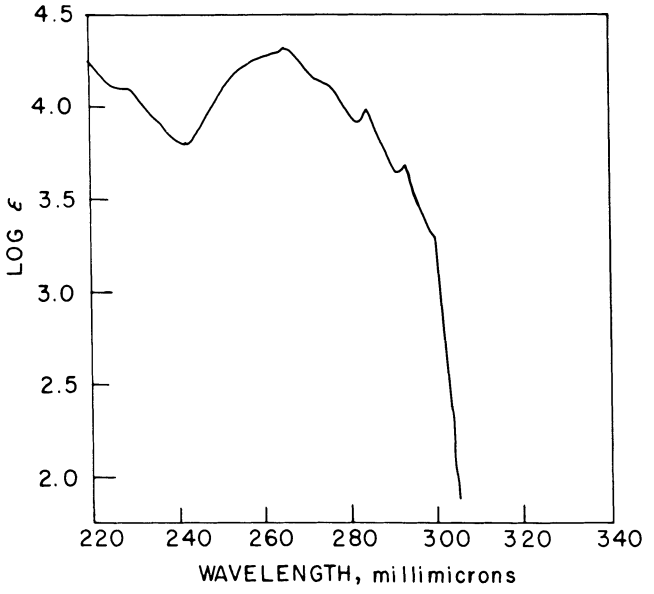
Infrared band, μ : 12.12 (s), 11.26 (m), 10.89 (w), 9.66 (w), 9.51 (s), 8.74 (m), 8.61 (w), 8.36 (m), 8.20 (w), 7.98 (w), 7.85 (w). (25)

569705 O—61——10

1-FLUORENOL



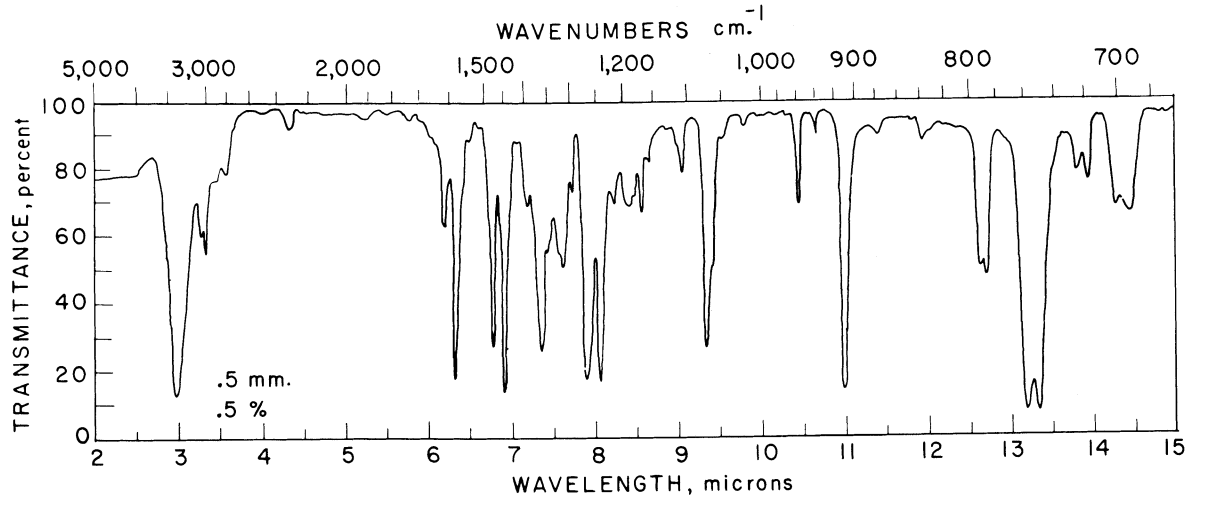
B.p. [est. 345°]



λ max, mμ (cyclohexane)	log ε
300	3.30
293	3.68
284	3.97
276	4.12
266	4.31
255	4.22
230	4.10

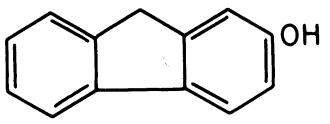
(37)

92

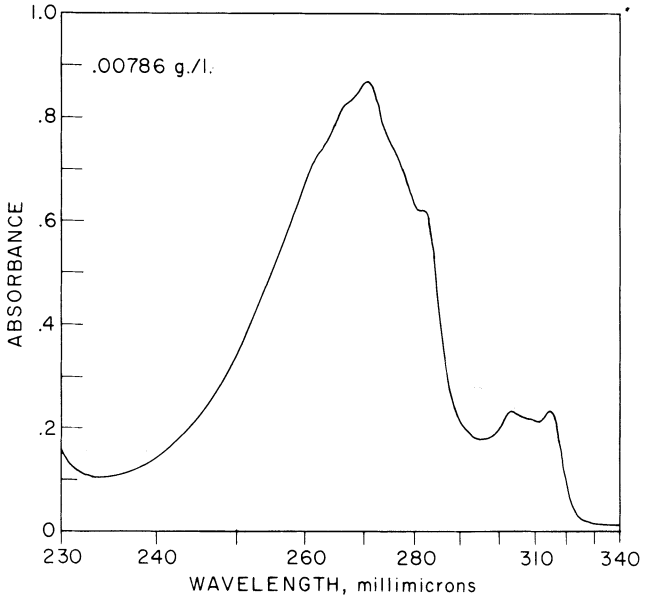


λ_{max}^{KBr}: 14.47 (m), 14.28 (m), 13.96 (w), 13.83 (w), 13.37 (s), 13.22 (s), 12.74 (m), 12.68 (m), 11.94 (w), 11.22 (w), 11.01 (s), 10.68 (w), 10.48 (m), 9.82 (w), 9.55 (w), 9.41 (w), 9.35 (s), 9.06 (w), 9.00 (w), 8.89 (w), 8.64 (w), 8.57 (w), 8.48 (w), 8.42 (m), 8.23 (w), 8.07 (s), 7.90 (s), 7.73 (w), 7.62 (m), 7.56 (w), 7.43 (w), 7.35 (s), 7.18 (w), 7.07 (w). (99)

2-FLUORENOL

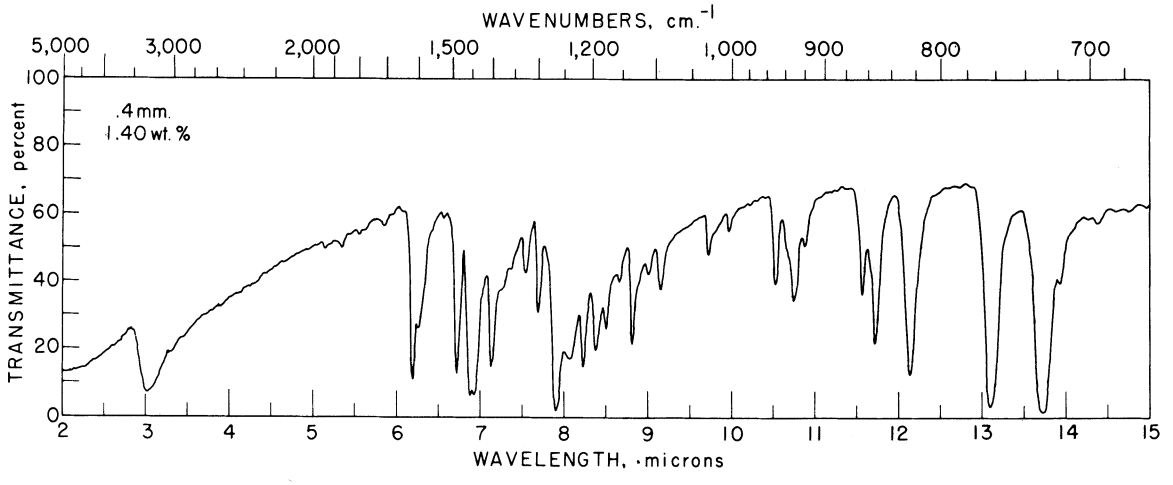


B.p. 340-350 (64)



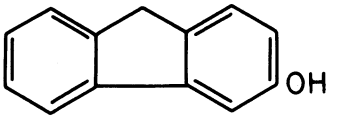
λ max, mμ (cyclohexane)	log ε
315.0	3.83
308.0	3.80
303.2	3.83
282.2	4.25
276.0	4.32
271.0	4.39
266.5	4.37
262.0	4.31

93

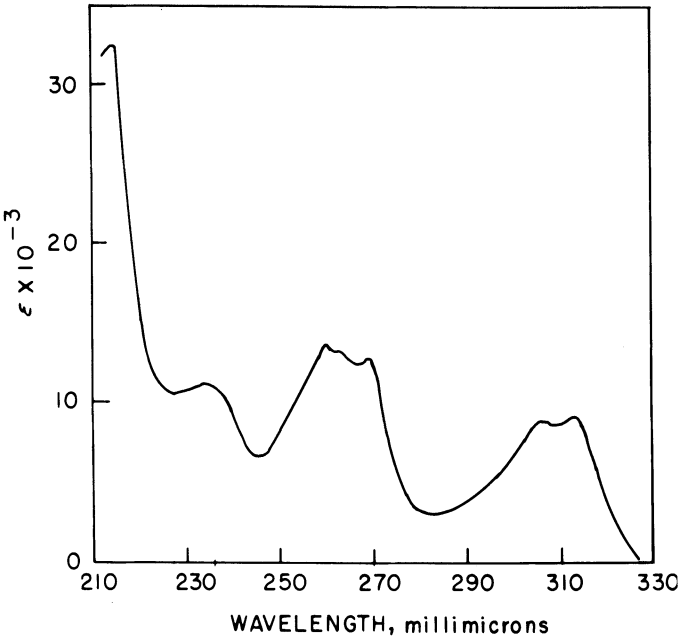


λ_{max}^{KBr} : 14.38 (w), 13.94 (w), 13.74 (s), 13.12 (s), 12.14 (s), 11.72 (m), 11.57 (m), 10.88 (w), 10.75 (m), 10.52 (m), 9.97 (w), 9.73 (w), 9.15 (w), 9.02 (w), 8.82 (m), 8.66 (w), 8.50 (w), 8.38 (m), 8.22 (m), 8.07 (w), 7.90 (s), 7.68 (m), 7.54 (w), 7.37 (w); 7.25 (w), 7.12 (m).

3-FLUORENOL



B.p. [est. 350°]



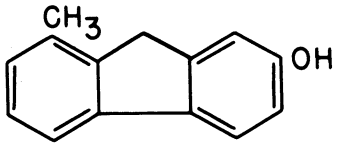
λ_{max}^{EtOH}, mμ	log ε
313	3.94
305	3.93
269	4.11
263	4.12
260	4.14
235	4.05

(114)

94

95

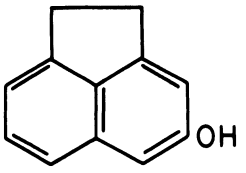
8-METHYL-2-FLUORENOL



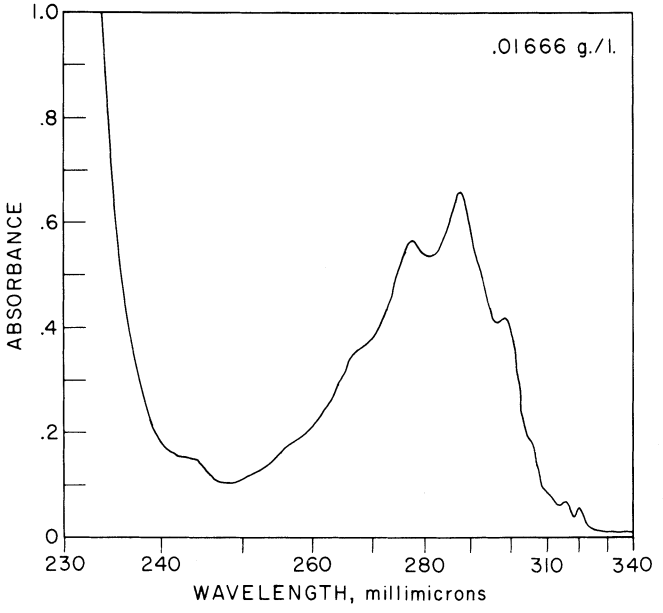
B.p. [est. 355°]

λ_{max}^{EtOH}, mμ: ~313 (3.66), 304 (3.70), ~283 (4.17), 274 (4.26). (78)

4 - ACENAPHTHENOL

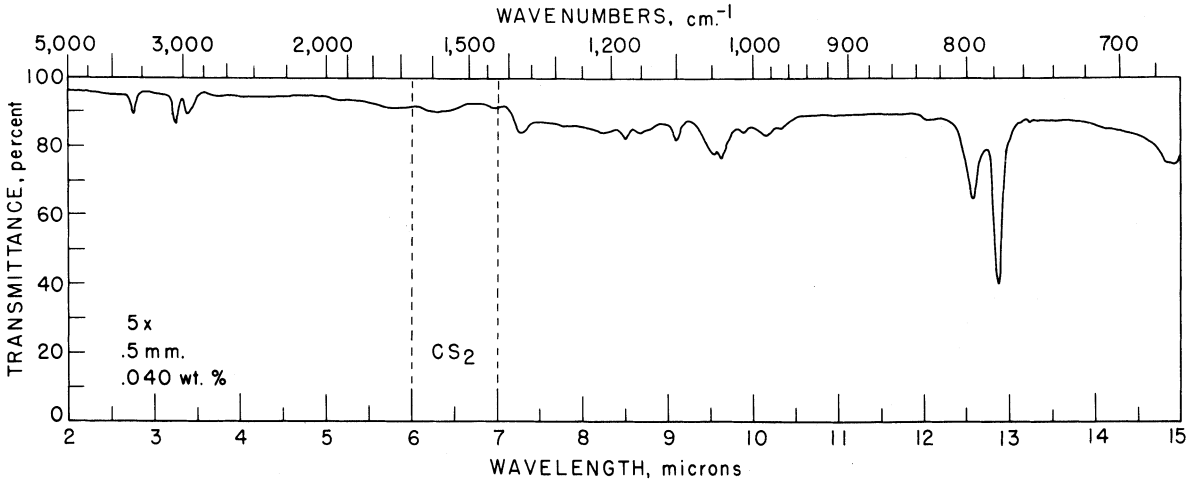


B.p. [est. 338°]



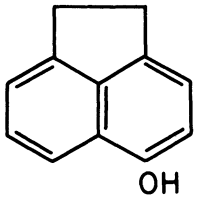
λ max, mμ (cyclohexane)	log ε
320.2	2.75
315.7	2.84
310.0	2.95
305.5	3.29
298.5	3.63
287.5	3.82
277.2	3.76
266.8	3.56
256.3	3.26
243.5	3.20

96

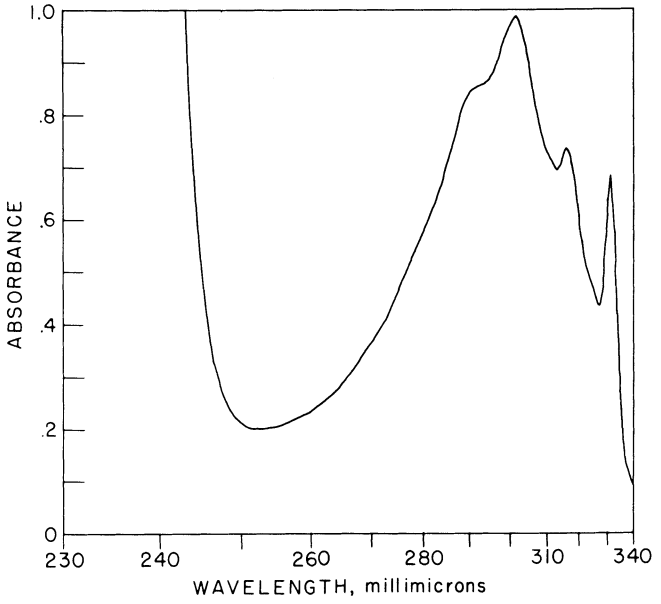


λ^{CS_2}: 14.85 (w), 14.82 (w), 12.87 (s), 12.57 (s), 10.35 (w), 10.17 (w), 9.90 (w), 9.65 (m), 9.55 (m), 9.12 (m), 8.80 (w), 8.70 (w), 8.54 (w), 8.30 (w), 7.30 (w).

5-ACENAPHTHENOL

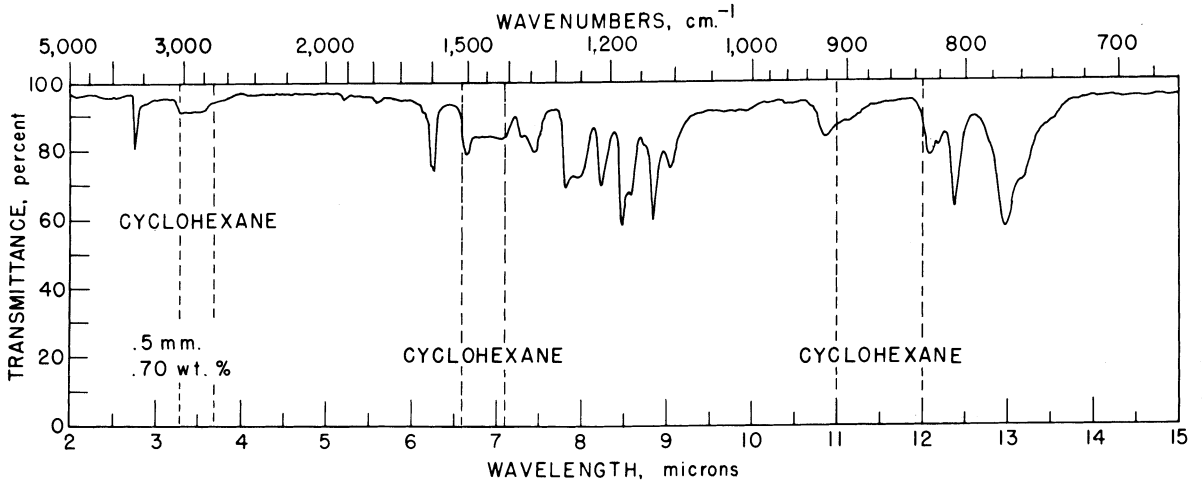


B.p. 221°/40 mm. (43)
[est. 332°]



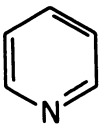
λ cyclohexane max, mμ
331.0
323.5
316.0
301.2
290.5

97

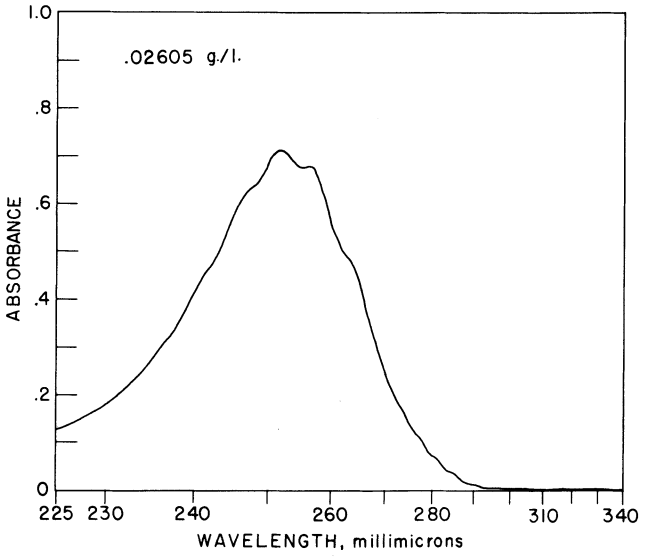


$\lambda^{\text{cyclohexane}}$: 13.19 (w), 12.97 (s), 12.38 (s), 12.18 (w), 12.10 (w), 11.18 (w), 10.87 (m), 9.05 (m), 8.85 (s), 8.75 (w), 8.59 (w), 8.49 (s), 8.24 (m), 8.00 (m), 7.82 (m), 7.44 (m), 7.30 (w), 7.10 (w).

PYRIDINE

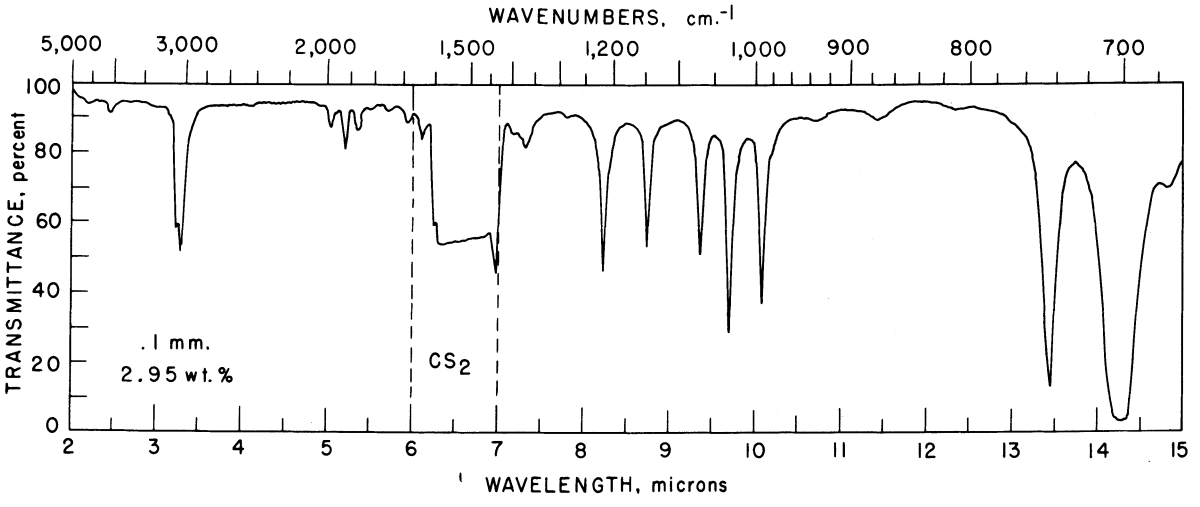


B.p. 115.4° (24)



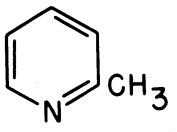
λ max, mμ (cyclohexane)	log ε
289.0	1.66
284.3	2.04
280.5	2.32
276.5	2.54
263.0	3.17
256.3	3.31
251.5	3.33
247.2	3.28
241.3	3.15

98

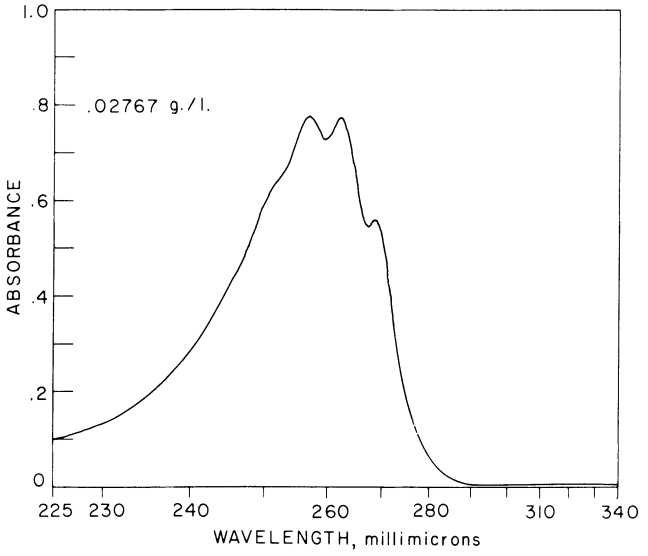


λ^{CS_2}: 14.82 (w), 14.30 (s), 13.45 (m), 10.08 (m), 9.70 (m), 9.36 (m), 8.74 (m), 8.23 (m), 7.78 (w), 7.32 (w), 7.17 (w).

2-METHYLPYRIDINE

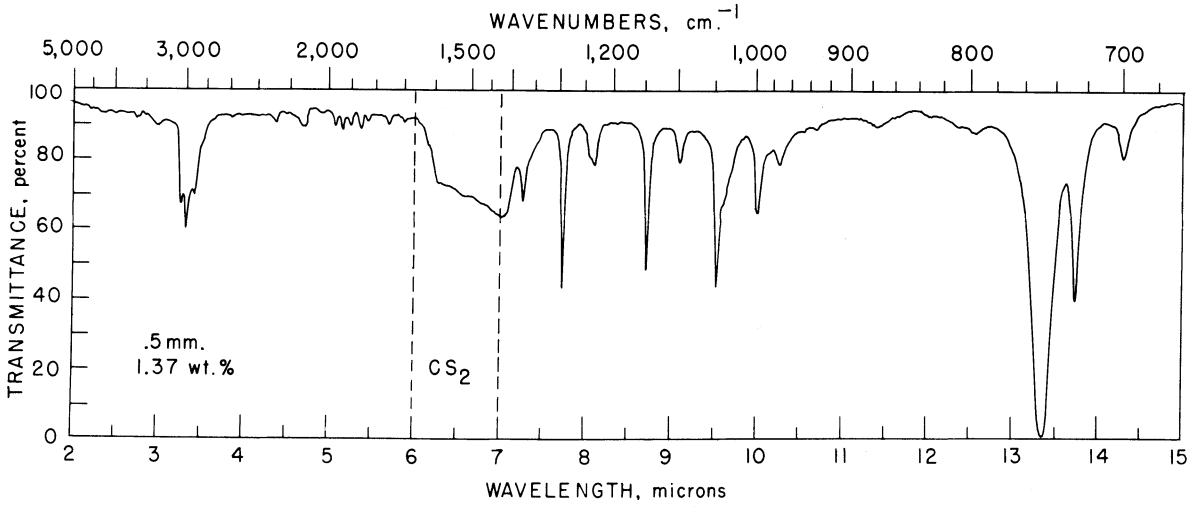


B.p. 129.41° (24)



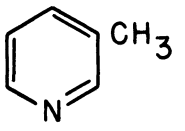
λ max, mμ (cyclohexane)	log ε
268.5	3.27
262.3	3.42
256.6	3.42
251.5	3.33

99

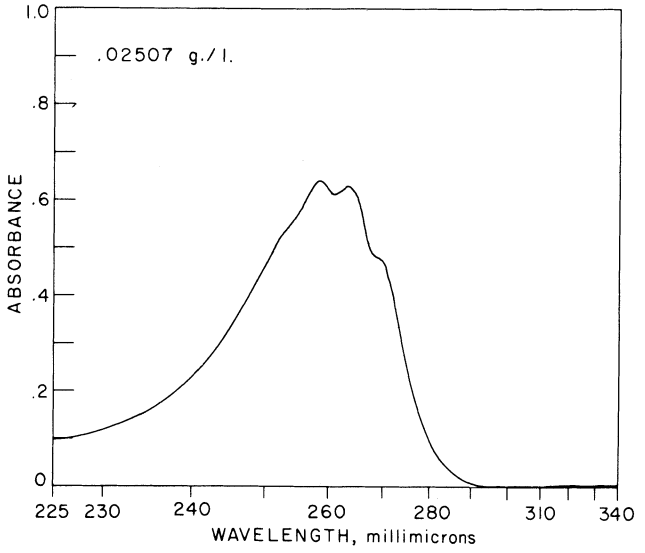


λ^{CS_2}: 14.31 (w), 13.74 (m), 13.35 (s), 12.55 (w), 11.42 (w), 10.27 (w), 10.02 (w), 9.64 (w), 9.54 (m), 9.11 (w), 8.72 (m), 8.12 (w), 7.74 (m), 7.27 (w).

3-METHYLPYRIDINE

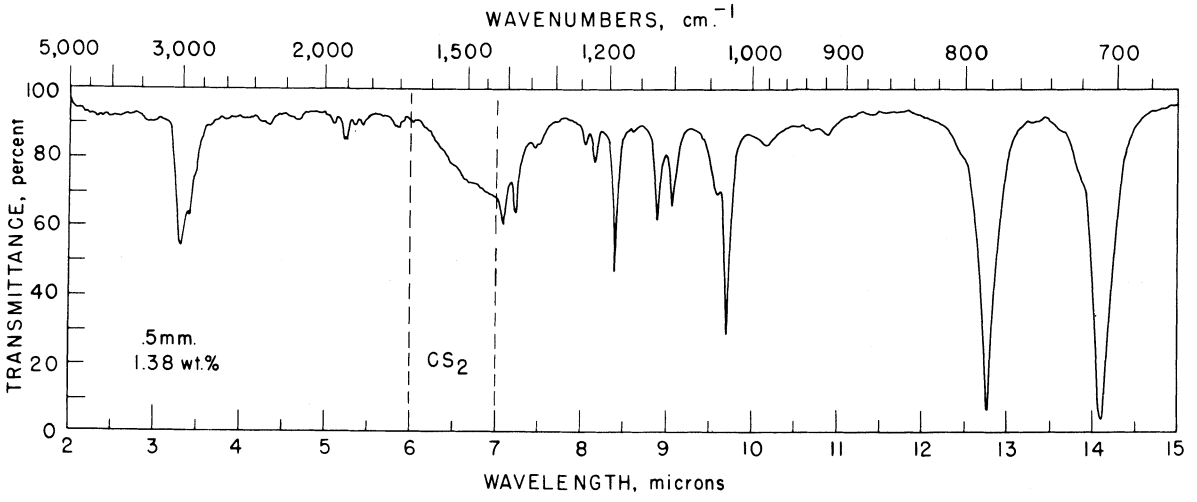


B.p. 144.14° (24)



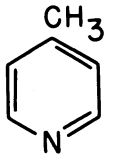
λ max, mμ cyclohexane	log ε
269.0	3.25
263.5	3.37
258.2	3.37
252.5	3.29

100

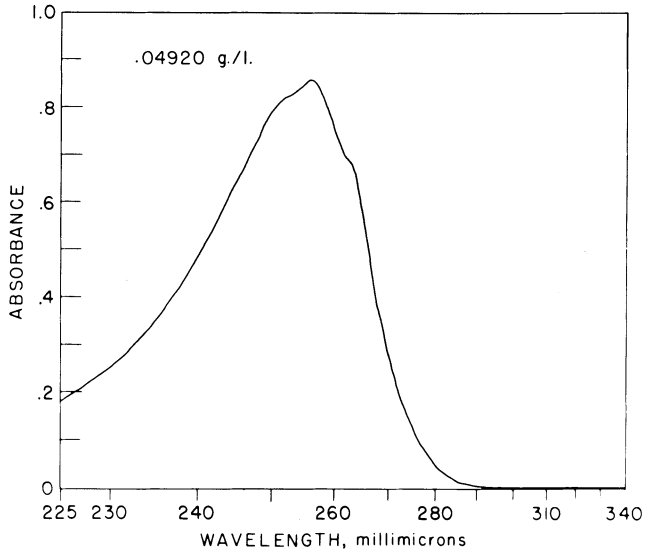


$\lambda_{max}^{CS_2}$: 14.11 (s), 13.87 (w), 12.78 (s), 10.90 (w), 10.18 (w), 9.72 (m), 9.60 (w), 9.08 (w), 8.90 (w), 8.40 (m), 8.15 (w), 8.05 (w), 7.52 (w), 7.45 (w), 7.23 (w), 7.09 (w).

4-METHYLPYRIDINE

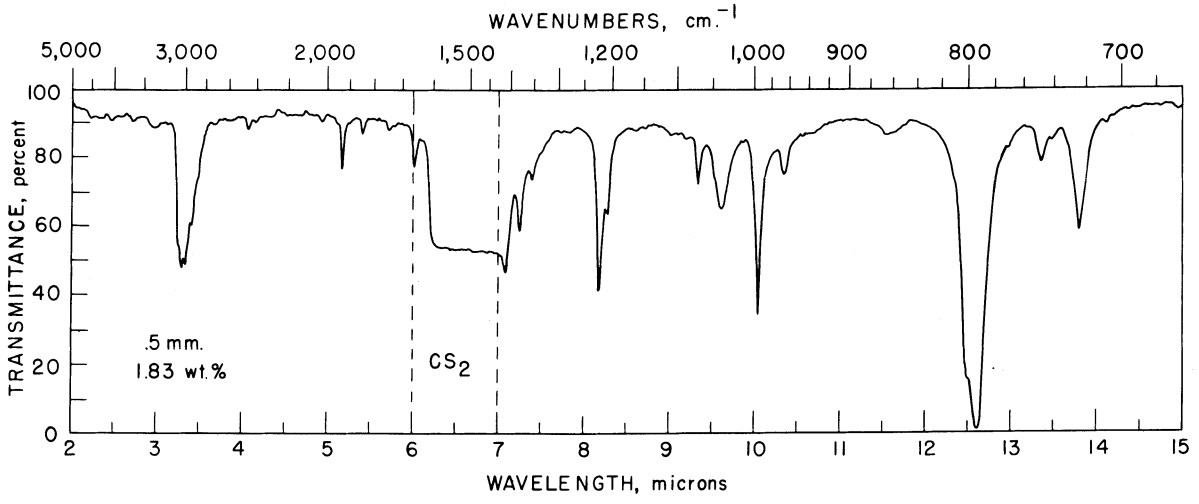


B.p. 145.0° (24)



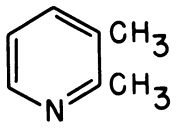
λ max, mμ (cyclohexane)	log ε
262.3	3.12
256.0	3.21
251.0	3.19

101

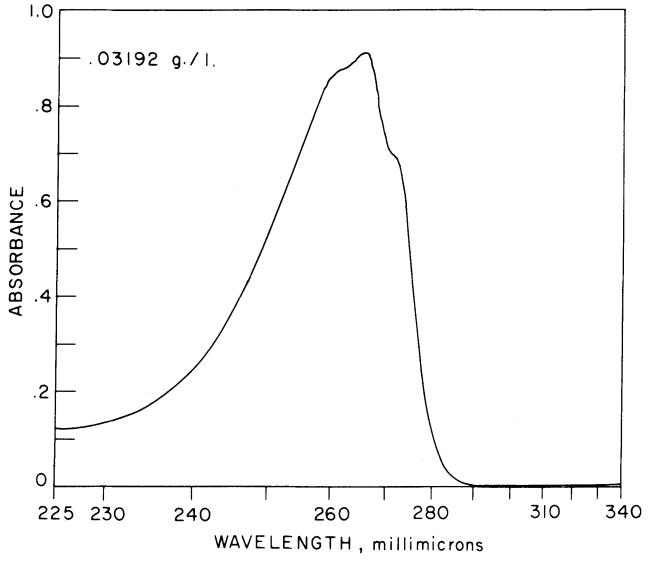


λ^{CS_2}: 13.80 (m), 13.48 (w), 13.35 (w), 12.61 (s), 12.48 (w), 11.54 (w), 10.35 (w), 10.05 (m), 9.62 (w), 9.35 (w), 8.28 (w), 8.19 (m), 7.84 (w), 7.74 (w), 7.30 (w), 7.25 (w), 7.08 (m).

2, 3 - DIMETHYLPYRIDINE

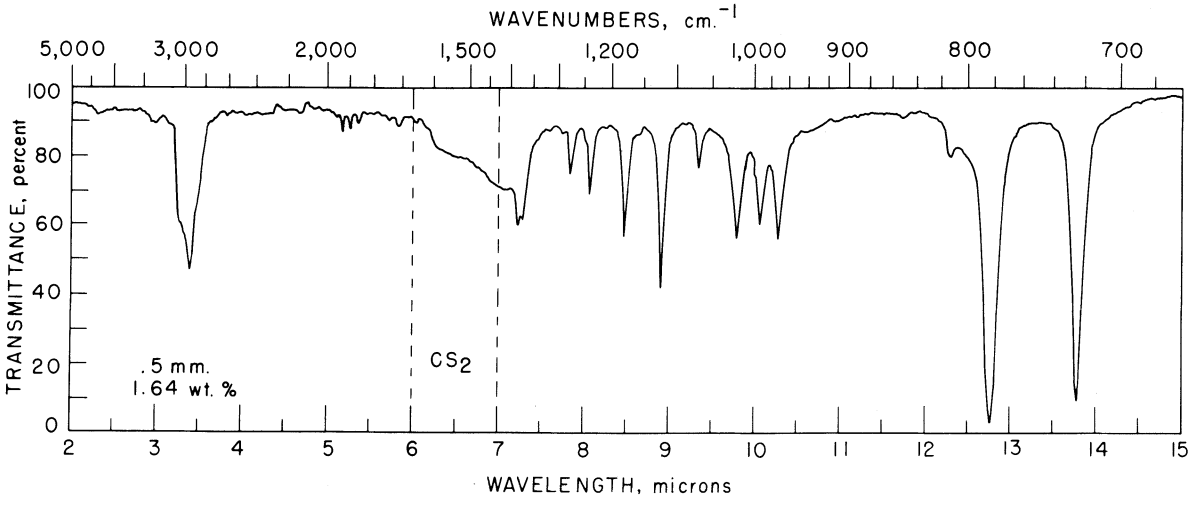


B.p. 161.16° (27)



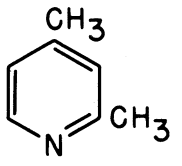
λ cyclohexane max, mμ	log ε
271.4	3.37
265.5	3.49
260.0	3.46

102

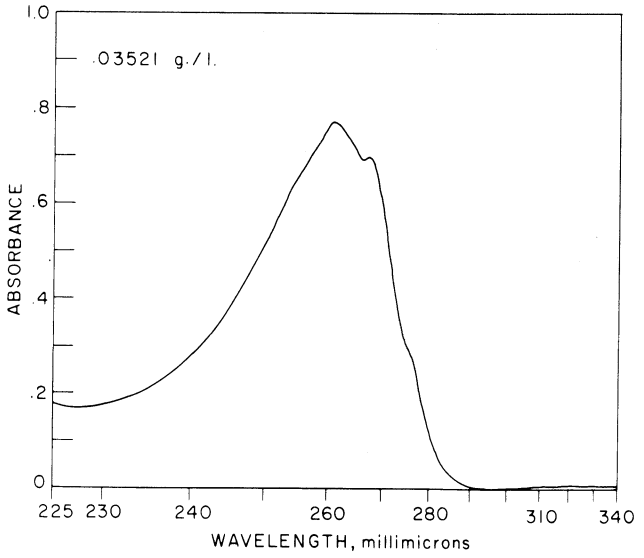


λ^{CS_2}: 13.78 (s), 12.76 (s), 12.30 (w), 11.75 (w), 10.98 (w), 10.28 (m), 10.07 (m), 9.80 (m), 9.35 (w), 8.91 (m), 8.47 (m), 8.07 (m), 7.84 (w), 7.74 (w), 7.62 (w), 7.30 (w), 7.22 (m).

2, 4 - DIMETHYLPYRIDINE

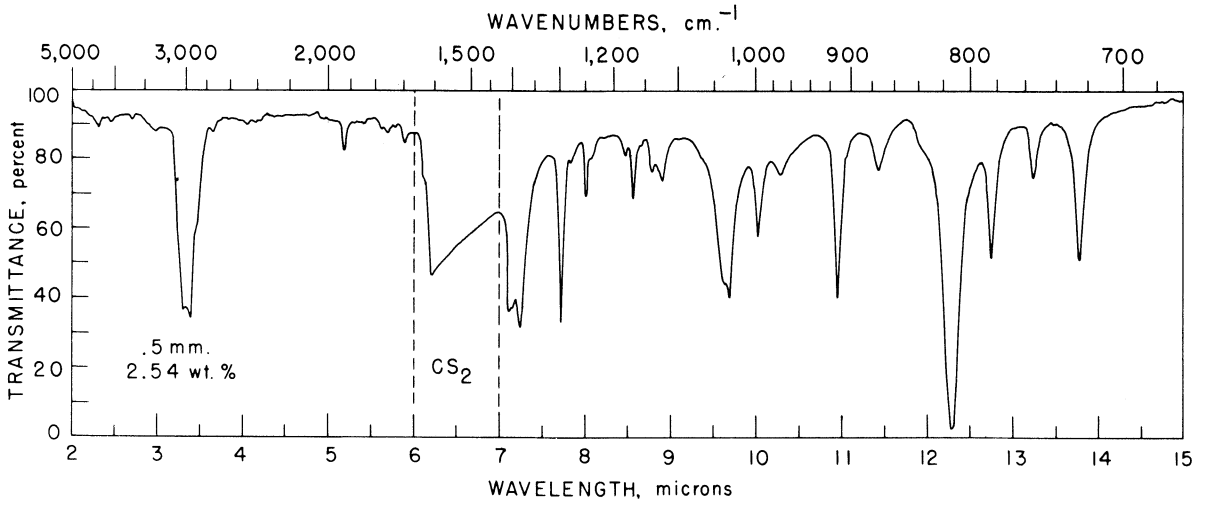


B.p. 158.40° (27)



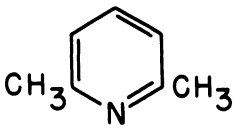
λ max, mμ (cyclohexane)	log ε
275.5	2.95
267.4	3.33
261.0	3.37
255.5	3.31

103

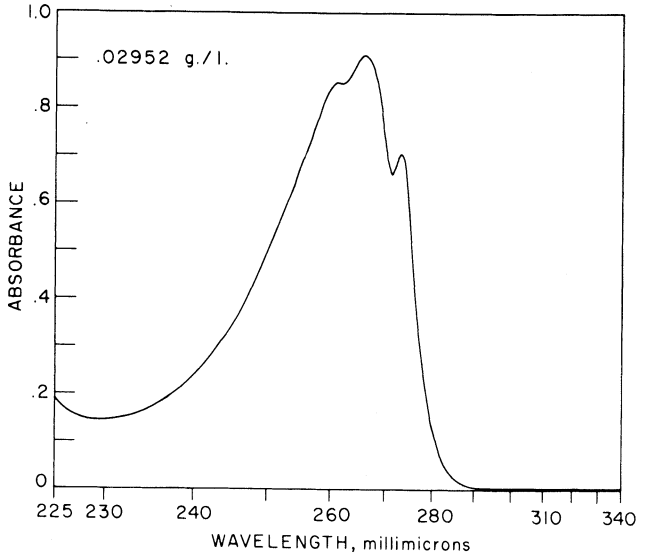


λ^{CS_2}: 13.79 (m), 13.25 (w), 12.75 (m), 12.30 (s), 11.95 (w), 11.43 (w), 10.96 (m), 10.30 (w), 10.02 (m), 9.69 (m), 9.64 (w), 9.35 (w), 8.90 (w), 8.79 (w), 8.57 (w), 8.48 (w), 8.08 (w), 8.02 (w), 7.84 (w), 7.73 (m), 7.25 (m), 7.16 (m).

2, 6 - DIMETHYLPYRIDINE

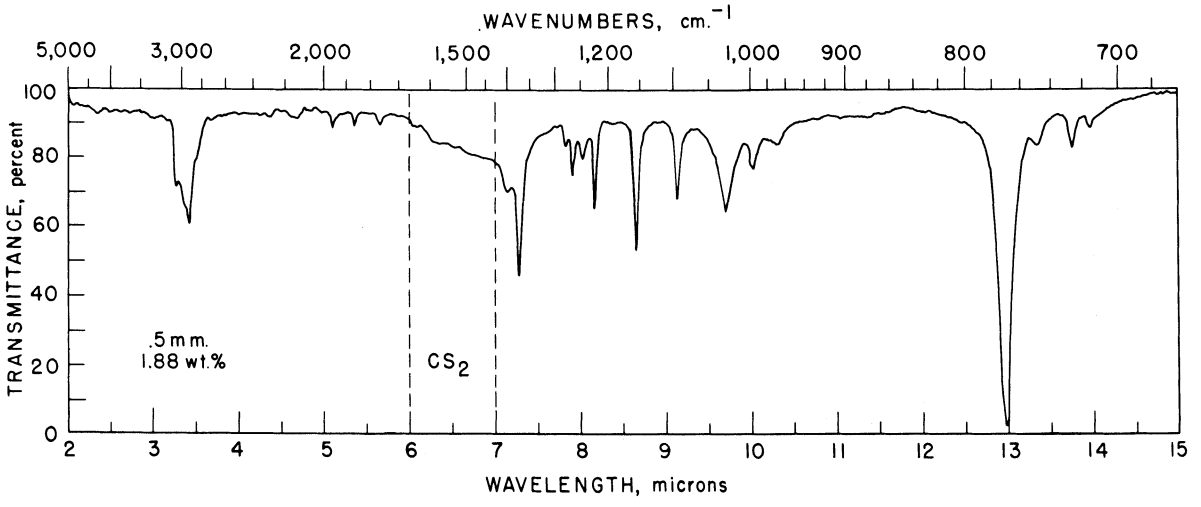


B.p. 144.05° (27)



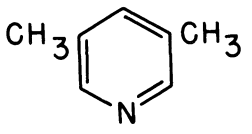
λ max, mμ (cyclohexane)	log ε
273.0	3.41
265.7	3.52
261.0	3.49

104

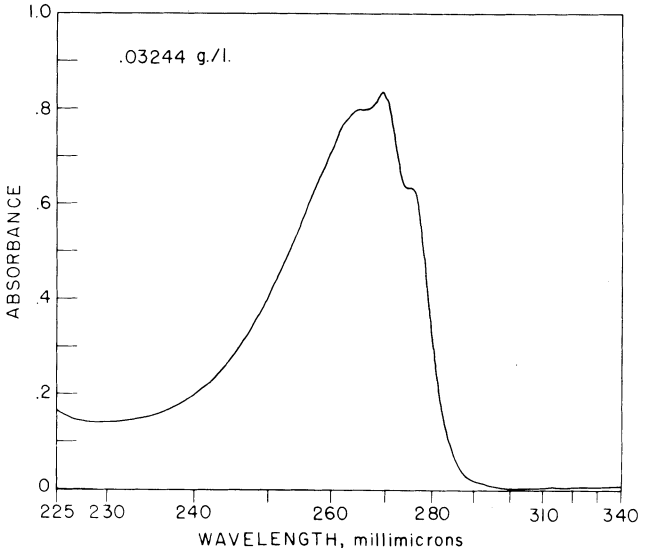


λ^{CS_2} : 13.98 (w), 13.76 (w), 13.35 (w), 12.98 (s), 10.32 (w), 10.03 (w), 9.72 (m), 9.14 (m), 8.66 (m), 8.17 (m), 8.04 (w), 7.92 (w), 7.84 (m), 7.28 (m), 7.14 (w).

3, 5 - DIMETHYLPYRIDINE

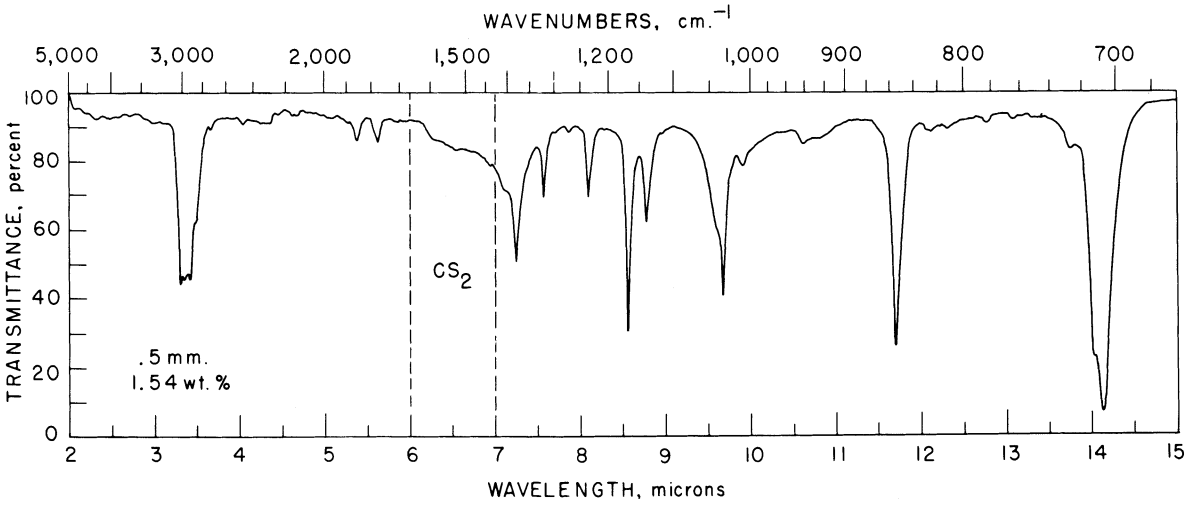


B.p. 171.91° (27)



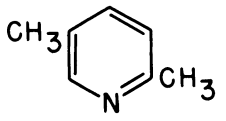
λ max, mμ (cyclohexane)	log ε
275.2	3.32
269.3	3.44
264.7	3.42

105

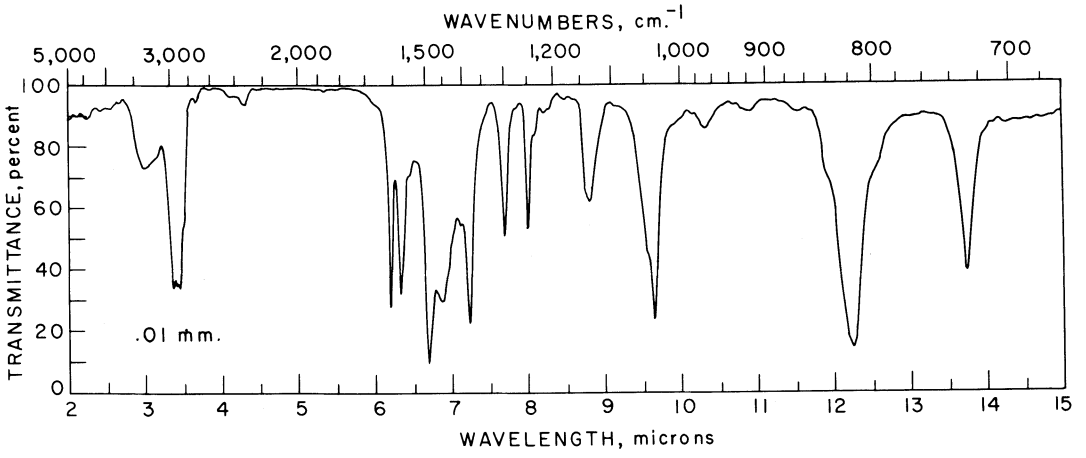


λ^{CS_2}: 14.13 (s), 14.03 (w), 13.76 (w), 11.70 (m), 10.62 (w), 9.92 (w), 9.67 (m), 9.60 (w), 8.78 (w), 8.57 (m), 8.10 (w), 7.87 (w), 7.57 (w), 7.25 (m), 7.07 (w).

2, 5 - DIMETHYLPYRIDINE



B.p. 157.01° (27)

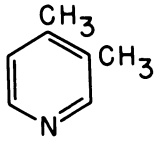


λ^{liquid} : 13.74 (m), 12.26 (s), 11.94 (w), 11.53 (w), 10.80 (w), 10.34 (w), 9.66 (s), 8.83 (m), 8.51 (w), 8.38 (w), 8.22 (w), 8.10 (w), 8.01 (m), 7.70 (m), 7.24 (s). (99)

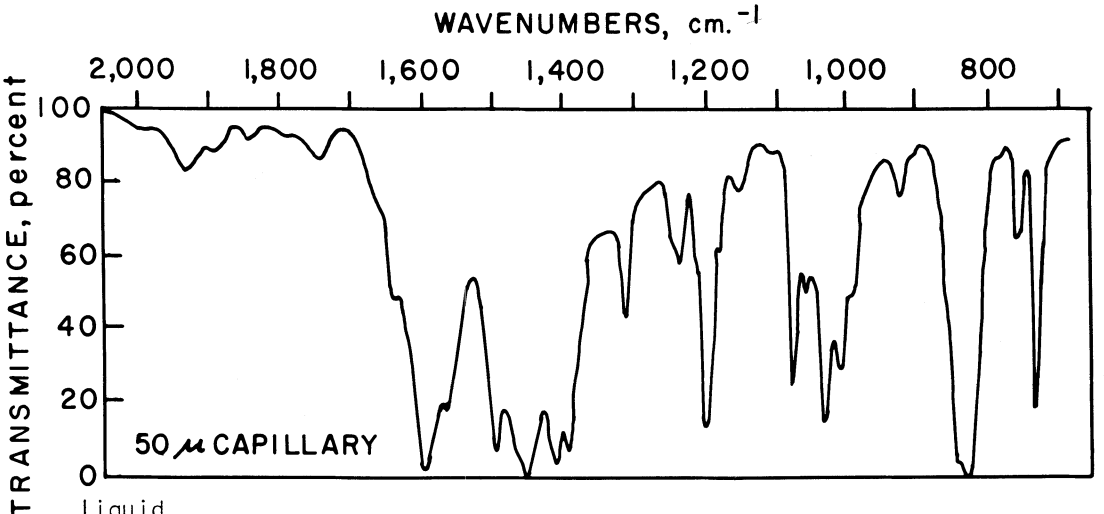
106

107

3, 4 - DIMETHYLPYRIDINE



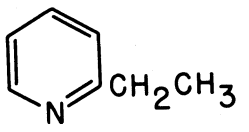
B.p. 179.13° (27)



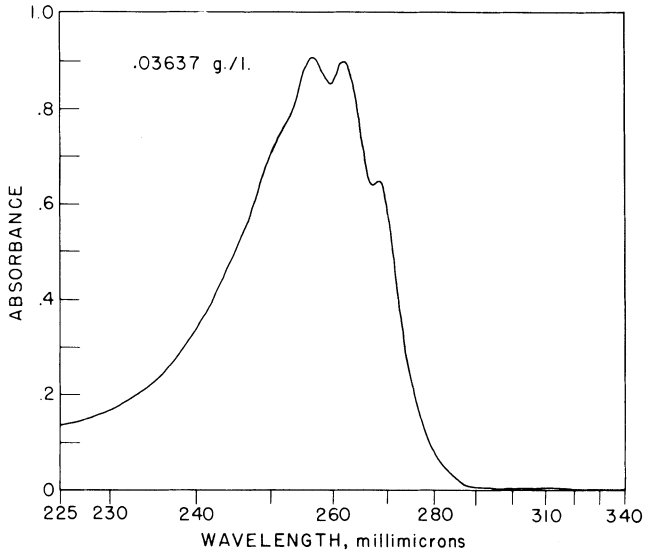
λ^{liquid} : 13.64 (s), 13.25 (m), 12.74 (w), 12.06 (s), 11.86 (s), 10.99 (w), 10.83 (w), 10.10 (w), 9.90 (m), 9.69 (s), 9.49 (w), 9.26 (s), 9.05 (w), 8.70 (w), 8.50 (w), 8.33 (s), 8.08 (m), 7.60 (m), 7.17 (s), 7.08 (s).1/

1/ Spectrum supplied by G. L. Cook, Laramie Petroleum Research Center, U. S. Bureau of Mines, Laramie, Wyo.

2-ETHYLPYRIDINE

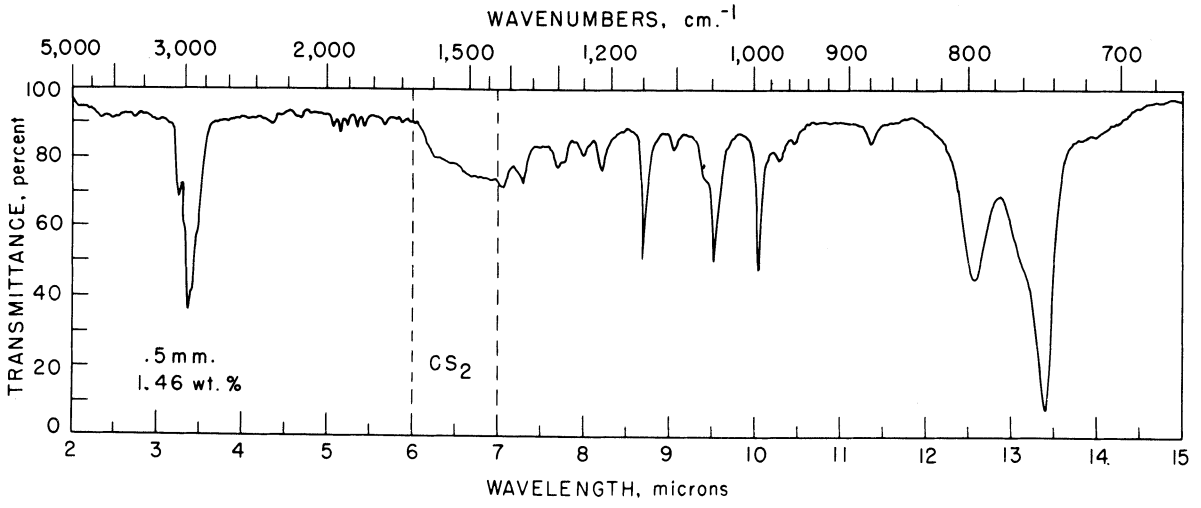


B.p. 148.6° (43)



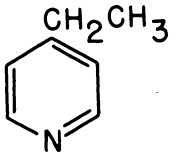
λ max, mμ (cyclohexane)	log ε
268.2	3.28
261.8	3.42
256.5	3.42
251.0	3.34

108

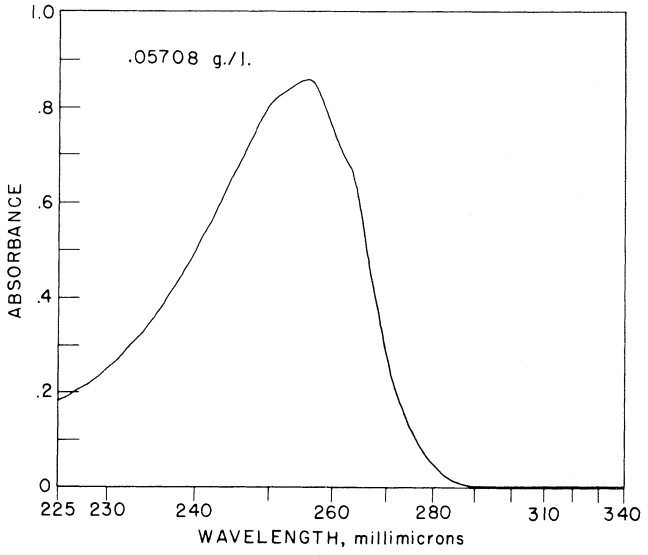


λ^{CS_2}: 13.41 (s), 12.57 (m), 11.37 (w), 10.47 (w), 10.30 (w), 10.05 (m), 9.54 (m), 9.47 (w), 9.05 (w), 8.72 (m), 8.22 (w), 8.00 (w), 7.77 (w), 7.70 (w), 7.29 (w), 7.05 (w).

4-ETHYLPYRIDINE

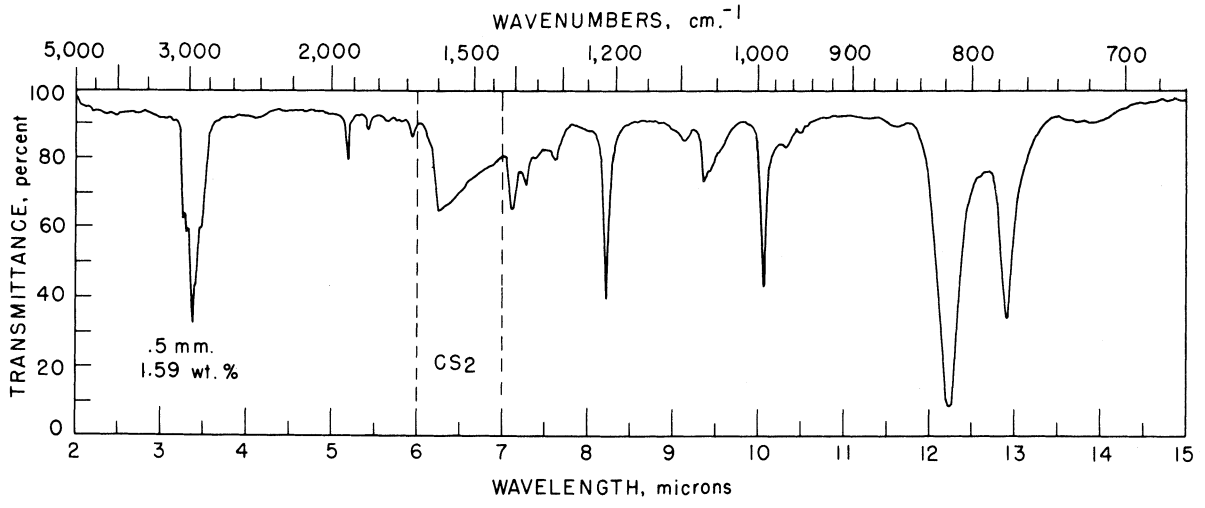


B.p. 169.6-170°/750 mm. (43)



λ max, mμ cyclohexane	log ε
262.8	3.10
255.7	3.21
251.2	3.19

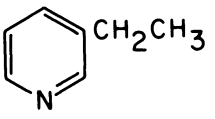
109



λ^{CS_2}: 12.90 (m), 12.22 (s), 10.50 (w), 10.32 (w), 10.05 (m), 9.42 (w), 9.36 (w), 9.14 (w), 8.22 (m), 7.60 (w), 7.39 (w), 7.27 (w), 7.10 (w).

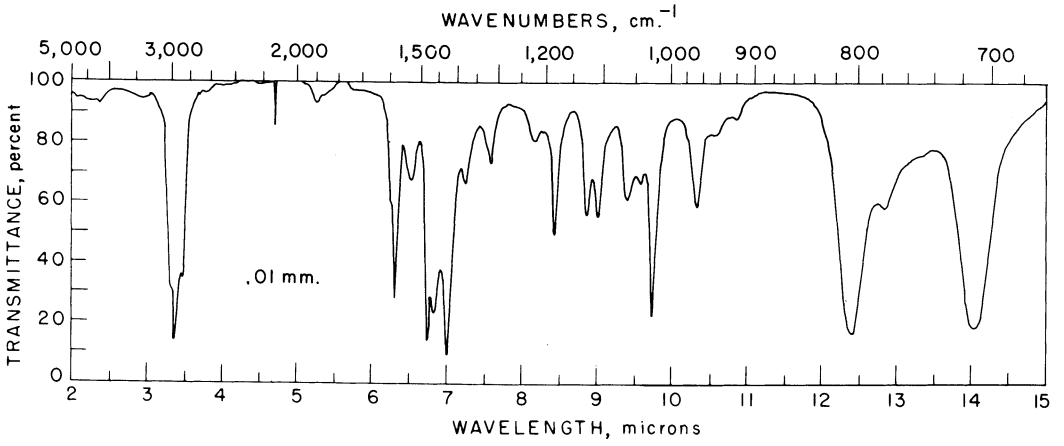
569705 O—61——11

3-ETHYLPYRIDINE



B.p. 162-165°/762 mm. (43)

$\lambda_{max,\ m\mu}^{10\%\ EtOH}$: 268 (3.25), 262 (3.36), 258 (3.37). (47)

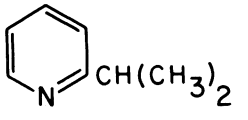


λ^{liquid}: 14.06 (s), 12.84 (w), 12.42 (s), 10.87 (w), 10.61 (w), 10.34 (m), 9.74 (m), 9.58 (w), 9.41 (m), 9.02 (m), 8.87 (m), 8.43 (m), 8.19 (w), 7.58 (w), 7.25 (w), 7.01 (s). (99)

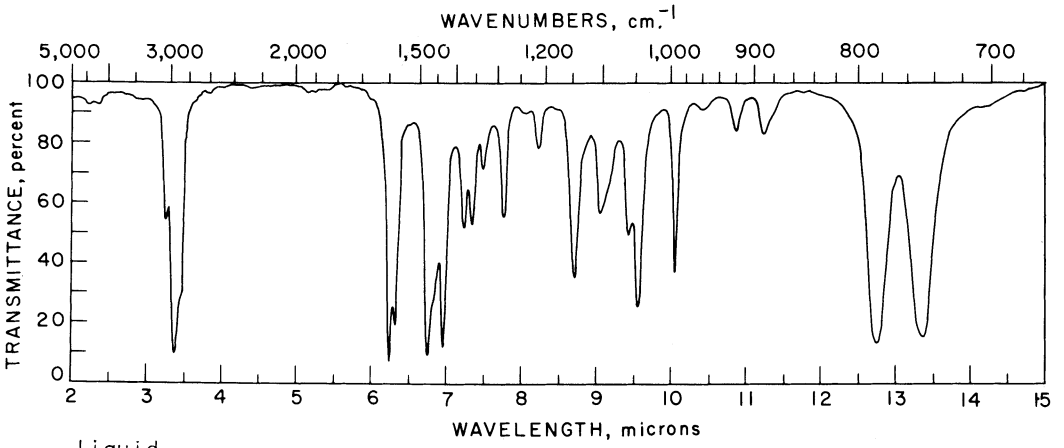
110

2-ISOPROPYLPYRIDINE

111

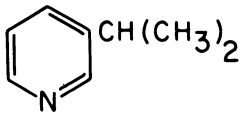


B.p. 158.9° (43)

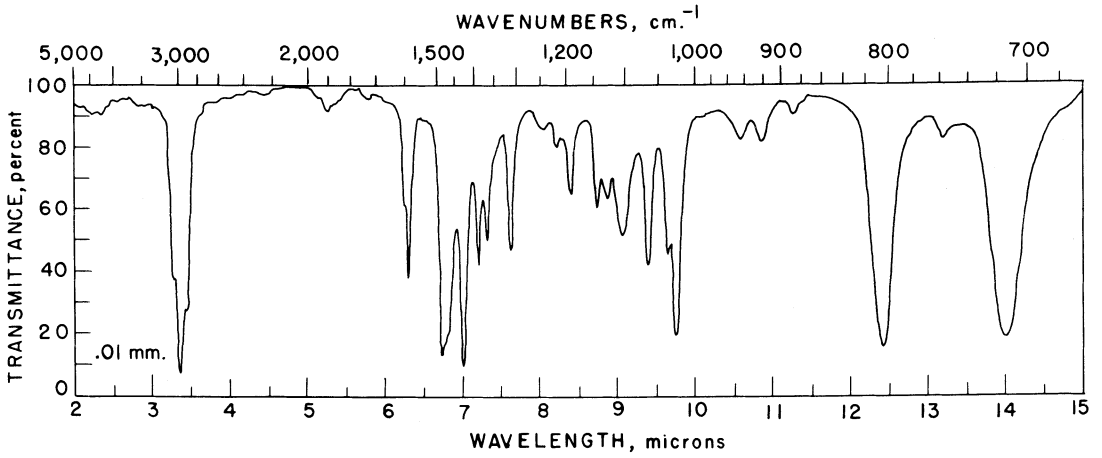


λ^{liquid}: 13.36 (s), 12.74 (s), 11.23 (w), 10.87 (w), 10.44 (w), 10.05 (m), 9.57 (m), 9.43 (w), 9.13 (w), 9.05 (m), 8.71 (m), 8.50 (w), 8.23 (w), 8.06 (w), 7.77 (m), 7.59 (w), 7.34 (m), 7.24 (m). (99)

3-ISOPROPYLPYRIDINE



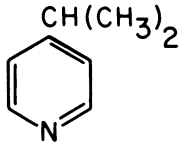
B.p. 177-178° (43)



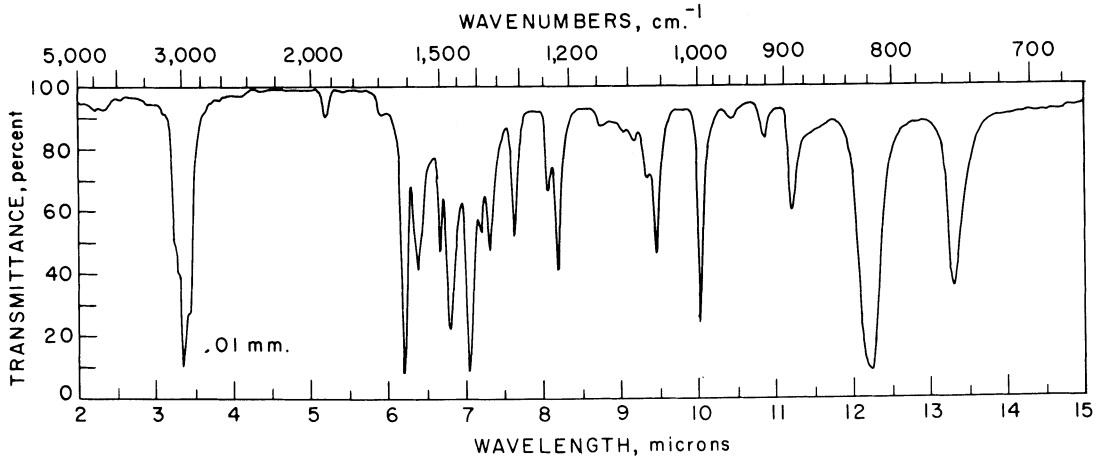
λ^{liquid}: 14.00 (s), 13.20 (w), 12.42 (s), 11.27 (w), 10.85 (w), 10.58 (w), 9.76 (s), 9.65 (w), 9.40 (m), 9.07 (m), 8.87 (m), 8.74 (m), 8.41 (m), 8.22 (w), 8.04 (w), 7.62 (m), 7.32 (m), 7.21 (m), 7.01 (s). (99)

112

4-ISOPROPYLPYRIDINE 113

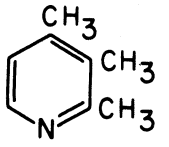


B.p. 173° (43)

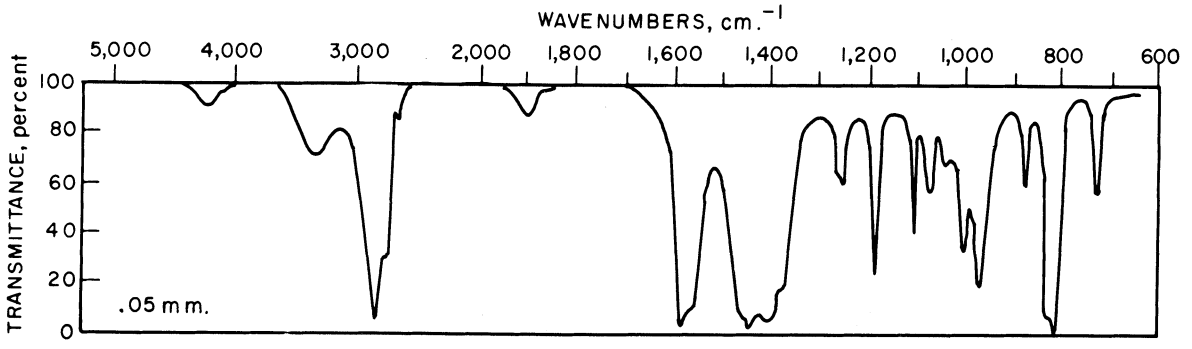


λ^{liquid}: 13.30 (s), 12.24 (s), 11.21 (m), 10.86 (w), 10.43 (w), 10.03 (m), 9.47 (m), 9.34 (w), 9.16 (w), 9.03 (w), 8.74 (w), 8.19 (m), 8.06 (w), 7.62 (m), 7.30 (m), 7.19 (w), 7.05 (s). (99)

2, 3, 4 - TRIMETHYLPYRIDINE



B.p. 192-193° (43)

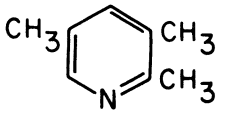


λ^{liquid}: 13.66 (m), 12.27 (s), 12.05 (s), 11.39 (m), 10.31 (s), 9.95 (m), 9.62 (w), 9.35 (m), 9.05 (m), 8.43 (s), 7.97 (m), 7.89 (w), 7.27 (w), 7.17 (s). (83)

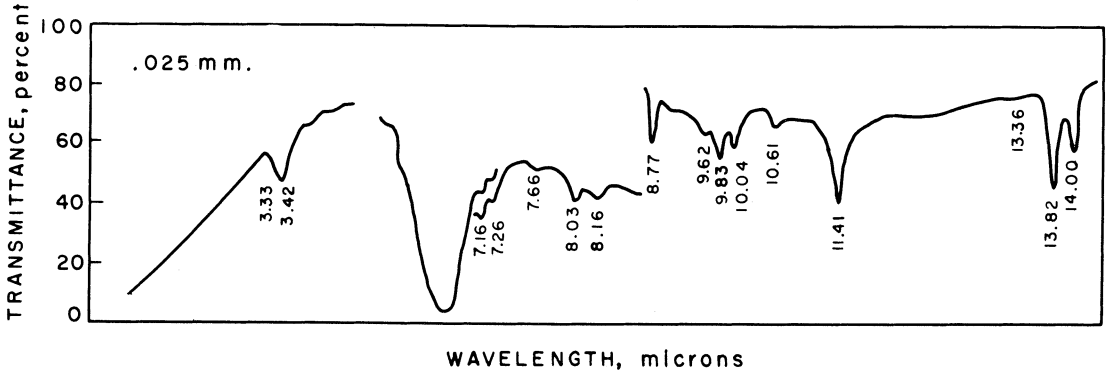
114

2, 3, 5 - TRIMETHYLPYRIDINE

115



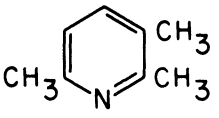
B.p. 182-183°/739 mm. (43)



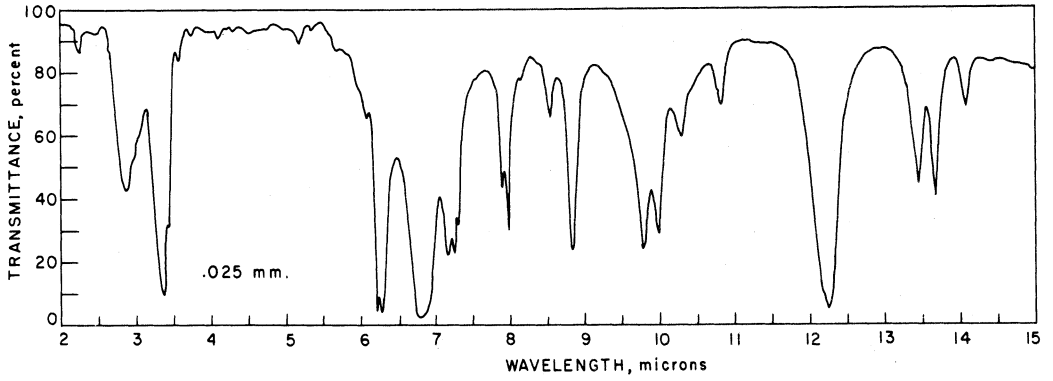
λ^{liquid}: 14.00 (m), 13.82 (s), 11.41 (s), 10.61 (w), 10.04 (w), 9.83 (m), 9.62 (w), 8.77 (m), 8.16 (w), 8.03 (w), 7.66 (w), 7.26 (w), 7.16 (w).[1/]

1/ Spectrum supplied by G. L. Cook, Laramie Petroleum Research Center, U. S. Bureau of Mines, Laramie, Wyo.

2, 3, 6 - TRIMETHYLPYRIDINE



B.p. 176-178°/759 mm. (43)

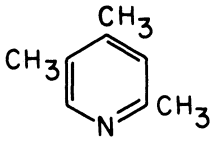


116

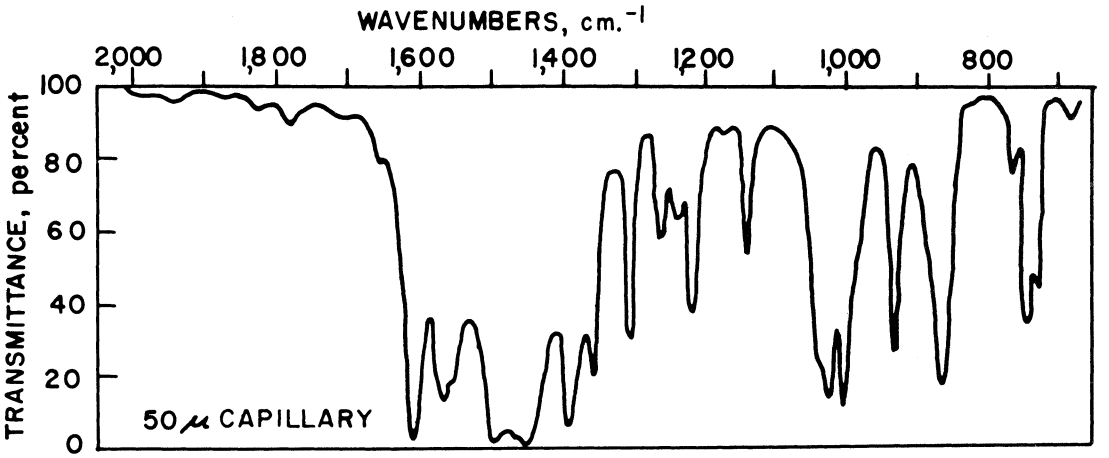
λ^{liquid}: 14.08 (m), 13.66 (s), 13.45 (s), 12.24 (s), 10.82 (w-m), 10.28 (w), 9.98 (s), 9.78 (s), 8.84 (s), 8.54 (w-m), 8.16 (sh), 7.98 (s), 7.89 (m), 7.30 (sh), 7.26 (m), 7.16 (m).[1/]

2, 4, 5 - TRIMETHYLPYRIDINE

117



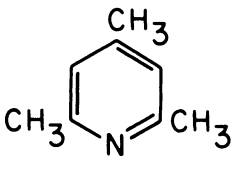
B.p. 165-168° (43)



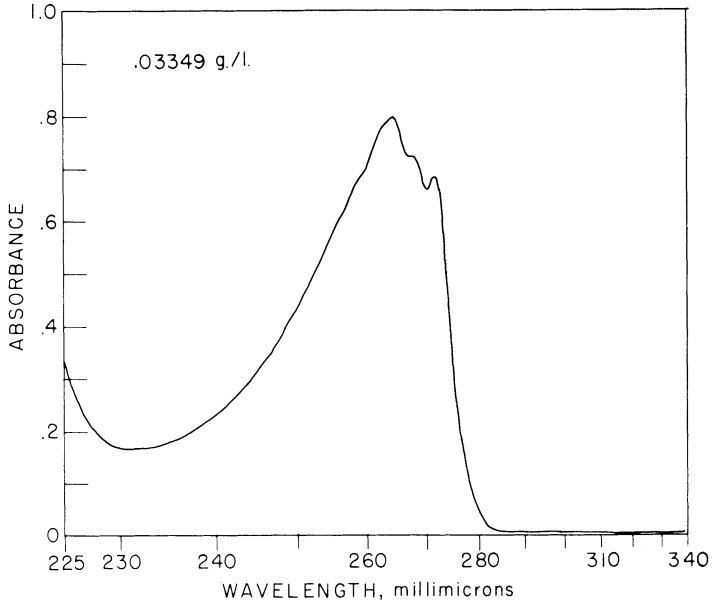
λ^{liquid}: 14.71 (w), 13.69 (m), 13.51 (m), 13.15 (w), 11.61 (s), 10.80 (s), 10.20 (w), 9.96 (s), 9.78 (s), 9.63 (m), 8.79 (m), 8.54 (w), 8.24 (m), 8.13 (w), 8.08 (w), 7.94 (m), 7.68 (m), 7.38 (m), 7.19 (s).[1/]

1/ Spectrum supplied by G. L. Cook, Laramie Petroleum Research Center, U. S. Bureau of Mines, Laramie, Wyo.

2, 4, 6 - TRIMETHYLPYRIDINE

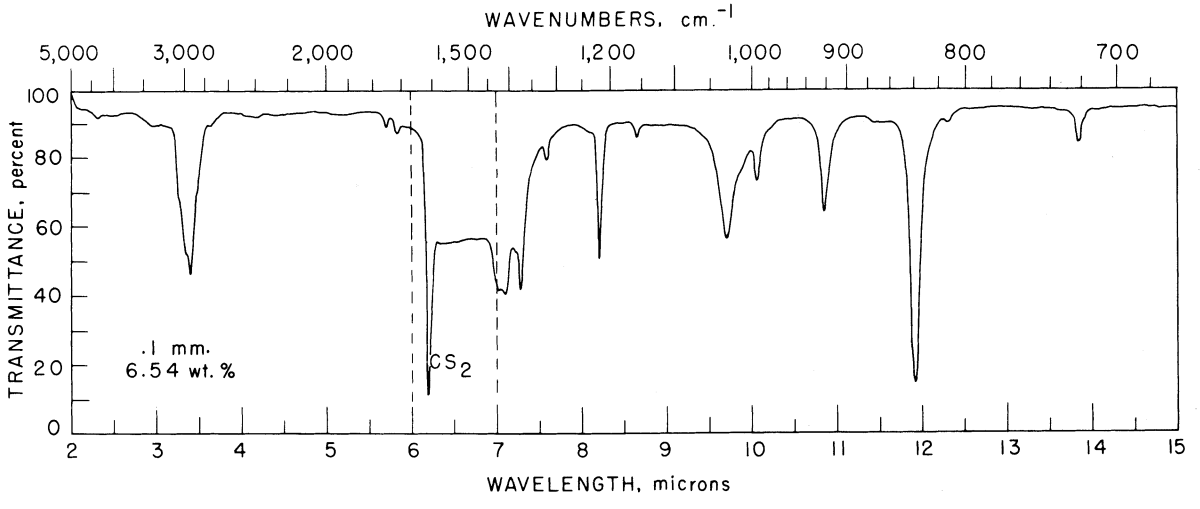


B.p. 171-172° (43)



λ max, mμ (cyclohexane)	log ε
271.5	3.39
267.7	3.42
264.4	3.46
262.3	3.45
259.3	3.40
256.0	3.34

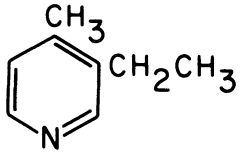
118



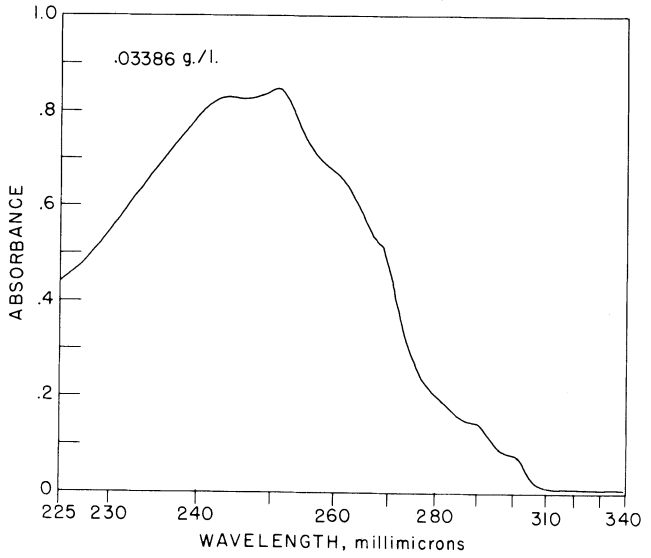
CS_2

λ : 13.85 (w), 12.30 (w), 11.91 (s), 10.84 (m), 10.05 (w), 9.70 (m), 8.64 (w), 8.20 (m), 7.57 (w), 7.26 (m), 7.08 (m), 7.00 (w).

3-ETHYL-4-METHYLPYRIDINE

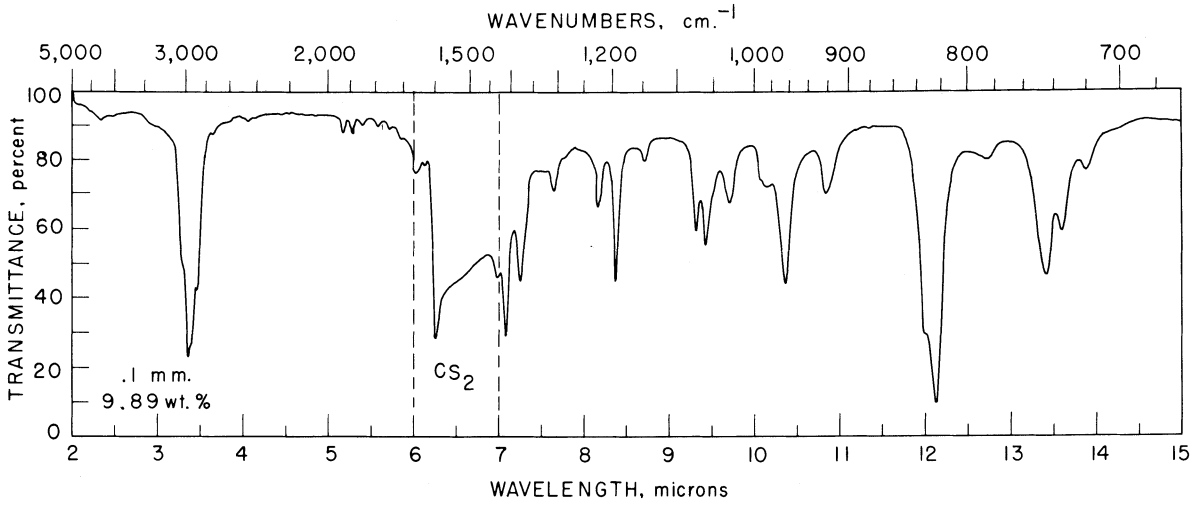


B.p. 195-196°/753 mm. (43)



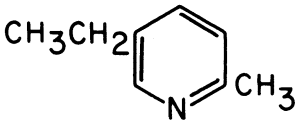
λ max, mμ (cyclohexane)	log ε
300.0	2.45
289.4	2.72
281.0	2.84
268.0	3.27
260.0	3.38
250.7	3.48
243.5	3.47

119

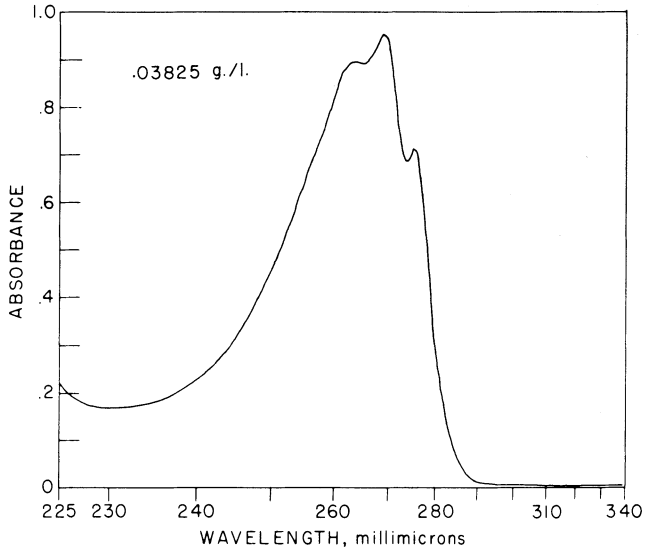


λ^{CS_2}: 13.90 (w), 13.60 (w), 13.43 (m), 12.74 (w), 12.12 (s), 12.00 (w), 10.84 (w), 10.36 (m), 10.15 (w), 10.07 (w), 9.71 (w), 9.43 (m), 9.32 (m), 8.72 (w), 8.38 (m), 8.17 (w), 7.64 (w), 7.25 (m), 7.08 (m), 7.00 (w).

5-ETHYL-2-METHYLPYRIDINE

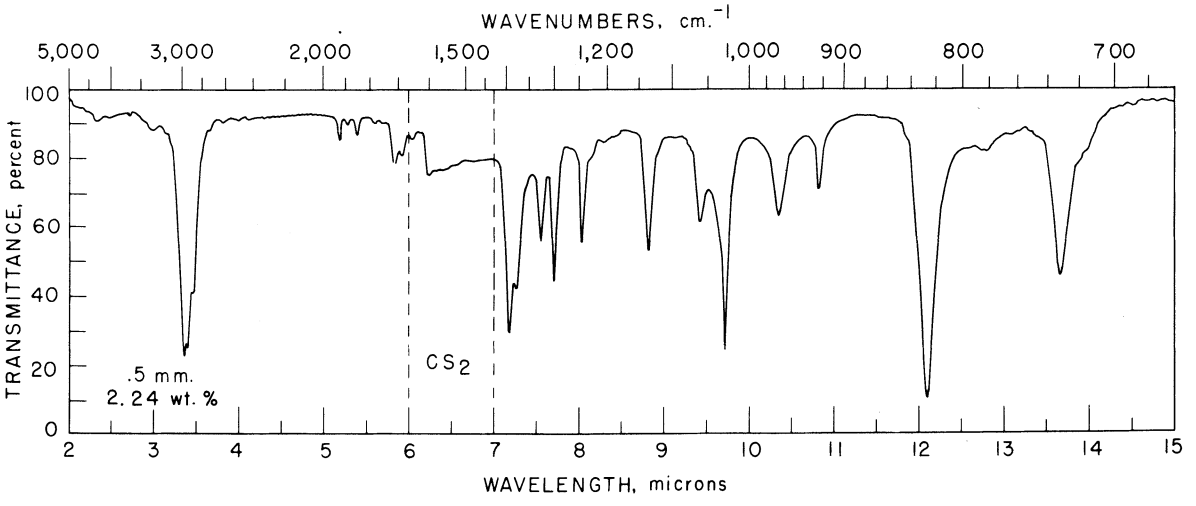


B.p. 174-176° (43)



λ max, mμ (cyclohexane)	log ε
275.2	3.35
268.8	3.47
263.0	3.45
256.0	3.33

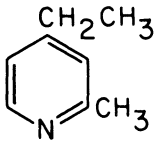
120



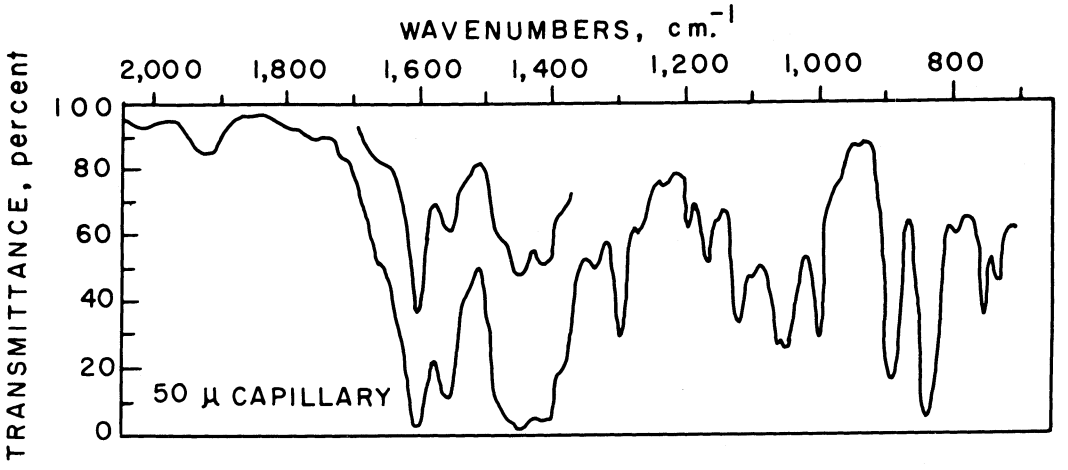
CS_2

λ : 13.95 (w), 13.65 (m), 12.78 (w), 12.10 (s), 10.82 (w), 10.35 (m), 9.72 (m), 9.42 (w), 8.82 (m), 8.28 (w), 8.04 (m), 7.71 (m), 7.61 (w), 7.27 (w), 7.18 (m).

4-ETHYL-2-METHYLPYRIDINE



B.p. 179-180° (43)



λ^{liquid} : 13.73 (m), 13.33 (m), 12.61 (w), 11.96 (s), 11.20 (s), 10.66 (w), 10.29 (w), 9.99 (m), 9.53 (m), 9.41 (m), 9.08 (w), 8.91 (m), 8.55 (w), 8.35 (w), 8.15 (w),1/ 7.87 (w), 7.69 (m), 7.52 (w), 7.23 (m), 7.06 (s).

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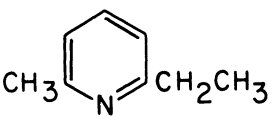
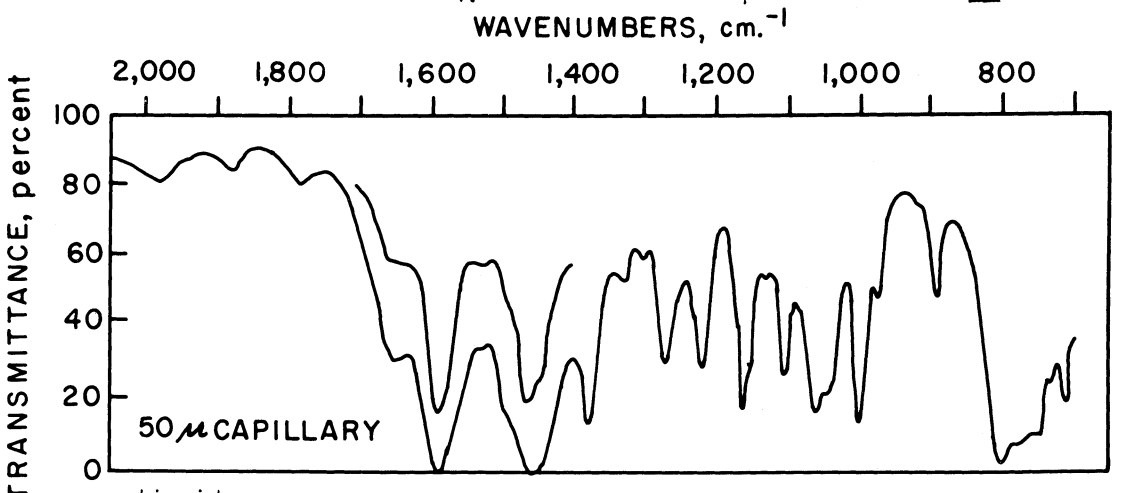
2-ETHYL-6-METHYLPYRIDINE



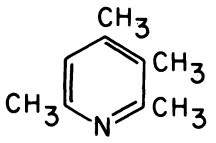
B.p. 160-161.5° (43)



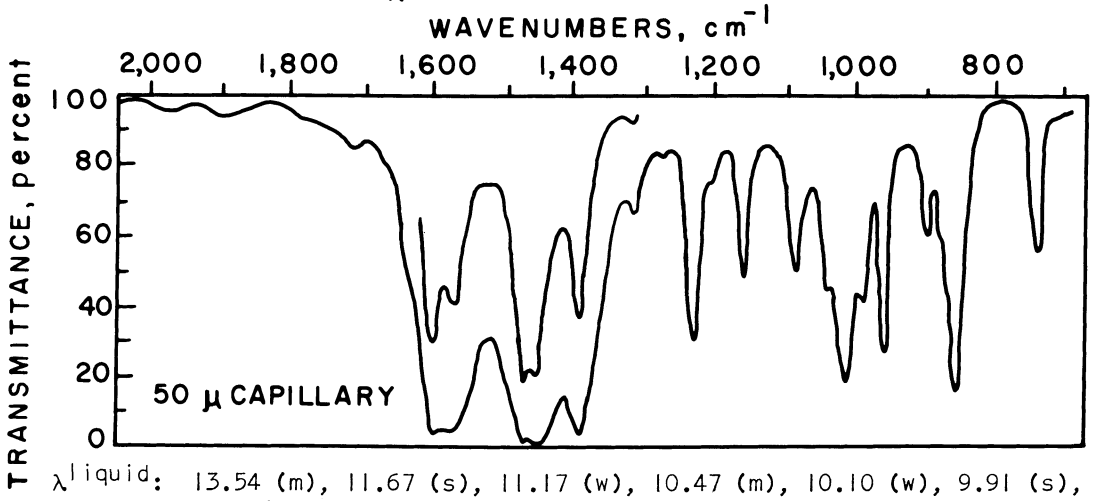
λ^{liquid} : 14.03 (m), 13.69 (w), 13.36 (s), 12.50 (s), 11.17 (m), 10.87 (w), 10.22 (w), 10.03 (m), 9.57 (m), 9.50 (m), 9.04 (m), 8.85 (w), 8.62 (m), 8.20 (m), 8.00 (w), 7.84 (m), 7.68 (w), 7.53 (w), 7.25 (m).1/

1/ Spectrum supplied by G. L. Cook, Laramie Petroleum Research Center, U. S. Bureau of Mines, Laramie, Wyo.

2, 3, 4, 6 - TETRAMETHYLPYRIDINE

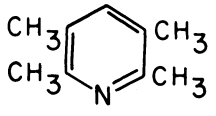


B.p. 203°/750 mm. (43)

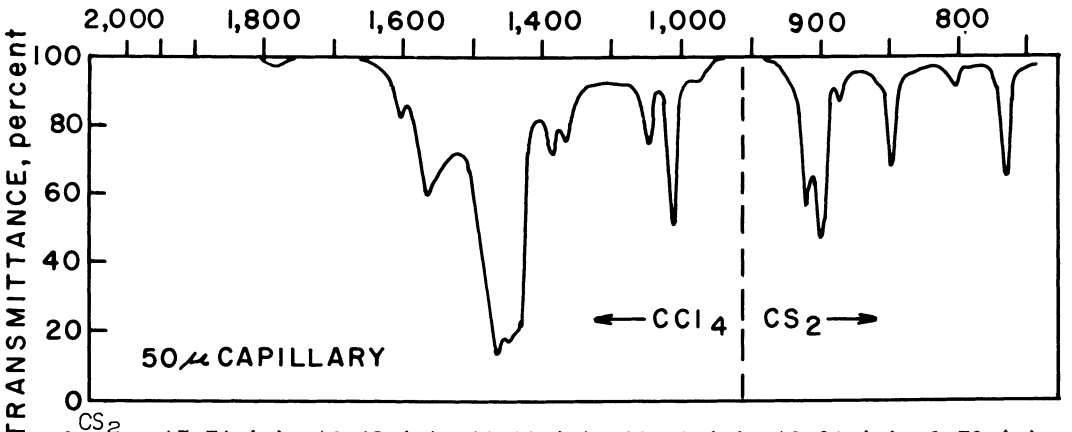


λ^{liquid}: 13.54 (m), 11.67 (s), 11.17 (w), 10.47 (m), 10.10 (w), 9.91 (s), 9.67 (w), 9.21 (m), 8.67 (w), 8.31 (m), 8.13 (m), 7.87 (w), 7.60 (w), 7.17 (s).[1/] 123

2, 3, 5, 6 - TETRAMETHYLPYRIDINE 124

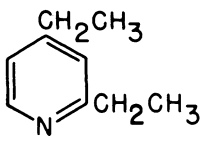


B.p. 197-198° (24)



λ^{CS_2}: 13.74 (m), 12.48 (w), 11.11 (m), 10.29 (w), 10.02 (m), 9.79 (m).
λ^{CCl_4}: 8.47 (w), 8.25 (m), 8.03 (m), 7.55 (w), 7.34 (m), 7.22 (m).[1/]

2, 4 - DIETHYLPYRIDINE 125

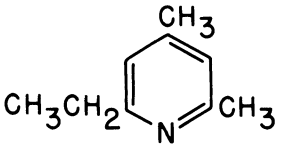


B.p. 187-188° (43)

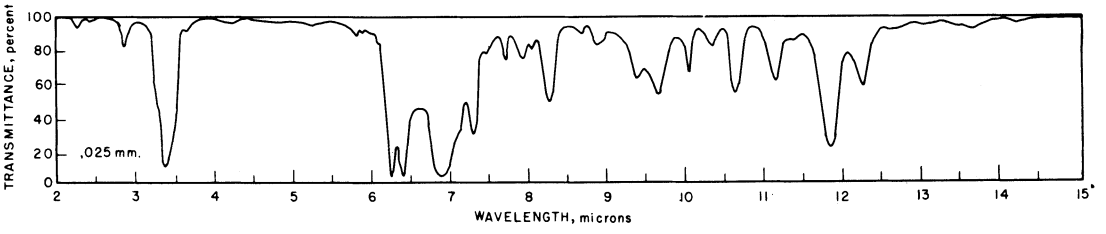
$\lambda_{max}^{cyclohexane}$, mμ : 260 (3.31). (47)

1/ Spectrum supplied by G. L. Cook, Laramie Petroleum Research Center, U. S. Bureau of Mines, Laramie, Wyo.

2, 4 - D I M E T H Y L - 6 - E T H Y L P Y R I D I N E



B.p. 181-182° (26)



λ^{liquid}: 12.25 (s), 11.82 (s), 11.13 (s), 10.62 (s), 10.32 (m), 10.04 (s), 9.64 (s), 9.39 (s), 8.84 (m), 8.24 (s), 8.01 (w), 7.89 (m), 7.68 (m), 7.45 (w), 7.28 (s), 7.07 (sh).1/

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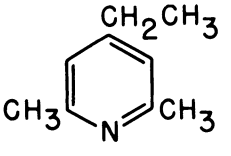
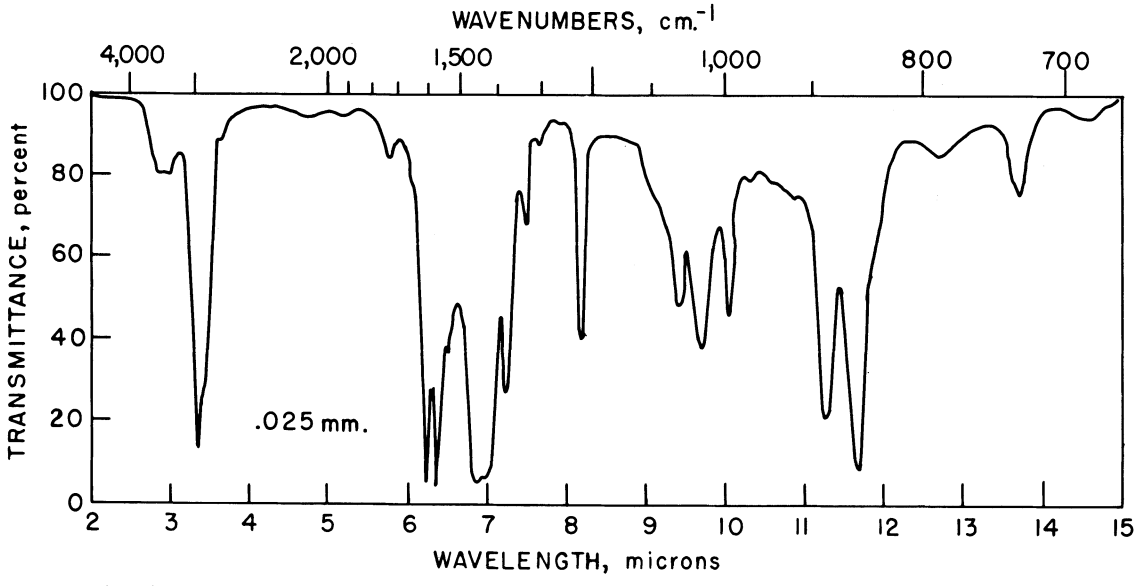
2, 6 - D I M E T H Y L - 4 - E T H Y L P Y R I D I N E

127



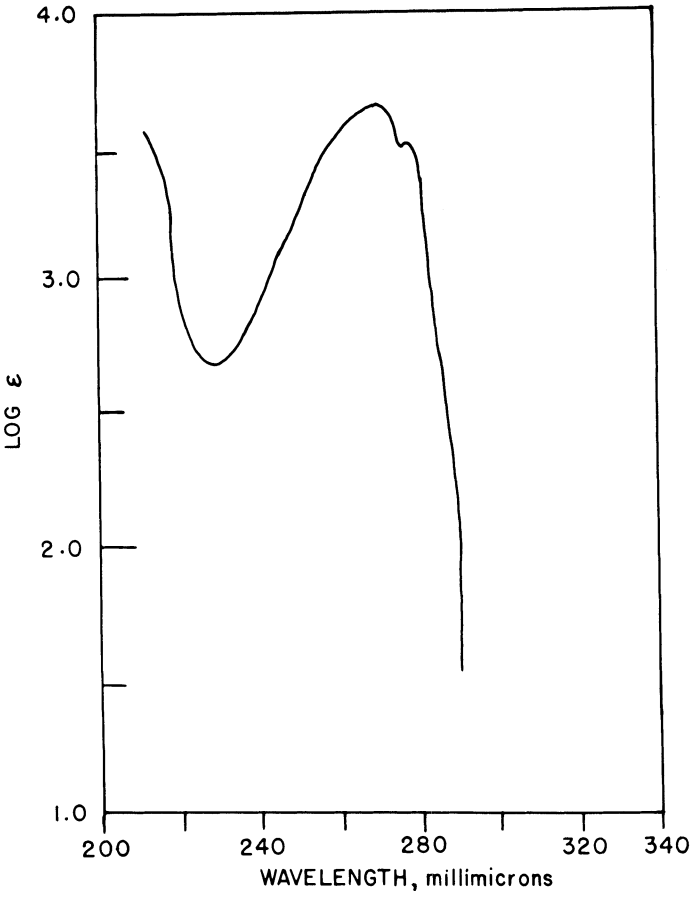
B.p. 186° (43)

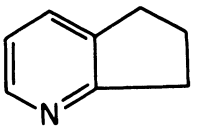


λ^{liquid}: 14.60 (w), 13.67 (m), 12.67 (w), 11.90 (w), 11.67 (s), 11.24 (s), 10.85 (w), 10.60 (w), 10.30 (w), 10.03 (m), 9.69 (m), 9.39 (m), 9.00 (w), 8.17 (m), 7.90 (w), 7.64 (w), 7.47 (w), 7.22 (m), 6.99 (s). (113)

1/ Spectrum supplied by G. L. Cook, Laramie Petroleum Research Center, U. S. Bureau of Mines, Laramie, Wyo.

2, 3 - CYCLOPENTENOPYRIDINE



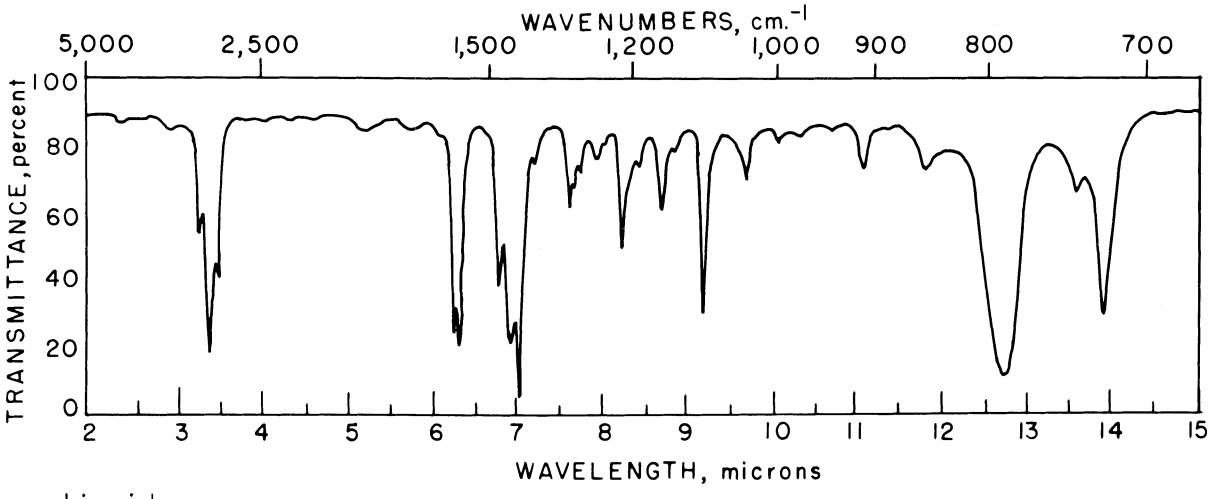


B.p. 199.5° (40)

λ max, mμ (cyclohexane)	log ε
277	3.20
272	3.63

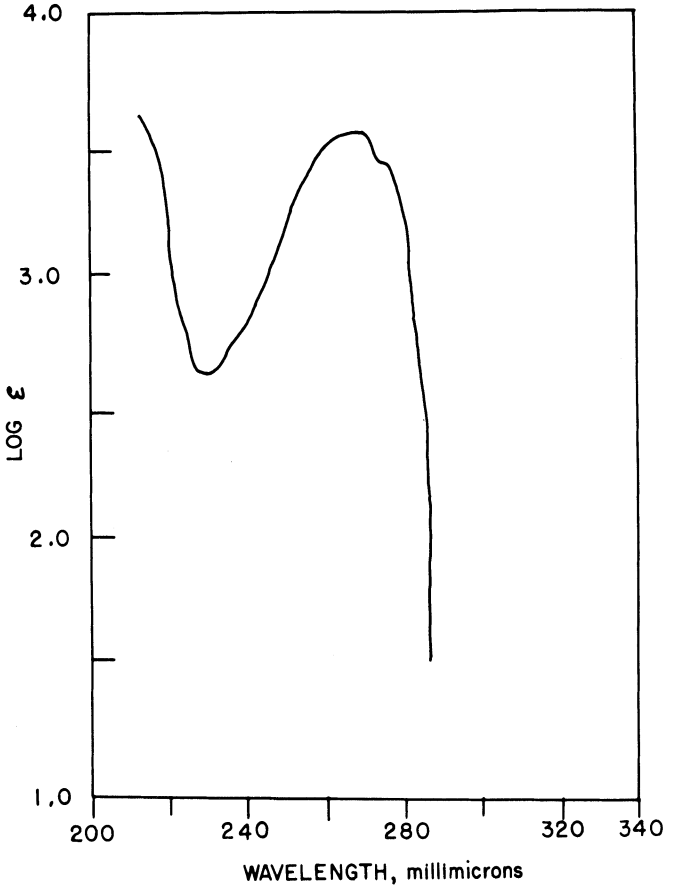
(40)

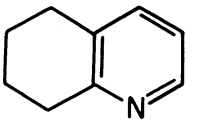
128



λ^{liquid}: 13.9 (m), 13.6 (w), 12.7 (s), 11.8 (w), 11.3 (w), 11.2 (w), 10.7 (w), 10.3 (w), 10.1 (w), 9.6 (w), 9.3 (m), 8.9 (w), 8.7 (w), 8.5 (m), 8.3 (w), 8.0 (w), 7.8 (w), 7.6 (w), 7.4 (w), 7.1 (s), 7.0 (w). (40)

5, 6, 7, 8 - TETRAHYDROQUINOLINE



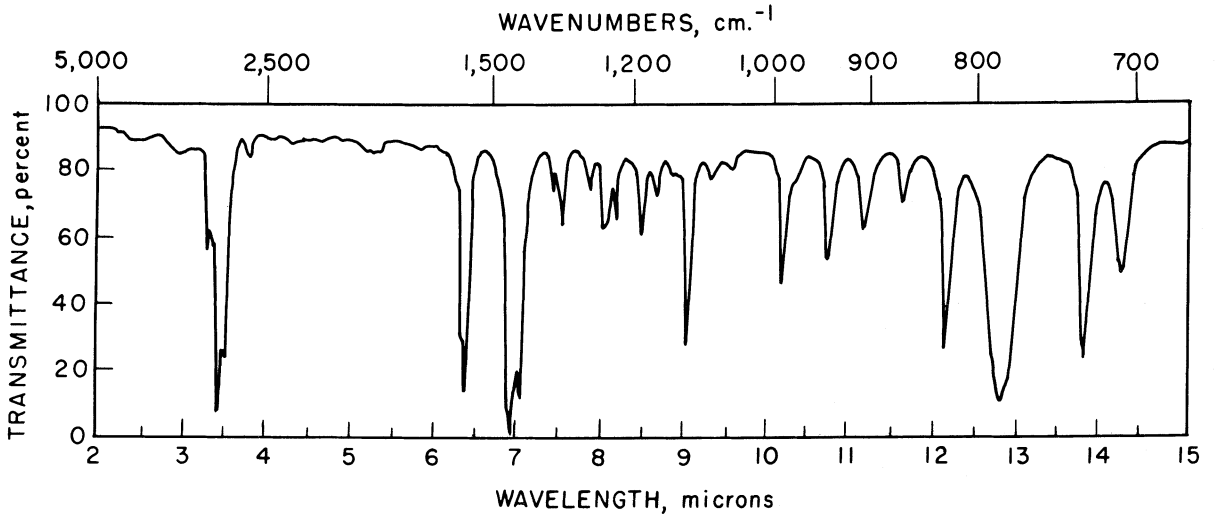


B.p. 222.2° (40)

λ max, mμ (cyclohexane)	log ε
275	2.60
268	3.54

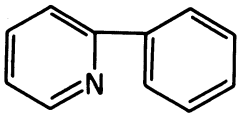
(40)

129

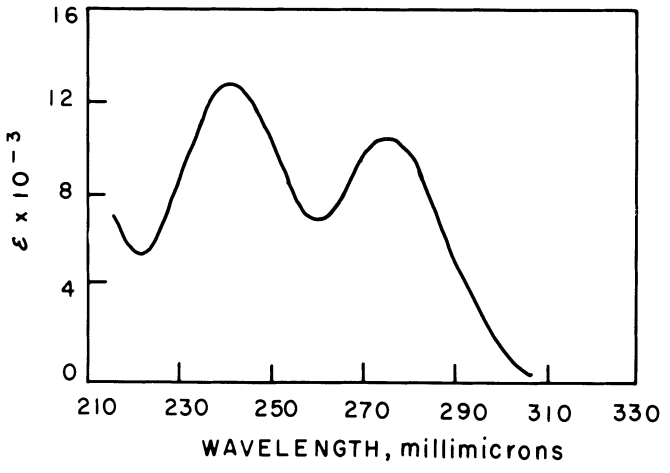


λ liquid : 14.3 (m), 13.8 (s), 12.8 (s), 12.2 (s), 11.6 (w), 11.2 (m), 10.7 (m), 10.3 (w), 10.2 (m), 9.5 (w), 9.3 (w), 9.0 (s), 8.8 (w), 8.7 (w), 8.5 (m), 8.1 (w), 8.0 (m), 7.8 (w), 7.5 (m), 7.4 (w), 7.1 (s). (40)

2-PHENYLPYRIDINE



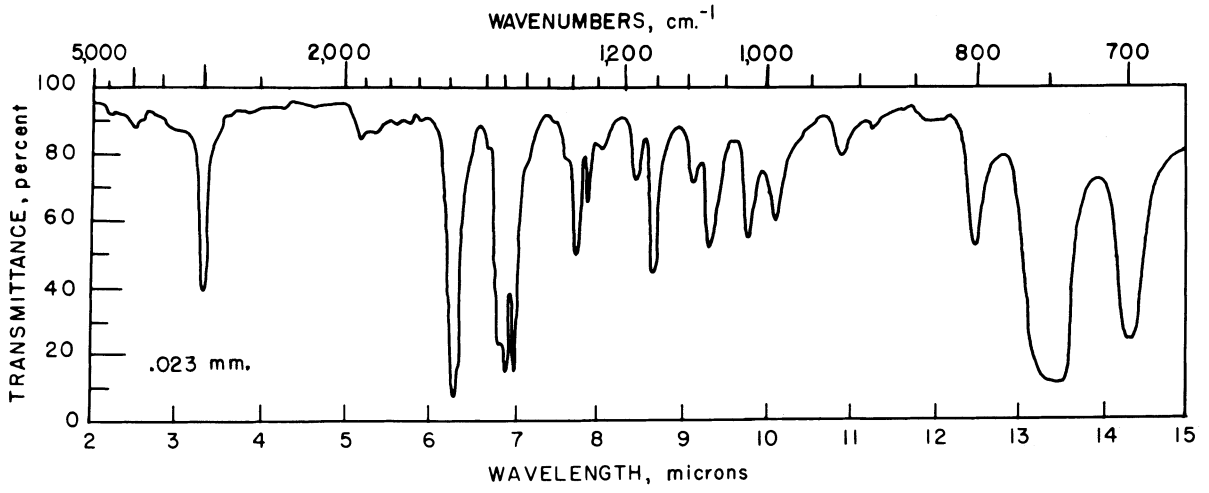
B.p. 268-269° (43)



λ max, mμ (H_2O (1% EtOH))	log ε
276	4.01
241	4.11

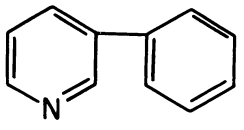
(67)

130

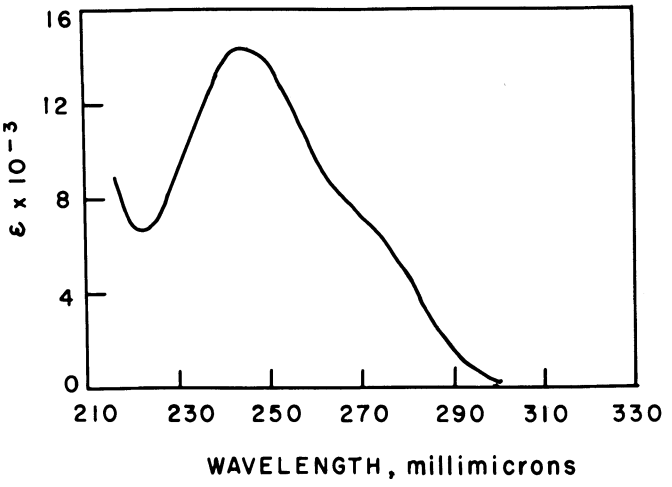


λ^{melt}: 14.30 (s), 13.35 (s), 12.50 (m), 12.10 (w), 11.90 (w), 11.25 (w), 10.90 (w), 10.13 (m), 9.80 (m), 9.35 (m), 9.15 (w), 8.65 (m), 8.45 (w), 8.10 (w), 7.88 (w), 7.75 (m), 7.65 (w). (31)

3-PHENYLPYRIDINE



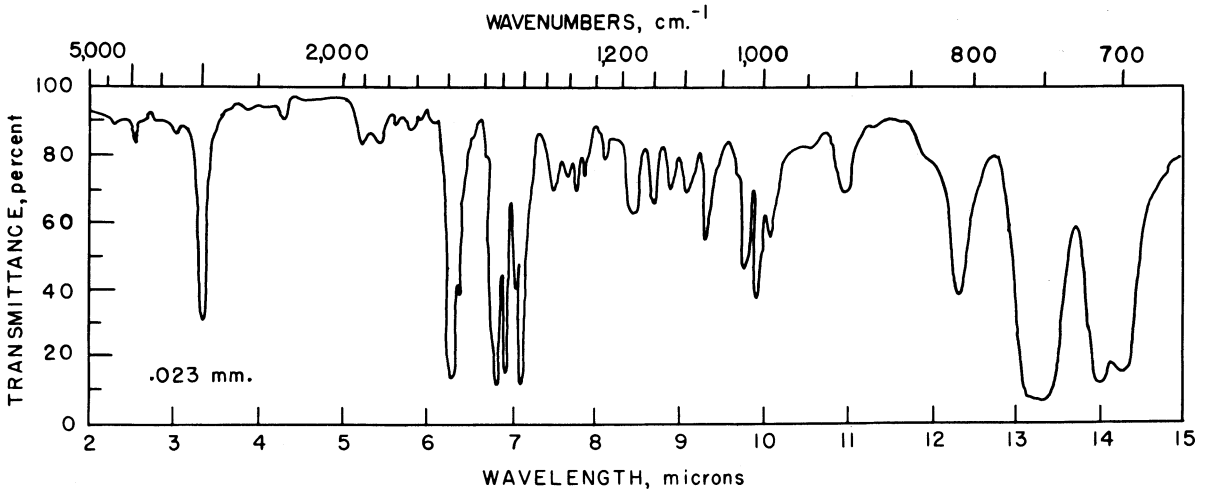
B.p. 269-270°/749 mm. (43)



λ_{max}, mμ (H_2O (1% EtOH))	log ε
270	3.87
246	4.16

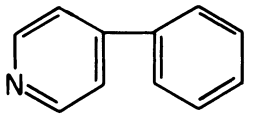
(67)

131

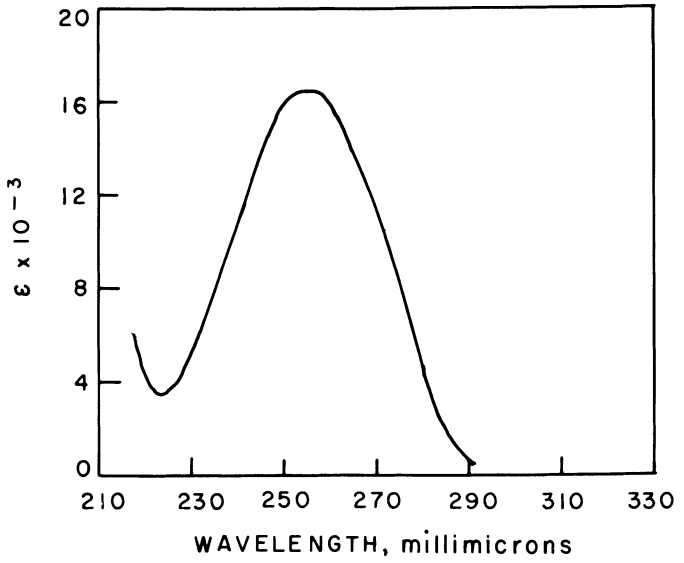


λ_{max}^{melt} : 14.25 (s), 14.00 (s), 13.25 (s), 12.30 (m), 11.90 (w), 10.98 (w), 10.55 (w), 10.08 (w), 9.92 (w), 9.78 (w), 9.35 (m), 9.12 (w), 8.92 (w), 8.70 (w), 8.46 (w), 8.13 (w), 7.88 (w), 7.80 (w), 7.67 (w), 7.50 (w), 7.15 (m), 7.05 (w). (31)

4-PHENYLPYRIDINE

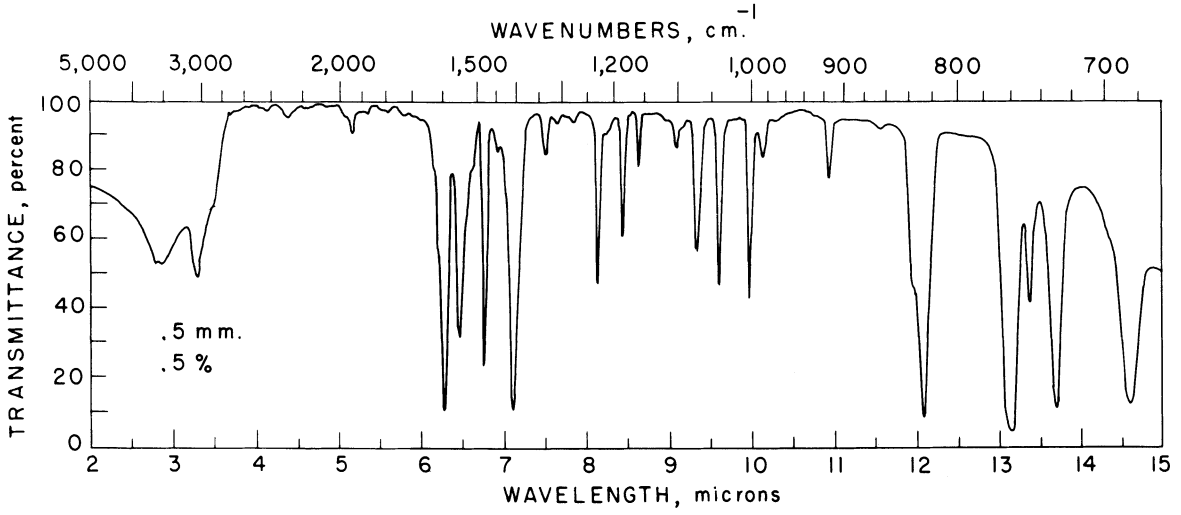


B.p. 274-275° (43)



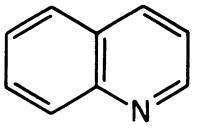
λ max, mμ (H_2O (1% EtOH))	log ε
255 (67)	4.22

132

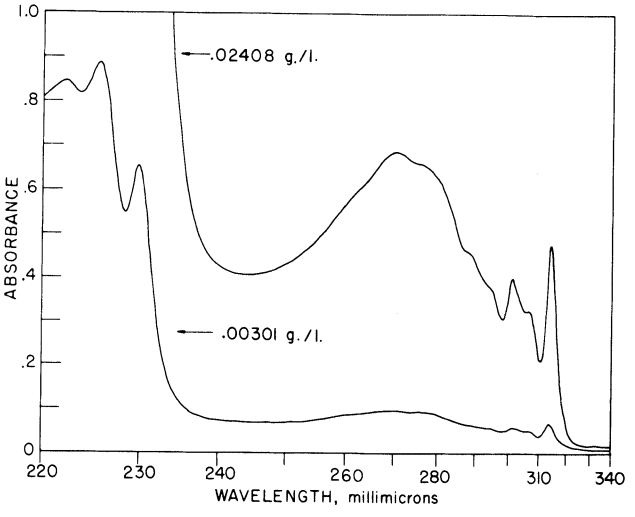


λ_{max}^{KBr} : 14.62 (s), 13.72 (s), 13.40 (m), 13.15 (s), 12.10 (s), 12.00 (w), 11.58 (w), 10.95 (w), 10.31 (w), 10.14 (w), 9.99 (m), 9.62 (m), 9.35 (m), 9.10 (w), 8.98 (w), 8.64 (w), 8.45 (m), 8.28 (w), 8.23 (w), 8.15 (s), 7.85 (w), 7.65 (w), 7.51 (w), 7.11 (s). (99)

QUINOLINE

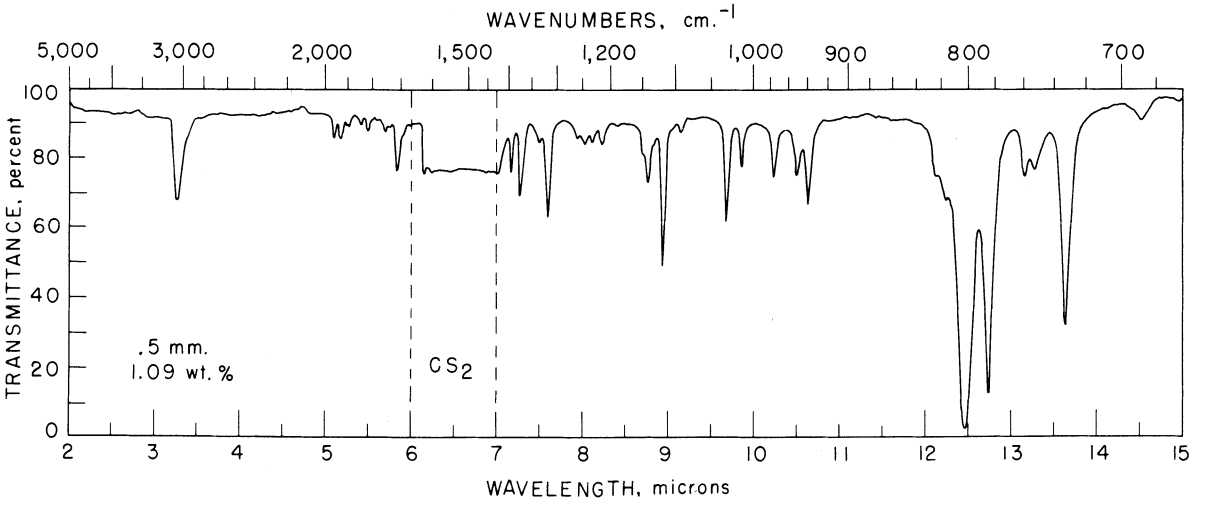


B.p. 237.1° (24)



λ max, mμ (cyclohexane)	log ε
314.2	3.41
306.2	3.24
301.0	3.33
294.0	3.31
288.0	3.39
277.0	3.54
270.0	3.57
261.0	3.49

133

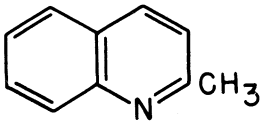


CS_2

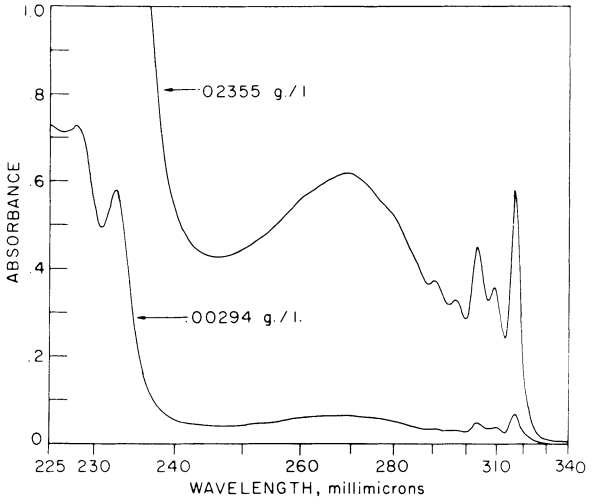
λ : 14.52 (w), 13.65 (s), 13.28 (w), 13.17 (w), 12.76 (s), 12.46 (s), 12.25 (w), 12.15 (w), 11.61 (w), 10.65 (m), 10.52 (w), 10.25 (w), 9.87 (w), 9.69 (m), 9.16 (w), 8.95 (m), 8.78 (w), 8.74 (w), 8.42 (w), 8.24 (w), 8.13 (w), 8.04 (w), 7.95 (w), 7.61 (m), 7.51 (w), 7.28 (m), 7.18 (w).

569705 O—61——12

2-METHYLQUINOLINE

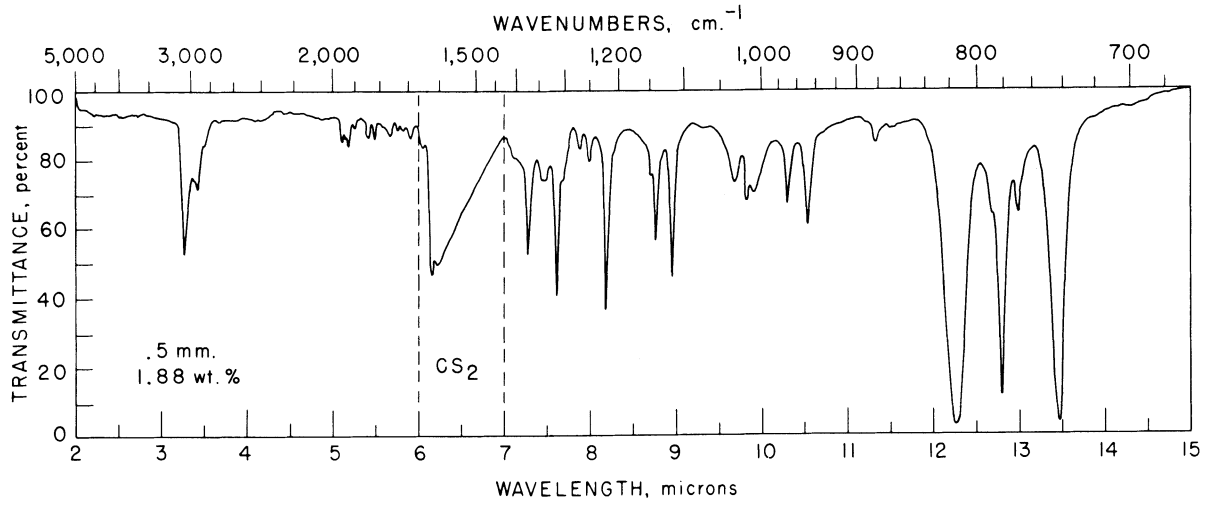


B.p. 245.8° (24)



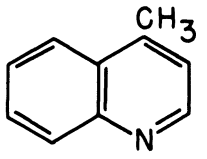
λ max, mμ (cyclohexane)	log ε
316.6	3.55
309.1	3.34
303.2	3.43
296.4	3.30
290.4	3.36
280.0	3.50
269.7	3.57
260.4	3.53
232.4	4.45
227.8	4.55

134

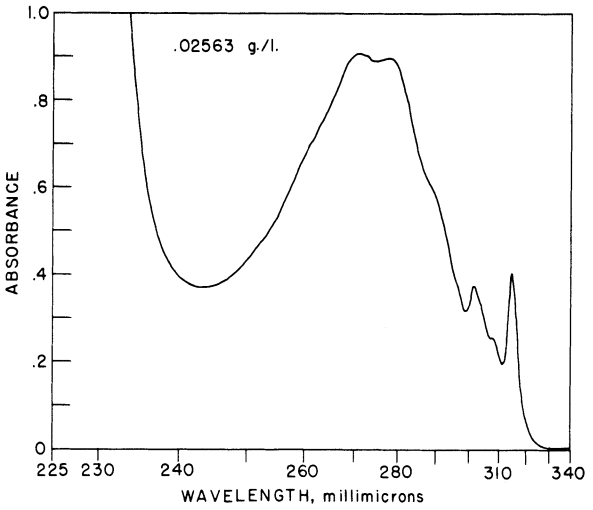


λ^{CS_2}: 13.47 (s), 13.00 (w), 12.80 (s), 12.26 (s), 11.33 (w), 10.55 (m), 10.32 (w), 9.92 (w), 9.83 (w), 9.68 (w), 8.97 (m), 8.77 (m), 8.71 (w), 8.19 (m), 8.00 (w), 7.88 (w), 7.68 (w), 7.62 (m), 7.48 (w), 7.45 (w), 7.28 (m), 7.13 (w).

4-METHYLQUINOLINE

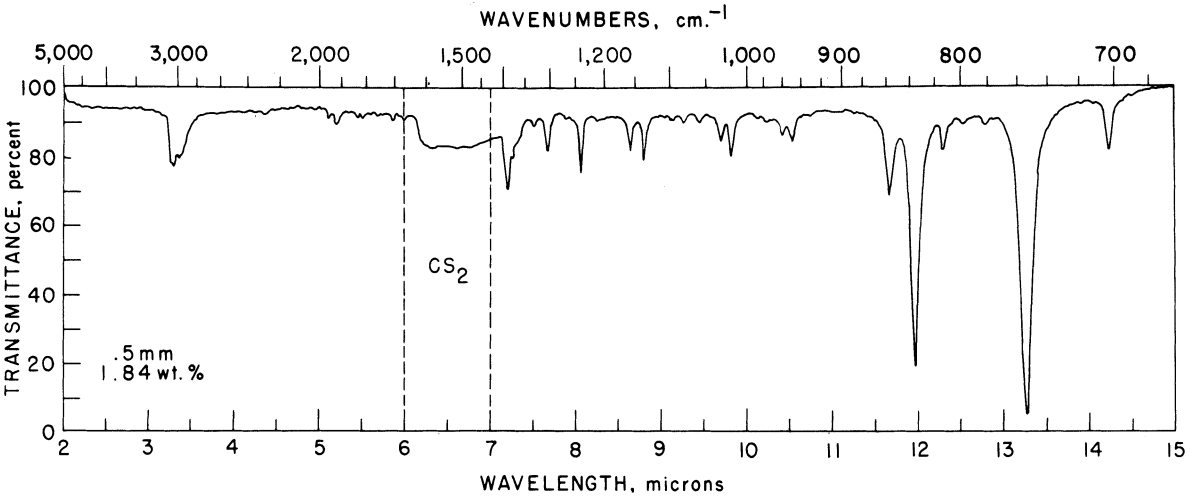


B.p. 264.2° (24)



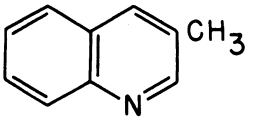
λ max, mμ (cyclohexane)	log ε
314.7	3.35
308.0	3.15
301.6	3.32
289.0	3.52
278.0	3.70
270.7	3.71
261.0	3.59

135



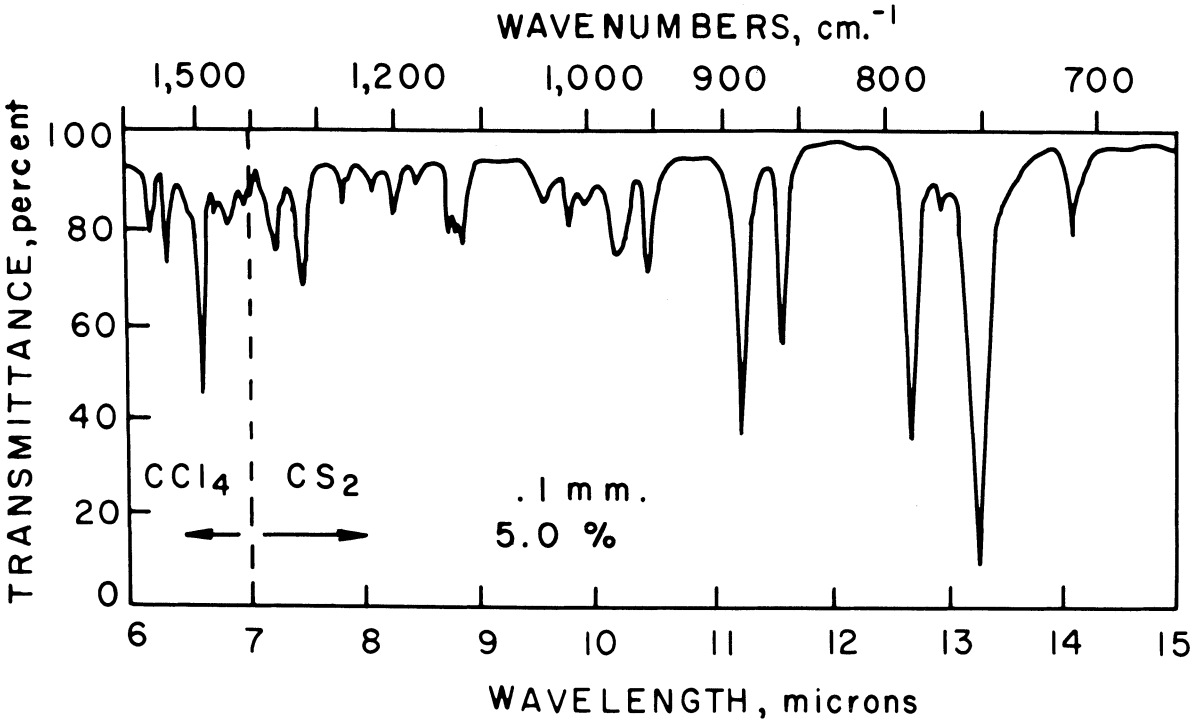
CS_2 λ : 14.22 (m), 13.52 (w), 13.26 (s), 12.78 (w), 12.53 (w), 12.28 (w), 11.97 (s), 11.65 (m), 10.52 (w), 10.42 (w), 10.23 (w), 9.82 (w), 9.69 (w), 9.45 (w), 9.26 (w), 9.14 (w), 9.02 (w), 8.80 (w), 8.63 (w), 8.25 (w), 8.05 (m), 7.95 (w), 7.90 (w), 7.66 (w), 7.50 (w), 7.26 (w), 7.19 (m).

3-METHYLQUINOLINE



B.p. 252°/735 mm. (43)

10% EtOH
λ_{max}, mμ : 318.0 (3.49), 286.0 (3.53). (62)



λ^{CS_2} : 14.10 (w), 13.30 (s), 12.94 (w), 12.68 (m), 11.50 (m), 11.22 (m), 10.45 (w), 10.18 (w), 9.95 (w), 9.75 (w), 9.55 (w), 8.90 (w), 8.75 (w), 8.50 (w), 8.30 (w), 8.10 (w), 7.85 (w), 7.48 (w), 7.28 (w), 7.10 (w). (104)

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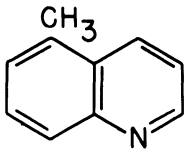
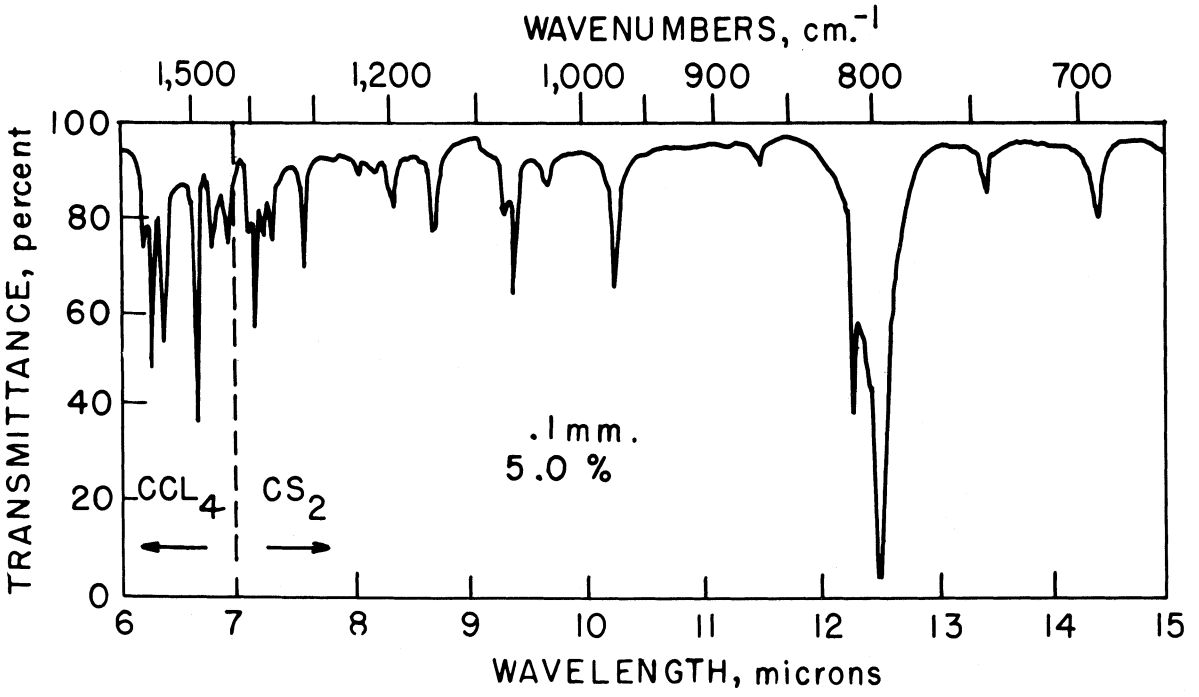
5-METHYLQUINOLINE



B.p. 253-255°/735 mm. (43)



λ^{CS_2}: 14.70 (w), 14.38 (w), 13.45 (w), 12.68 (w), 12.52 (s), 12.30 (m), 11.48 (w), 10.25 (m), 9.72 (w), 9.40 (m), 9.30 (w), 9.18 (w), 8.70 (w), 8.37 (w), 8.25 (w), 8.10 (w), 7.95 (w), 7.85 (w), 7.60 (w), 7.40 (w), 7.33 (w), 7.25 (w), 7.20 (m), 7.13 (w). (104)

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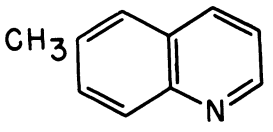
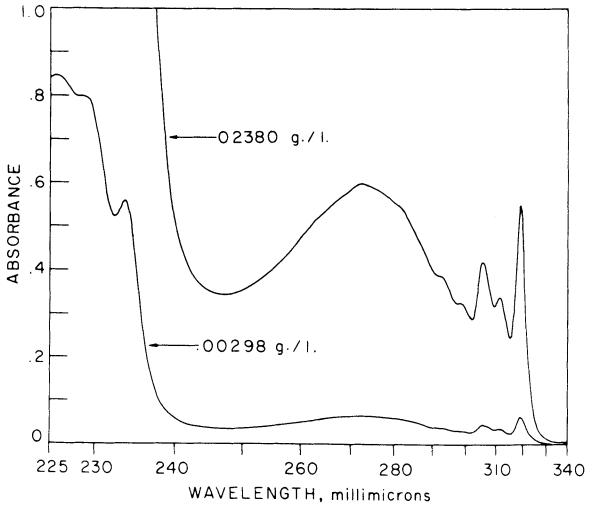
6-METHYLQUINOLINE

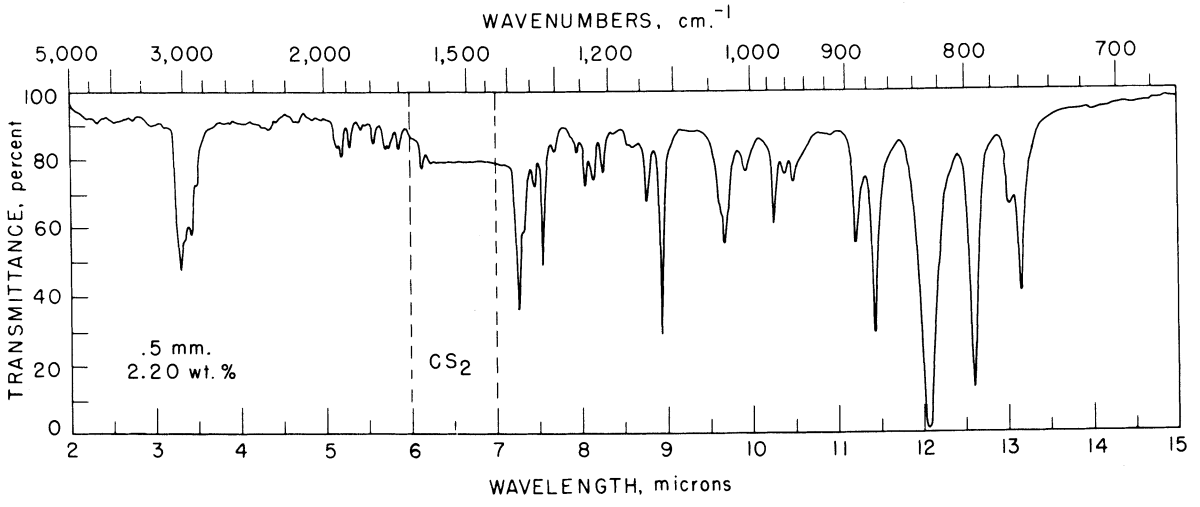


B.p. 257.4-258.6°/745 mm. (43)



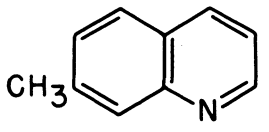
λ max, mμ cyclohexane	log ε
319.1	3.52
311.4	3.31
305.4	3.40
298.3	3.30
292.3	3.37
281.0	3.52
272.3	3.56
233.4	3.53
229.0	3.68
225.6	3.71

138

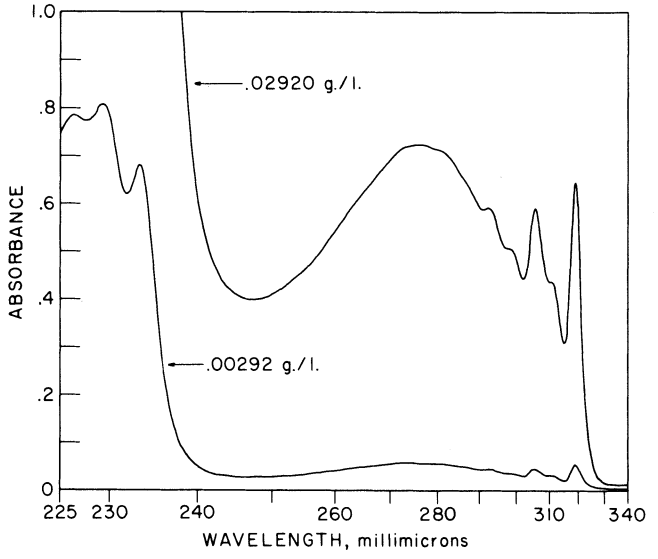


λ^{CS_2}: 13.16 (m), 13.02 (w), 12.60 (s), 12.05 (s), 11.44 (m), 11.22 (w), 10.48 (w), 10.39 (w), 10.26 (w), 9.92 (w), 9.68 (w), 8.94 (m), 8.77 (w), 8.60 (w), 8.25 (w), 8.14 (w), 8.05 (w), 7.94 (w), 7.69 (w), 7.55 (w), 7.45 (w), 7.32 (w), 7.27 (m).

7-METHYLQUINOLINE



B.p. 251.5-252.5° (43)



λ max, mμ (cyclohexane)	log ε
318.7	3.50
310.6	3.33
305.2	3.46
298.0	3.40
292.0	3.46
285.0	3.50
281.0	3.54
276.0	3.55
233.2	4.53
229.4	4.60
226.3	4.59

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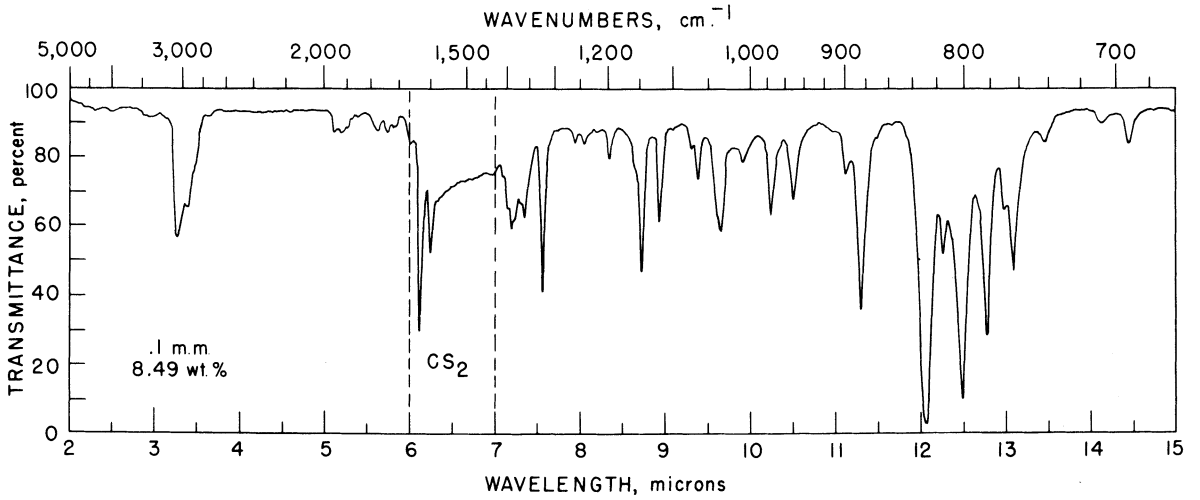
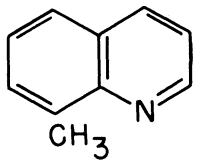
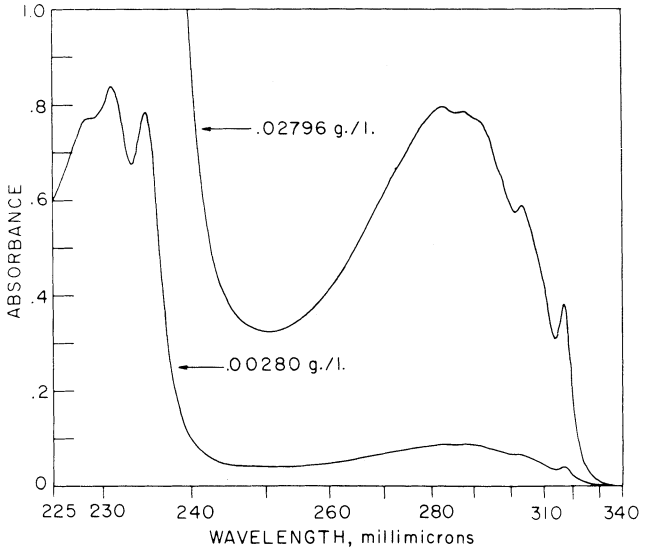


λ^{CS_2}: 14.45 (w), 14.14 (w), 13.46 (w), 13.09 (m), 12.99 (w), 12.78 (m), 12.50 (s), 12.27 (w), 12.07 (s), 11.49 (w), 11.30 (m), 11.12 (w), 10.51 (w), 10.25 (w), 9.92 (w), 9.66 (m), 9.38 (w), 9.30 (w), 9.10 (w), 8.94 (w), 8.72 (m), 8.34 (w), 8.21 (w), 8.05 (w), 7.94 (w), 7.56 (m), 7.35 (w), 7.30 (w), 7.23 (w), 7.20 (w), 7.15 (w), 7.10 (w).

8-METHYLQUINOLINE



B.p. 247.3-248.3°/751.3 mm. (43)



λ max, mμ (cyclohexane)	log ε
316.8	3.29
310.0	3.33
303.2	3.48
291.0	3.60
287.3	3.60
282.4	3.61
234.5	4.60
231.0	4.63
228.5	4.60

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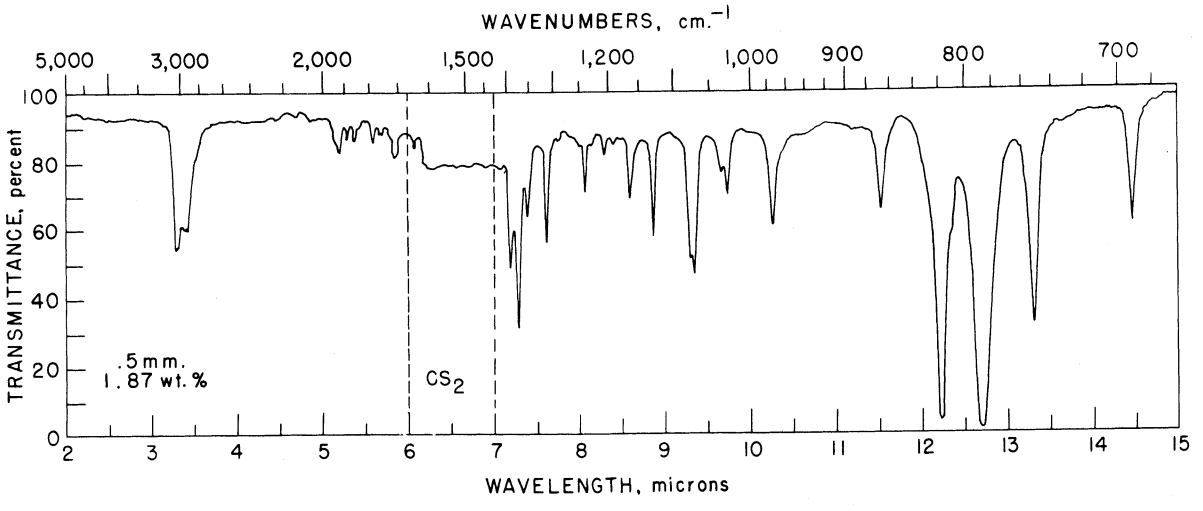
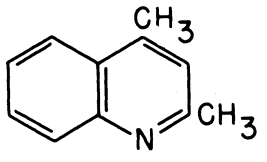
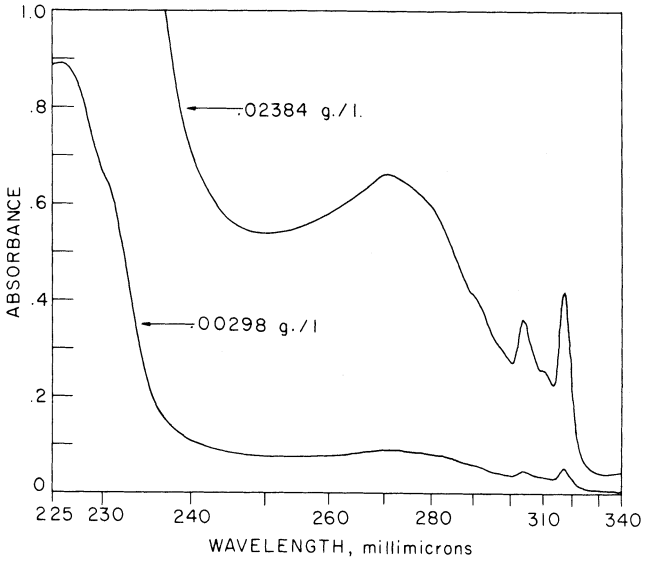


λ^{CS_2}: 14.46 (m), 13.32 (m), 12.71 (s), 12.35 (w), 12.23 (s), 11.52 (m), 10.26 (m), 9.73 (w), 9.65 (w), 9.34 (m), 9.30 (w), 9.17 (w), 8.87 (m), 8.59 (w), 8.40 (w), 8.30 (w), 8.15 (w), 8.07 (w), 8.00 (w), 7.76 (w), 7.62 (m), 7.40 (w), 7.29 (m), 7.20 (m).

2, 4 - DIMETHYLQUINOLINE



B.p. 264-265° (43)



λ max, mμ (cyclohexane)	log ε
317.0	3.44
310.4	3.22
303.8	3.37
298.0	3.29
290.5	3.43
280.0	3.59
270.6	3.64
230.2	4.54
225.6	4.67

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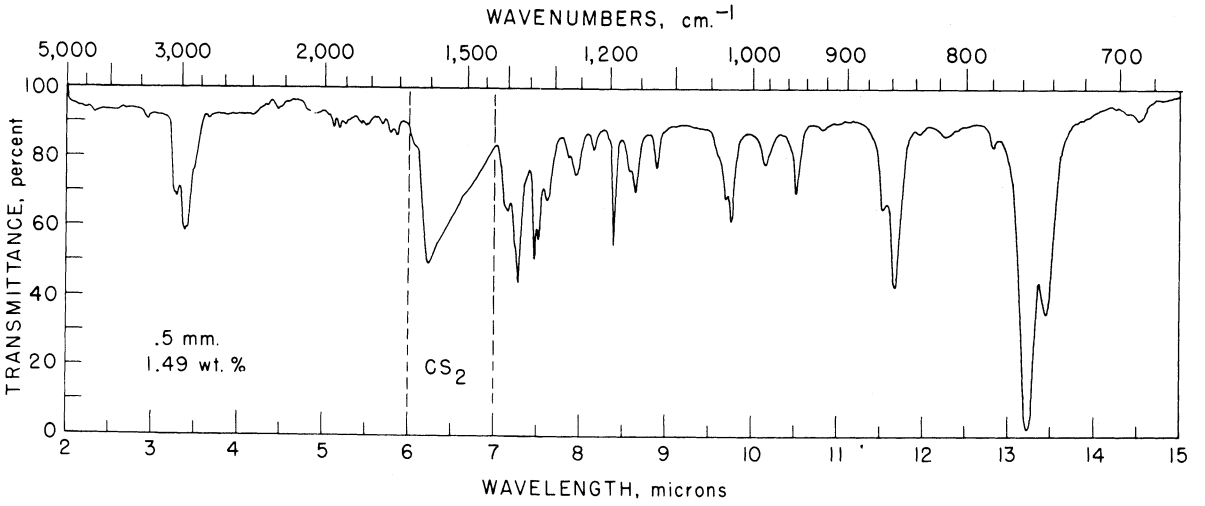
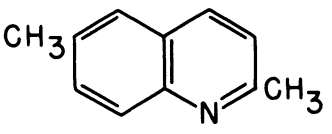


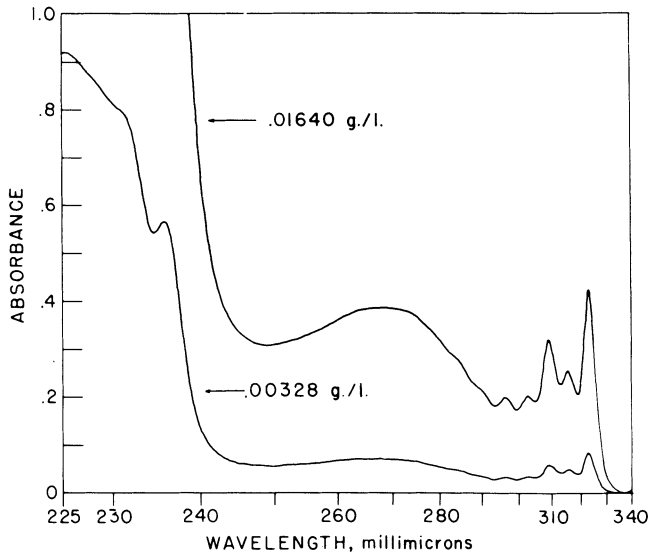
CS_2

λ 14.52 (w), 13.45 (m), 13.23 (s), 12.82 (w), 12.27 (w), 11.97 (w), 11.68 (m), 11.54 (w), 10.83 (w), 10.52 (w), 10.17 (w), 9.76 (m), 9.70 (w), 8.89 (w), 8.65 (w), 8.58 (w), 8.40 (m), 8.15 (w), 7.94 (w), 7.86 (w), 7.62 (w), 7.52 (w), 7.46 (m), 7.28 (w), 7.25 (m), 7.15 (w).

2, 6 - DIMETHYLQUINOLINE

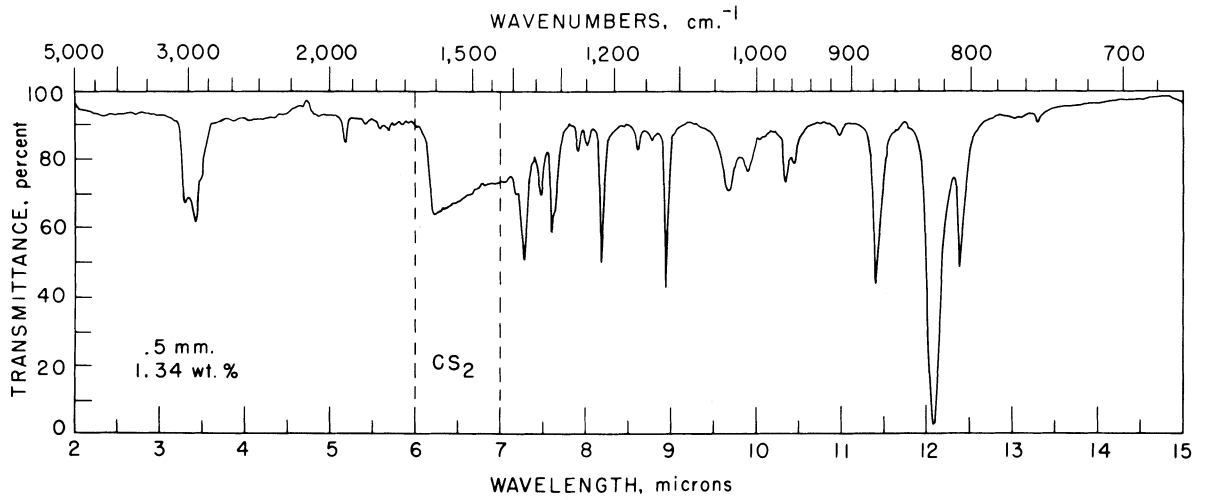


B.p. 266-267° (43)



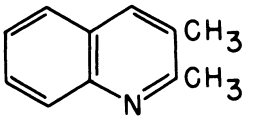
λ max, mμ cyclohexane	log ε
322.6	3.61
315.2	3.65
308.6	3.49
302.2	3.29
295.7	3.28
289.0	3.32
284.0	3.43
269.5	3.57
235.7	4.43
231.4	4.58
225.5	4.64

142

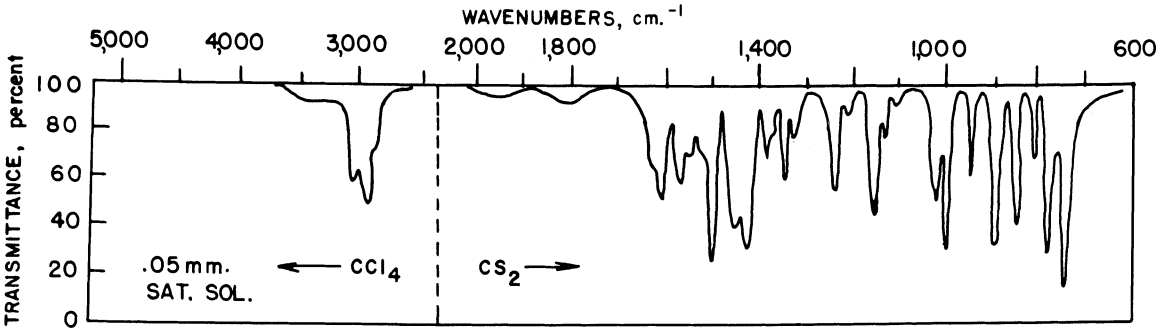


λ^{CS_2}: 13.30 (w), 12.39 (m), 12.10 (s), 11.41 (m), 10.97 (w), 10.45 (w), 10.35 (w), 9.91 (w), 9.68 (w), 8.95 (m), 8.78 (w), 8.61 (w), 8.19 (m), 8.02 (w), 7.92 (w), 7.64 (w), 7.62 (m), 7.48 (w), 7.43 (w), 7.28 (m), 7.18 (w).

2, 3 - DIMETHYLQUINOLINE



B.p. 261°/730 mm. (43)



λ^{CS_2}: 13.42 (s), 12.82 (s), 12.27 (m), 11.76 (s), 11.14 (s), 10.55 (m), 10.02 (s), 9.80 (m), 9.05 (w), 8.80 (w), 8.70 (s), 8.30 (w), 8.06 (m), 7.58 (w), 7.42 (m), 7.30 (w), 7.25 (m), 7.02 (s). (83)

143

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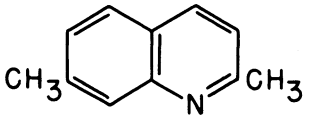
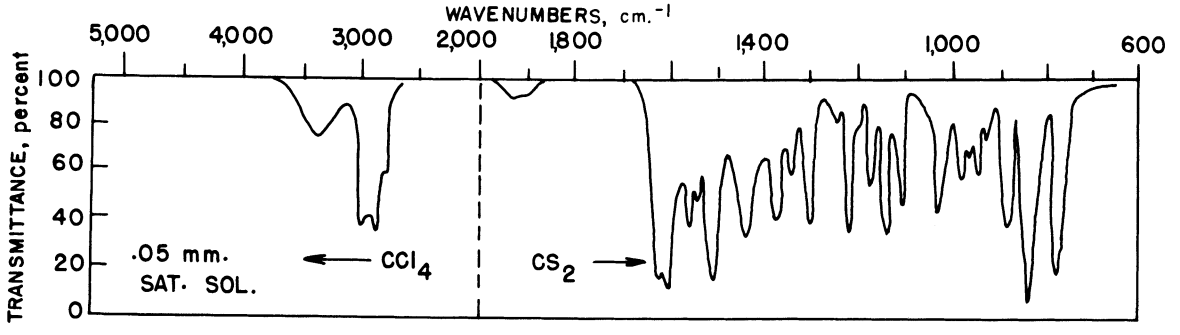
2, 7 - DIMETHYLQUINOLINE

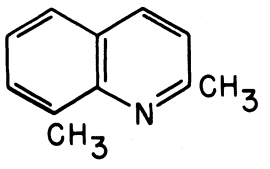


B.p. 264-265° (43)

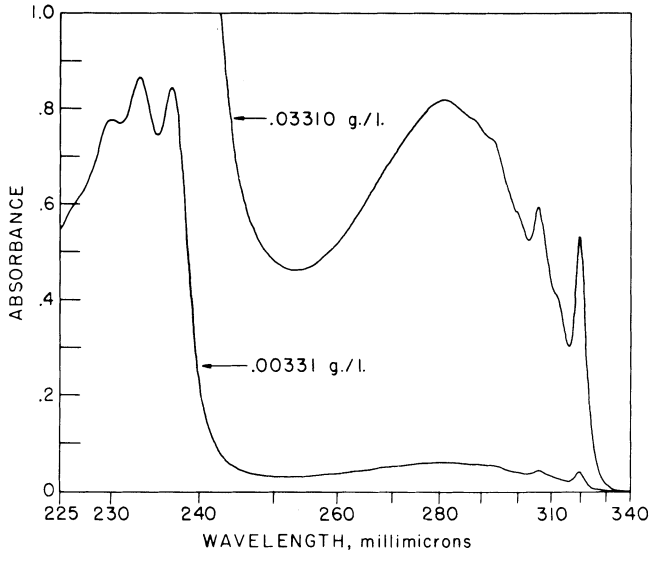


λ^{CS_2}: 12.99 (s), 11.90 (s), 11.40 (m), 10.80 (w), 10.60 (w), 10.40 (w), 10.20 (w), 9.76 (m), 9.05 (w), 8.77 (m), 8.56 (w), 8.37 (w), 8.23 (m), 8.03 (w), 7.67 (m), 7.46 (w), 7.30 (m). (83)

2, 8 - DIMETHYLQUINOLINE

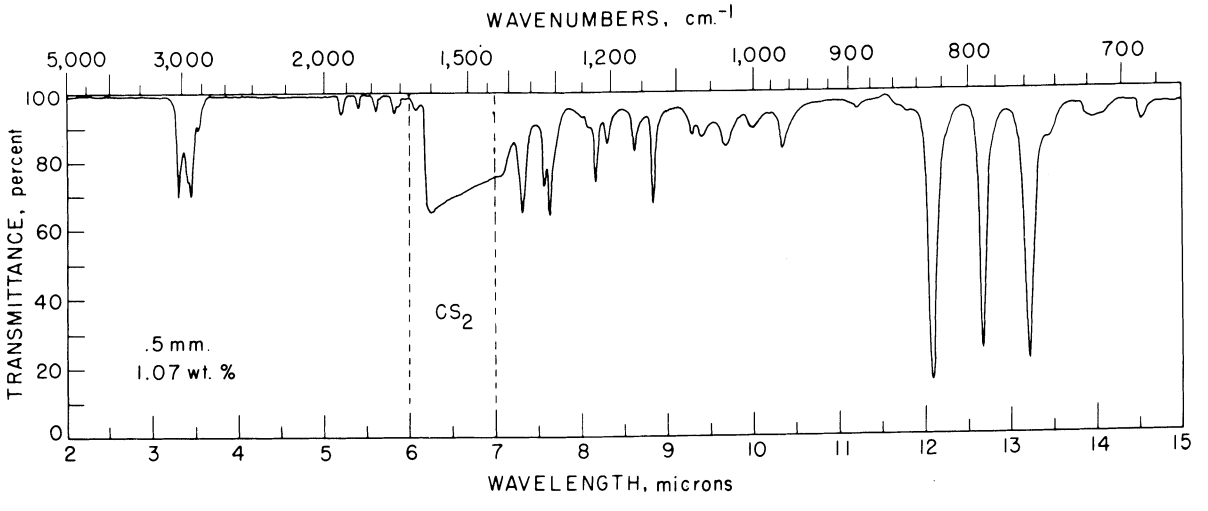


B.p. 252° (43)



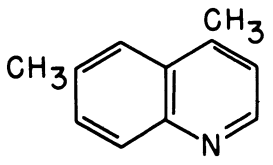
λ cyclohexane max, mμ	log ε
319.7	3.40
312.0	3.28
305.9	3.45
299.6	3.44
293.0	3.54
288.5	3.57
281.0	3.59
236.7	4.60
233.1	4.61
230.0	4.57
226.7	4.46

145

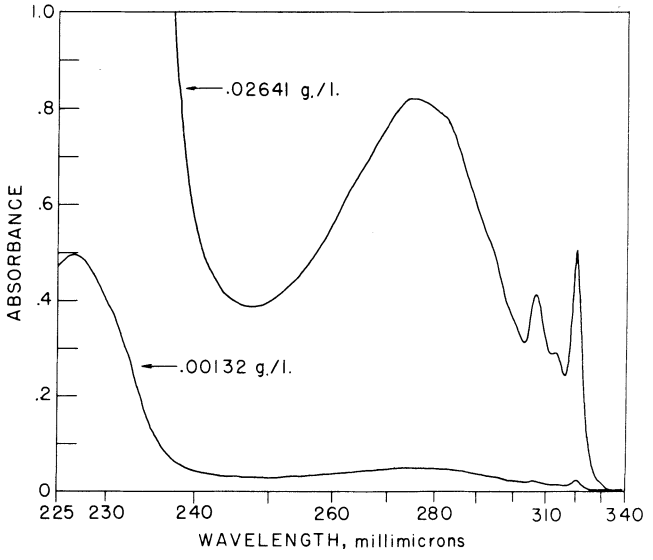


λ^{CS_2}: 14.52 (w), 14.05 (w), 13.88 (w), 13.45 (w), 13.20 (s), 12.66 (s), 12.08 (s), 11.77 (w), 10.34 (w), 10.00 (w), 9.67 (w), 9.38 (w), 9.27 (w), 8.82 (m), 8.61 (w), 8.29 (w), 8.16 (m), 8.08 (w), 8.00 (w), 7.63 (m), 7.57 (w), 7.32 (m).

4, 6 - DIMETHYLQUINOLINE

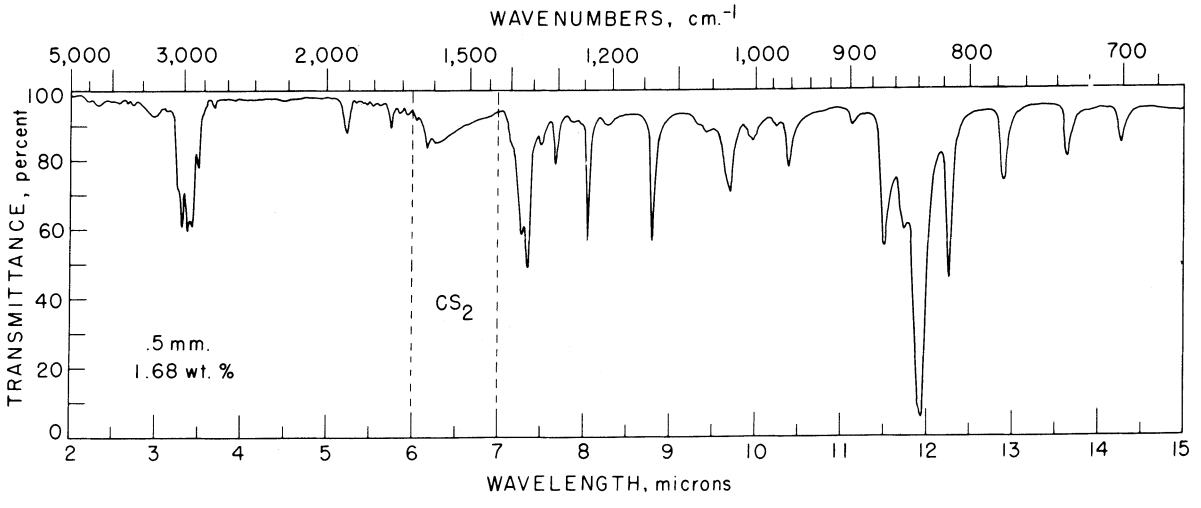


B.p. 273-274° (43)



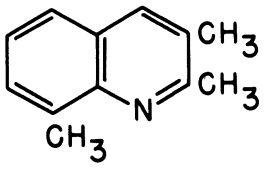
λ max, mμ (cyclohexane)	log ε
319.8	3.47
312.4	3.24
306.1	3.39
293.5	3.49
281.8	3.67
273.5	3.69
226.5	4.77

146

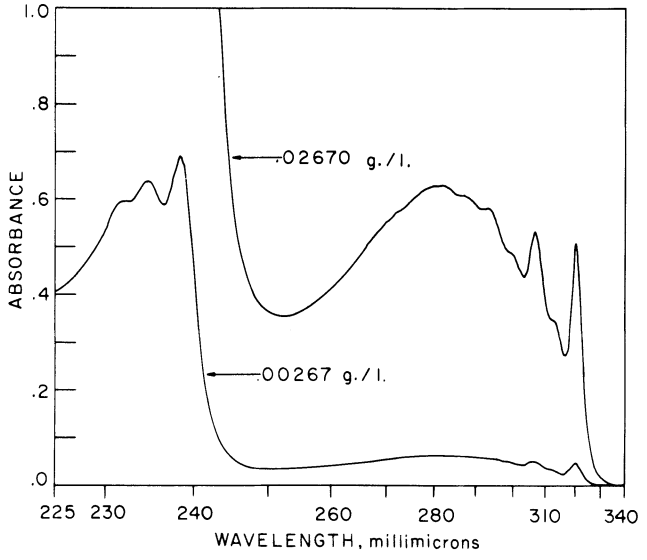


λ^{CS_2}: 14.25 (w), 13.62 (w), 12.87 (w), 12.24 (m), 11.92 (s), 11.72 (w), 11.48 (m), 11.12 (w), 10.37 (w), 10.24 (w), 9.95 (w), 9.68 (w), 9.63 (w), 9.41 (w), 9.30 (w), 8.79 (m), 8.25 (w), 8.04 (m), 7.87 (w), 7.66 (w), 7.50 (w), 7.34 (m), 7.27 (w), 7.15 (w).

2, 3, 8 - TRIMETHYLQUINOLINE

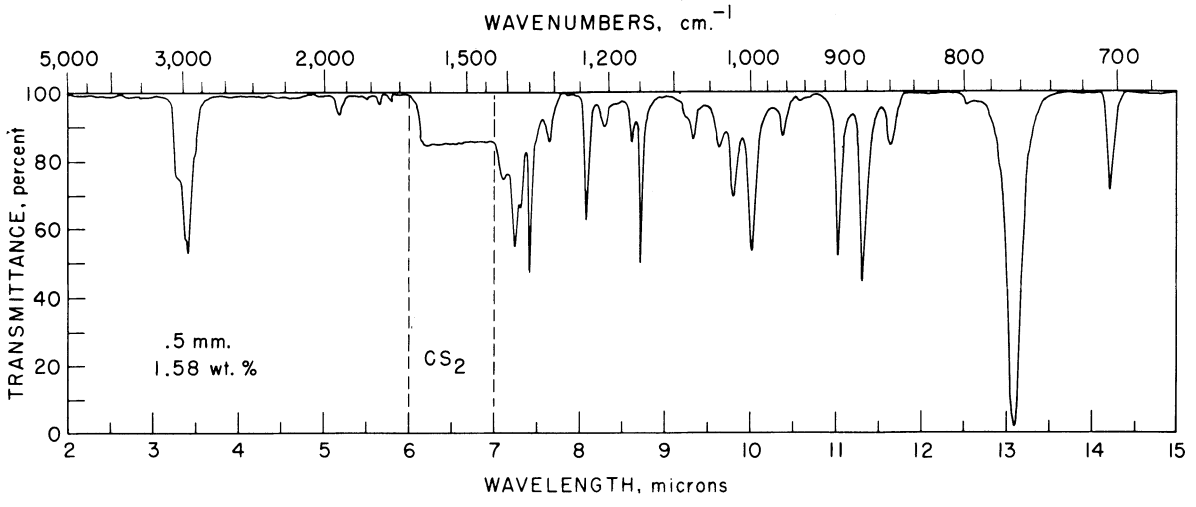


B.p. 280°/747 mm. (43)



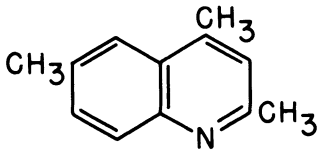
λ max, mμ (cyclohexane)	log ε
320.2	3.51
312.7	3.35
306.6	3.53
299.5	3.50
293.0	3.57
287.7	3.59
281.8	3.61
238.3	4.65
234.6	4.61
231.6	4.58

147

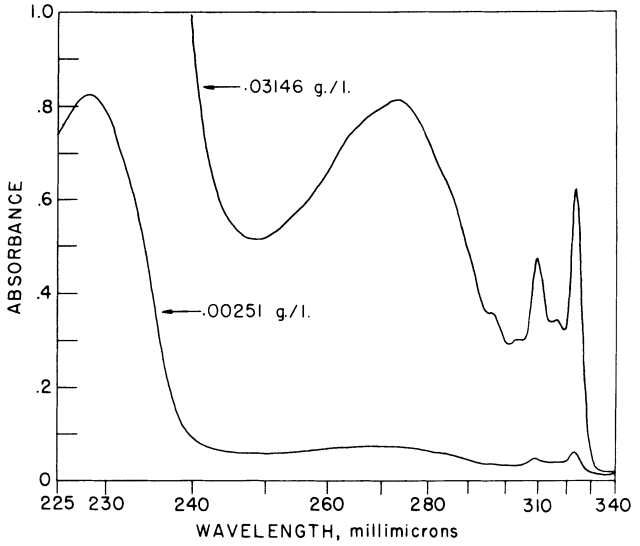


$\lambda_{max}^{CS_2}$: 14.22 (m), 13.10 (s), 12.53 (w), 11.65 (w), 11.32 (m), 11.03 (m), 10.38 (w), 10.02 (m), 9.80 (w), 9.64 (w), 9.34 (w), 9.26 (w), 8.72 (m), 8.61 (w), 8.30 (w), 8.09 (m), 7.65 (w), 7.42 (m), 7.31 (w), 7.25 (m), 7.10 (w).

2, 4, 6 - TRIMETHYLQUINOLINE

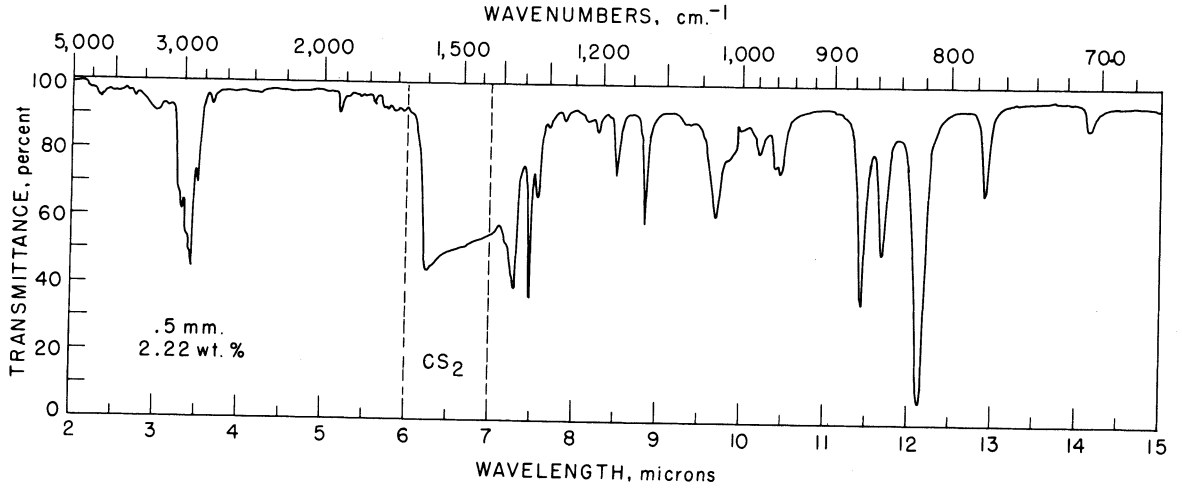


B.p. 287°/758 mm. (66)



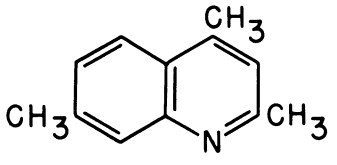
λ max, mμ (cyclohexane)	log ε
323.2	3.53
316.0	3.27
309.3	3.41
303.0	3.22
295.8	3.29
284.5	3.53
273.0	3.64
264.5	3.61
228.3	4.75

148

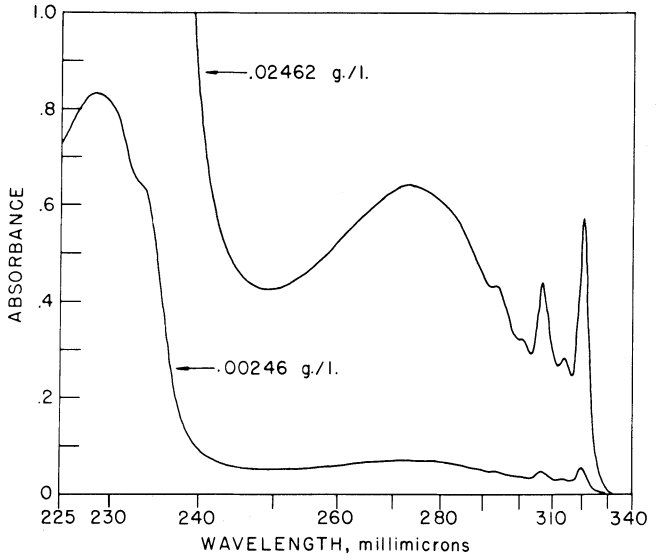


λ^{CS_2} : 14.15 (w), 12.92 (m), 12.14 (s), 11.68 (m), 11.44 (s), 10.47 (w), 10.41 (w), 10.22 (w), 9.70 (m), 8.85 (m), 8.52 (m), 8.28 (w), 8.17 (w), 7.90 (w), 7.70 (w), 7.57 (w), 7.48 (m), 7.30 (m), 7.20 (w).

2, 4, 7 - TRIMETHYLQUINOLINE

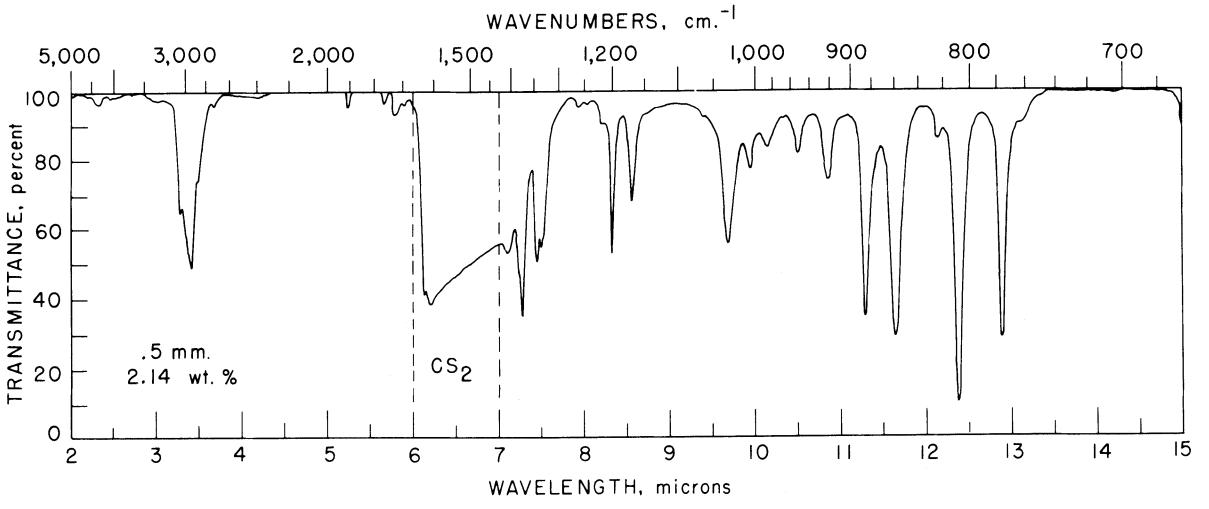


B.p. 280-281° (43)



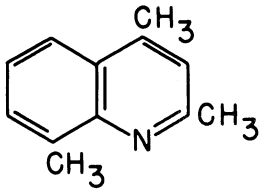
λ max, mμ (cyclohexane)	log ε
320.2	3.61
314.0	3.36
306.6	3.52
300.2	3.41
293.4	3.52
283.0	3.65
272.8	3.69
233.3	4.65
228.4	4.76

149

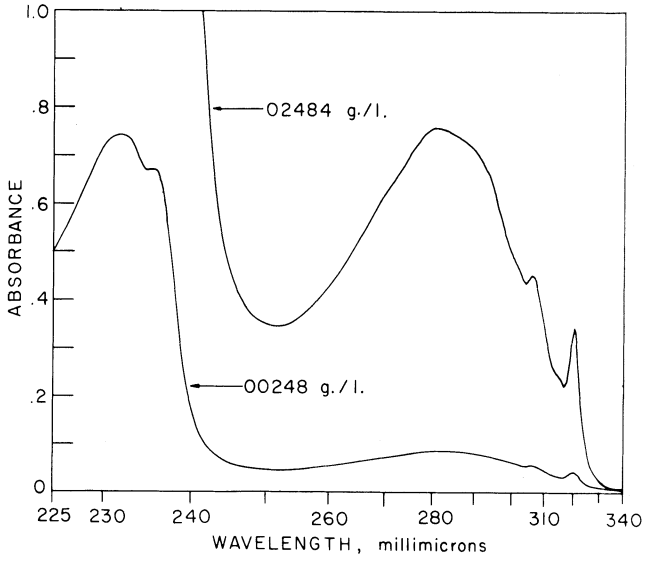


λ^{CS_2} : 13.12 (w), 12.88 (s), 12.37 (s), 12.13 (w), 11.64 (s), 11.28 (s), 10.85 (m), 10.50 (w), 10.13 (w), 9.94 (w), 9.68 (m), 8.56 (m), 8.33 (m), 8.20 (w), 7.93 (w), 7.52 (w), 7.50 (w), 7.45 (m), 7.27 (s), 7.10 (w).

2, 4, 8 - TRIMETHYLQUINOLINE

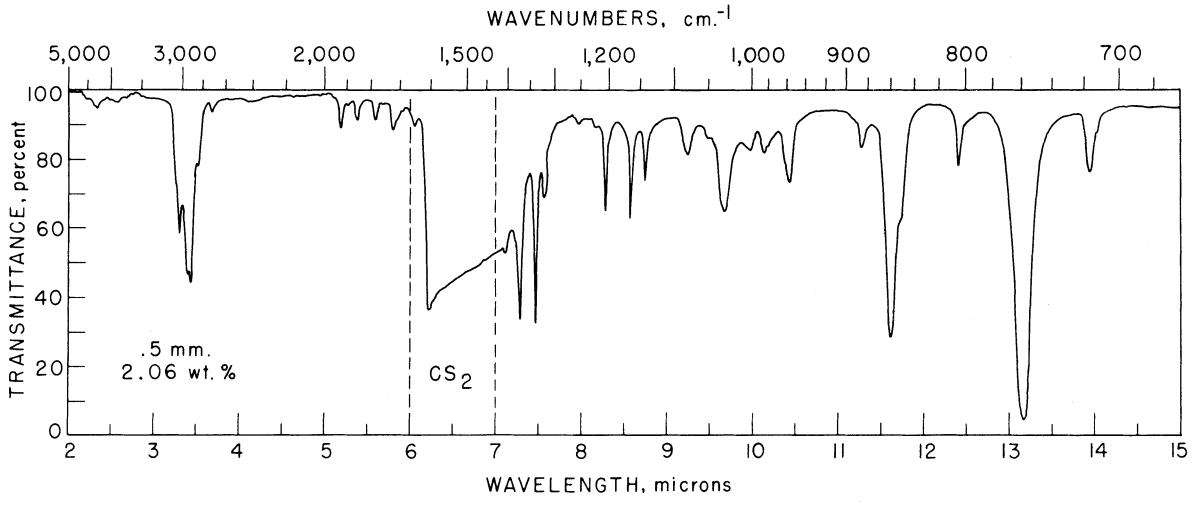


B.p. 275.8°/740 mm.



λ max, mμ (cyclohexane)	log ε
320.0	3.37
314.0	3.23
306.0	3.49
293.0	3.66
288.0	3.70
281.0	3.72
235.5	4.66
231.7	4.71

150



λ^{CS_2}: 13.95 (w), 13.15 (s), 12.42 (w), 11.73 (w), 11.62 (m), 11.27 (w), 10.44 (w), 10.40 (w), 10.15 (w), 9.68 (w), 9.49 (w), 9.25 (w), 8.75 (w), 8.58 (w), 8.28 (w), 8.18 (w), 7.98 (w), 7.57 (w), 7.47 (m), 7.28 (m), 7.12 (w).

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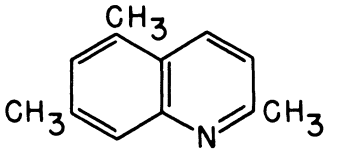
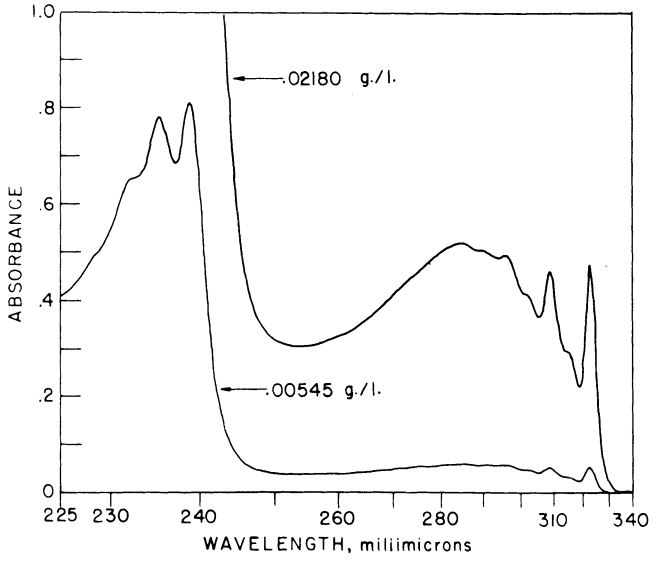
2, 5, 7 - TRIMETHYLQUINOLINE

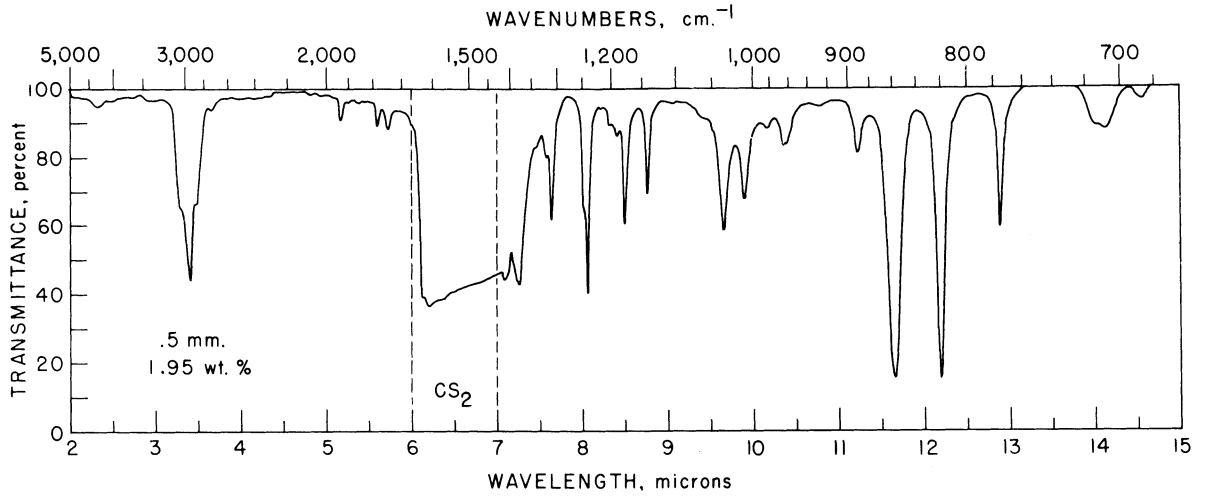


B.p. 286.6°/746 mm.



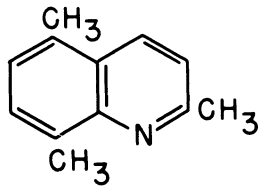
λ max, mμ (cyclohexane)	log ε
322.7	3.57
314.7	3.37
308.8	3.56
302.0	3.51
295.6	3.59
290.3	3.60
284.5	3.61
238.7	4.41
235.2	4.39
232.0	4.31
228.5	4.19

151

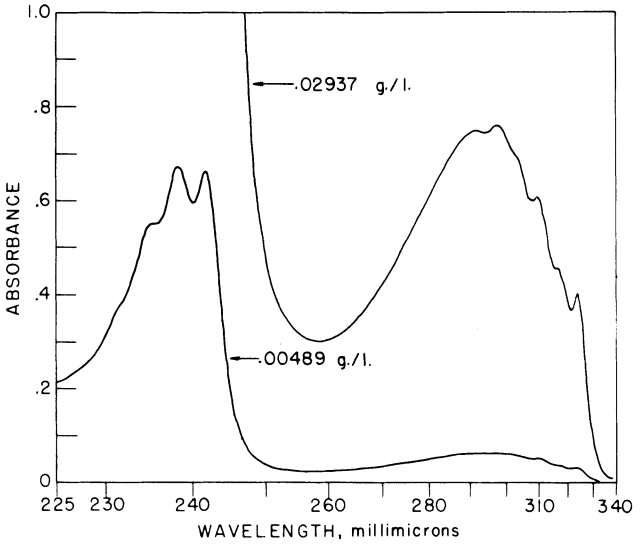


λ^{CS_2}: 14.55 (w), 14.14 (w), 14.02 (w), 12.89 (m), 12.20 (s), 11.65 (s), 11.22 (w), 10.40 (w), 10.36 (w), 10.17 (w), 9.90 (m), 9.65 (m), 9.40 (w), 8.76 (m), 8.50 (m), 8.41 (w), 8.32 (w), 8.22 (w), 8.07 (m), 8.02 (w), 7.64 (m), 7.58 (w), 7.56 (w), 7.47 (w), 7.26 (m), 7.23 (w), 7.20 (w), 7.14 (w), 7.08 (w).

2, 5, 8 - TRIMETHYLQUINOLINE

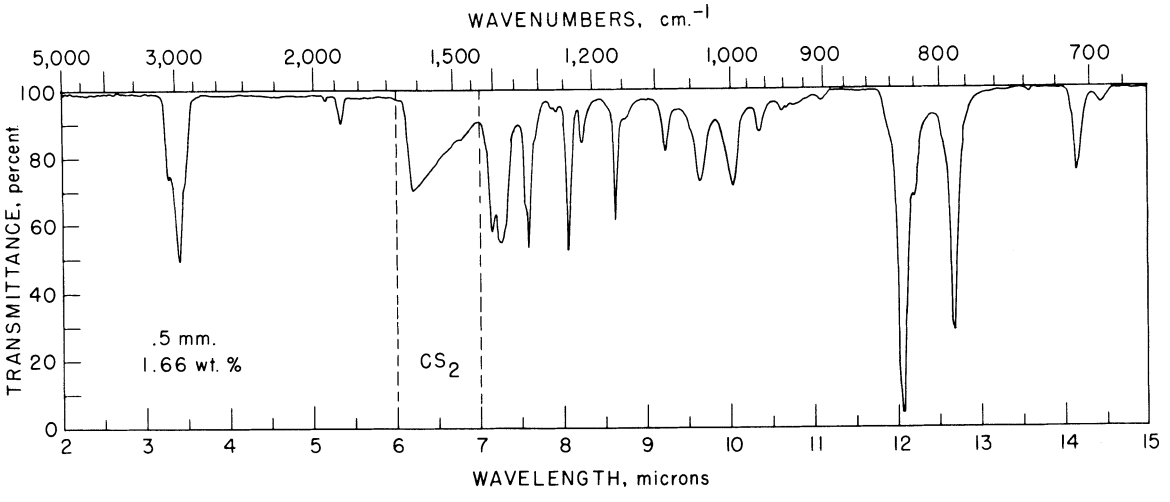


B.p. 143-145°/15 mm.
[est. 273°]



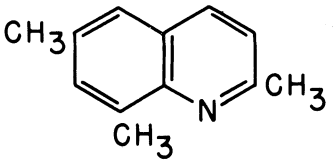
λ max, mμ (cyclohexane)	log ε
324.0	3.37
316.5	3.42
309.5	3.55
304.0	3.60
297.7	3.65
291.5	3.64
241.8	4.37
238.3	4.37
235.1	4.29
231.5	4.12

152

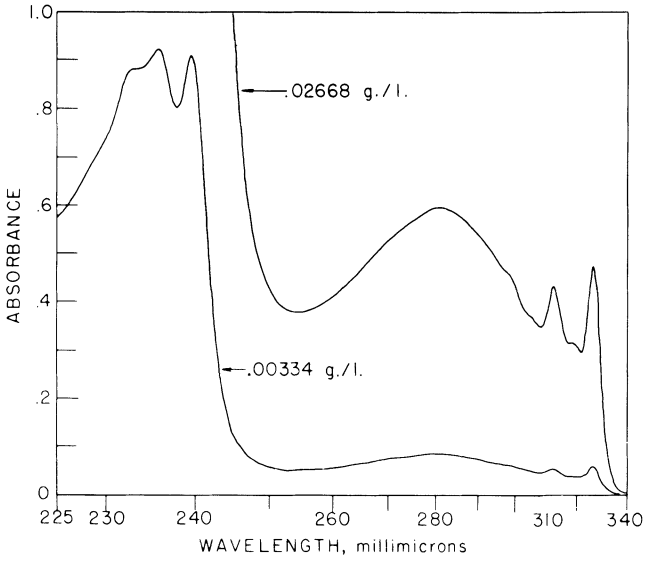


λ^{CS_2}: 14.15 (m), 13.59 (w), 12.68 (s), 12.21 (w), 12.07 (s), 11.10 (w), 10.62 (w), 10.35 (w), 10.04 (m), 9.65 (m), 9.53 (w), 9.24 (w), 8.78 (w), 8.63 (m), 8.23 (w), 8.07 (m), 7.93 (w), 7.88 (w), 7.67 (w), 7.59 (m), 7.56 (w), 7.32 (w), 7.26 (m), 7.24 (w), 7.15 (w).

2, 6, 8 - TRIMETHYLQUINOLINE

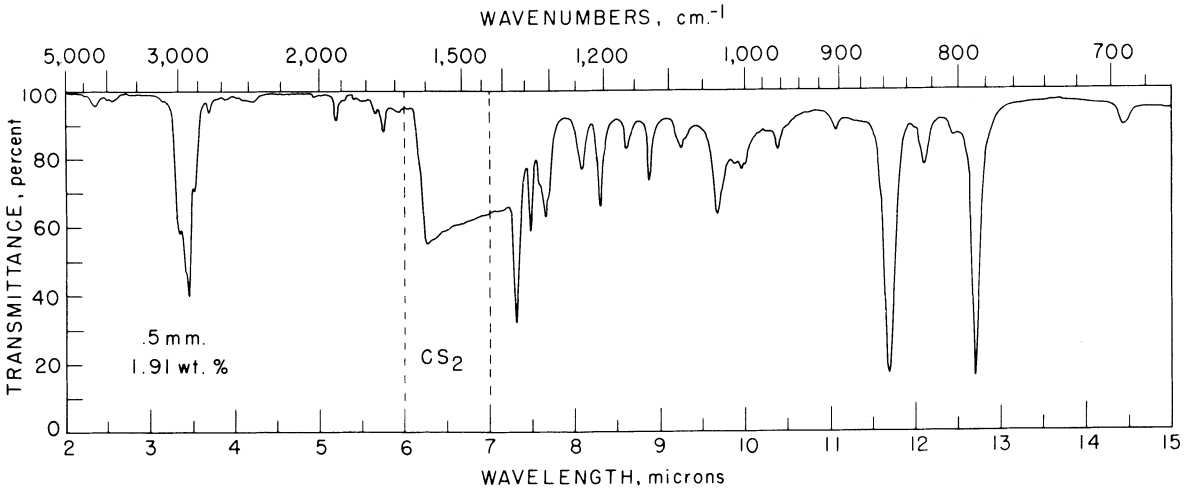


B.p. 267.4°/746 mm.



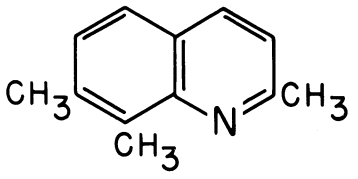
λ max, mμ (cyclohexane)	log ε
323.1	3.37
318.8	3.48
312.0	3.44
305.0	3.37
298.0	3.47
281.0	3.58
239.4	4.67
235.5	4.67
232.6	4.65

153

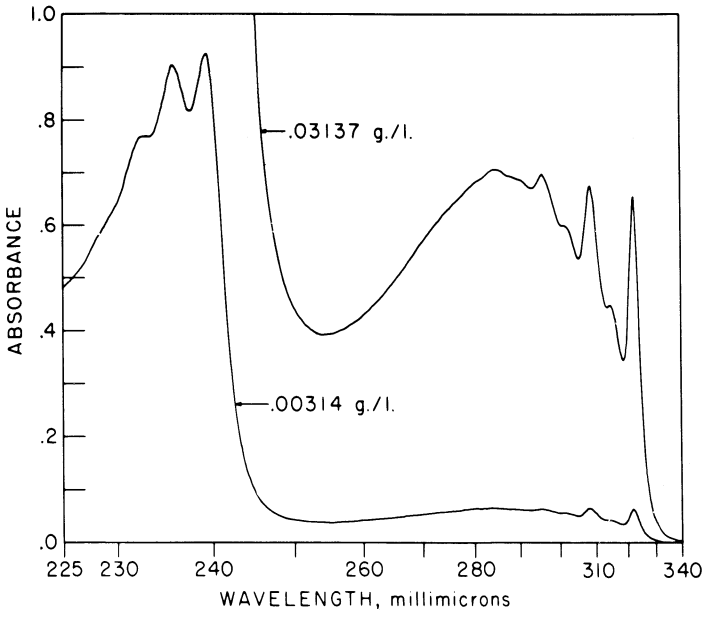


λ^{CS_2}: 14.43 (w), 12.68 (s), 12.42 (w), 12.08 (w), 11.67 (s), 11.04 (w), 10.36 (w), 9.95 (w), 9.66 (m), 9.24 (w), 8.86 (m), 8.58 (w), 8.29 (m), 8.07 (w), 7.95 (w), 7.69 (w), 7.64 (m), 7.57 (w), 7.47 (m), 7.30 (m).

2, 7, 8 - TRIMETHYLQUINOLINE

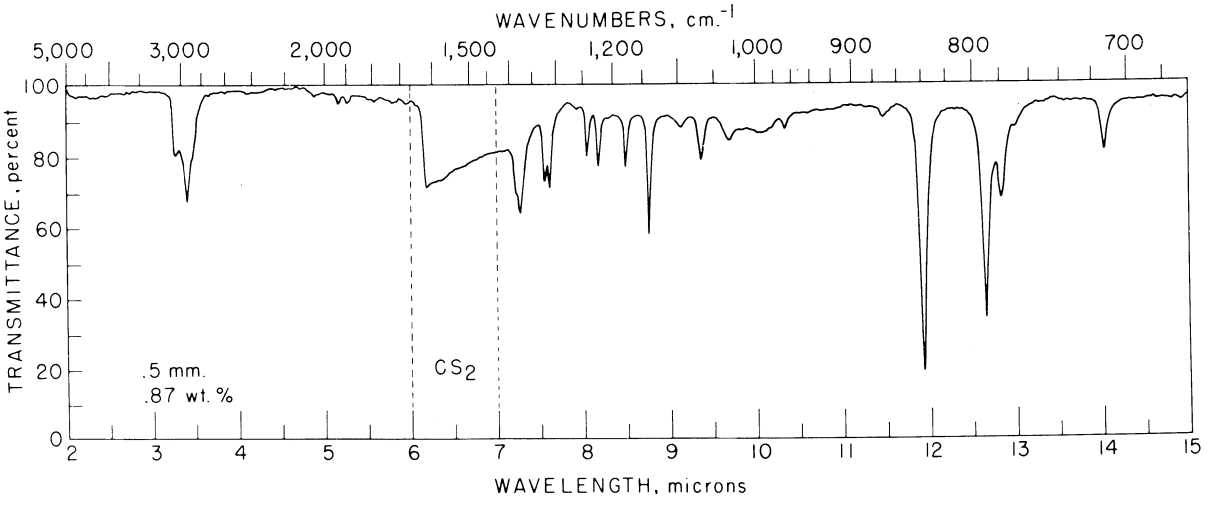


B.p. 276.1°/740 mm.



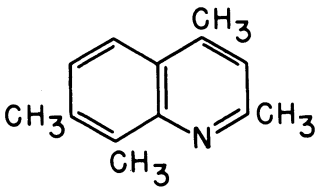
λ cyclohexane max, mμ	log ε
322.0	3.55
314.3	3.38
308.1	3.56
301.2	3.51
295.5	3.58
290.0	3.57
284.5	3.59
239.3	4.70
235.5	4.69
232.5	4.62
228.7	4.51

154

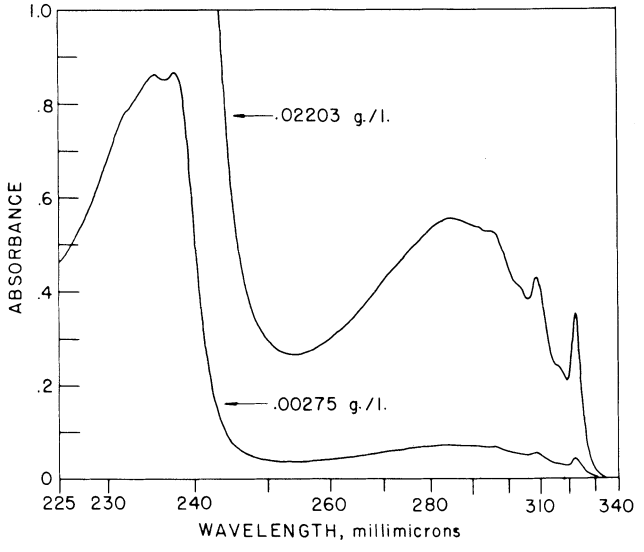


λ^{CS_2}: 14.03 (w), 13.00 (w), 12.84 (m), 12.65 (s), 11.93 (s), 11.48 (w), 10.34 (w), 9.70 (w), 9.36 (w), 9.14 (w), 8.77 (m), 8.50 (w), 8.30 (w), 8.17 (w), 8.05 (w), 7.94 (w), 7.62 (w), 7.56 (w), 7.27 (m), 7.23 (w).

2, 4, 7, 8 - TETRAMETHYLQUINOLINE [1/]

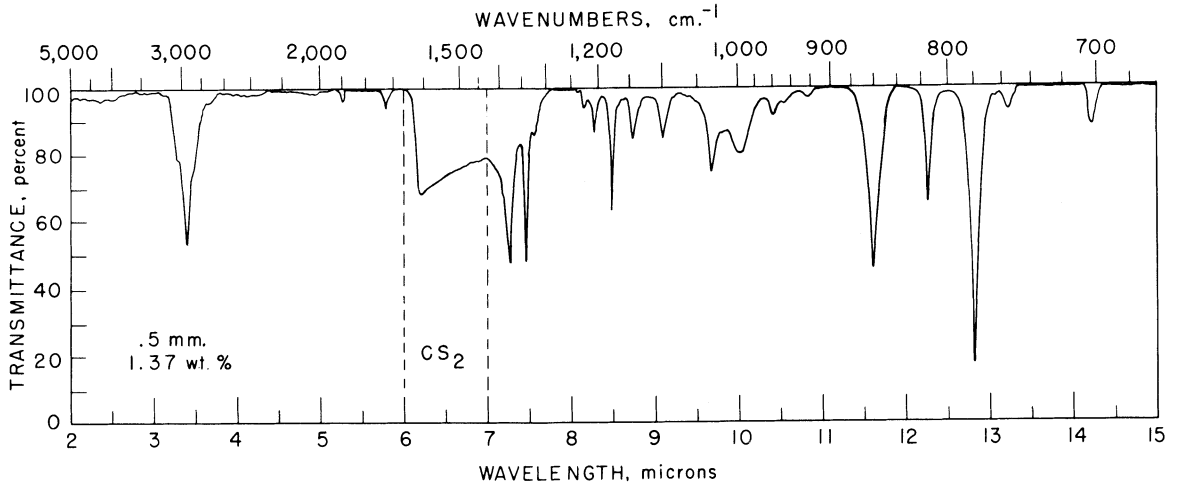


B.p. 295.5°/742 mm.



λ max, mμ (cyclohexane)	log ε
322.8	3.47
316.5	3.30
308.8	3.56
303.4	3.54
295.8	3.65
292.0	3.66
284.5	3.67
237.5	4.77
235.1	4.76
232.1	4.72

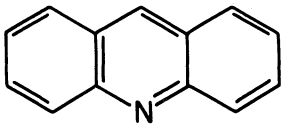
155



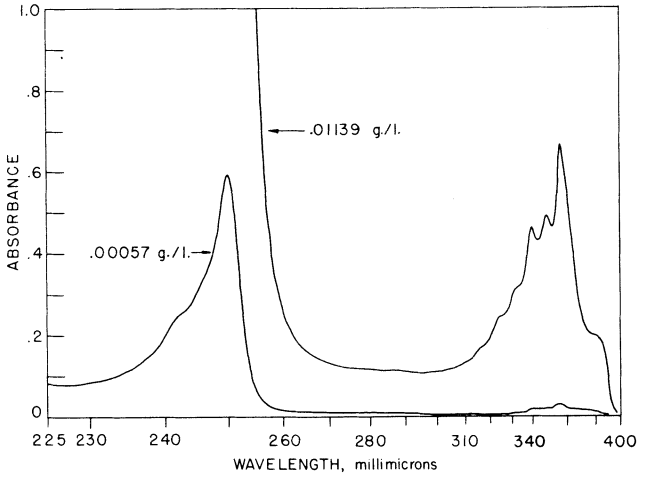
λ^{CS_2}: 14.24 (w), 13.24 (w), 12.83 (s), 12.27 (m), 11.62 (m), 10.85 (w), 10.55 (w), 10.44 (w), 10.05 (m), 9.70 (m), 9.11 (w), 8.75 (w), 8.50 (m), 8.29 (w), 8.17 (w), 8.10 (w), 7.57 (w), 7.47 (m), 7.27 (m), 7.24 (w).

1/ See no. 166.

2, 3 - BENZOQUINOLINE (ACRIDINE)

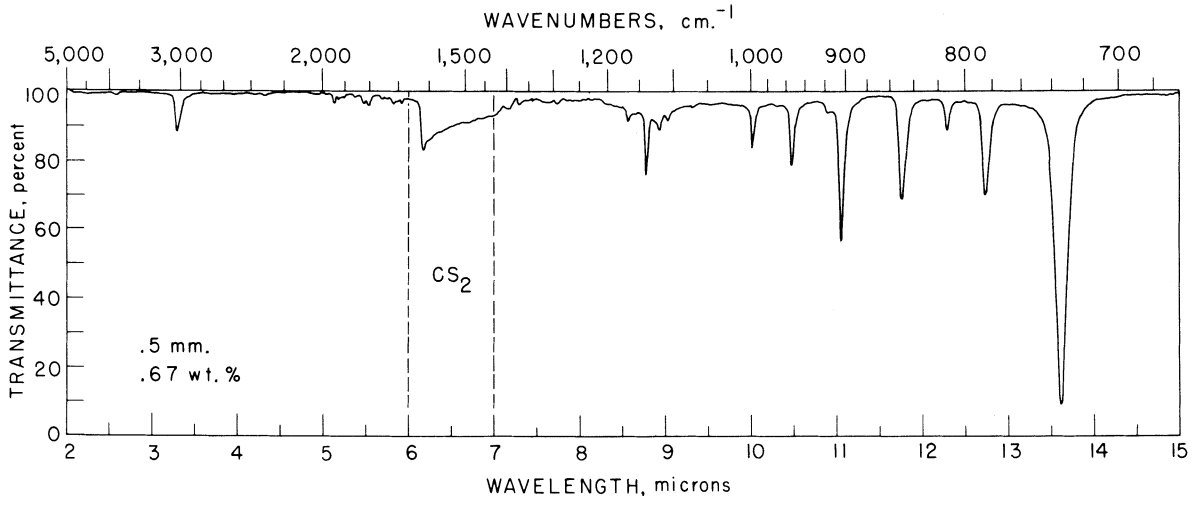


B.p. 345-346° (24)



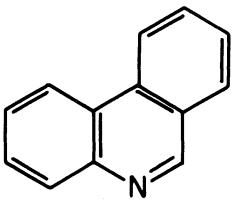
λ max, mμ (cyclohexane)	log ε
380.0	3.49
357.4	4.03
348.3	3.89
340.0	3.86
332.3	3.70
324.7	3.58
317.0	3.44
309.0	3.32
250.0	4.94
242.0	4.89

156



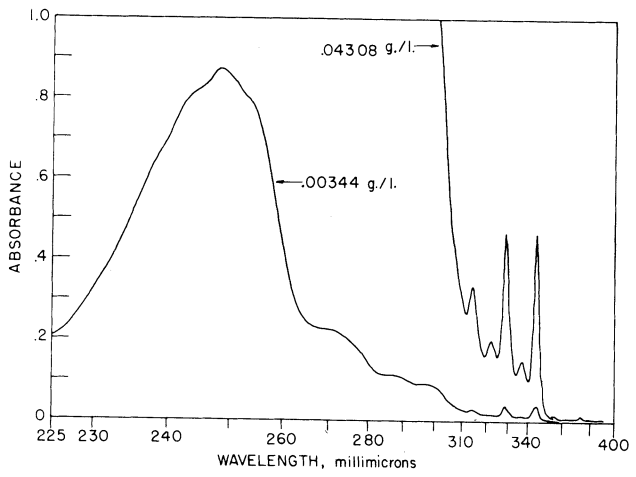
λ^{CS_2}: 13.62 (s), 12.73 (m), 12.29 (w), 11.75 (m), 11.05 (m), 10.89 (w), 10.47 (w), 10.00 (w), 9.03 (w), 8.93 (w), 8.78 (w), 8.56 (w), 7.75 (w), 7.30 (w), 7.18 (w).

3, 4 - BENZOQUINOLINE (PHENANTHRIDINE)

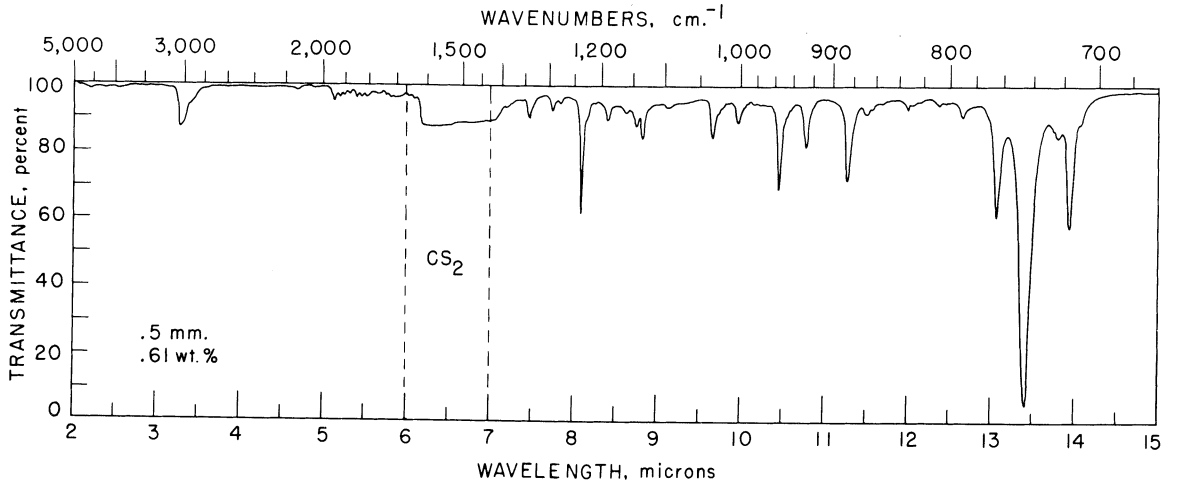


B.p. 349°/769 mm. (43)

157

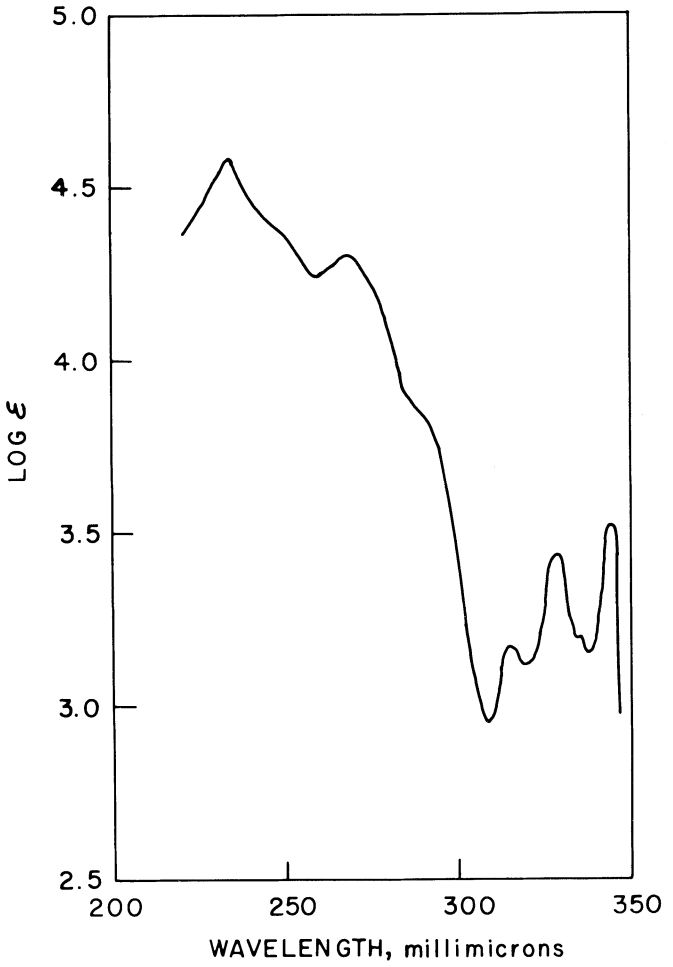


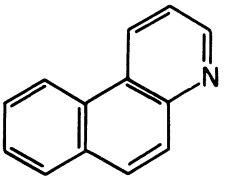
λ max, mμ (cyclohexane)	log ε
373.0	1.33
355.5	1.66
344.4	3.28
337.1	2.80
328.8	3.29
322.5	2.92
314.3	3.14
300.7	3.65
297.0	3.69
287.5	3.77
271.0	4.07
253.0	4.62
248.4	4.66
244.0	4.63



λ^{CS_2}: 14.07 (w), 13.94 (m), 13.42 (s), 13.06 (m), 12.65 (w), 12.36 (w), 12.00 (w), 11.50 (w), 11.28 (m), 10.78 (m), 10.47 (m), 9.97 (w), 9.66 (w), 9.12 (w), 8.83 (w), 8.75 (w), 8.62 (w), 8.40 (w), 8.08 (m), 7.84 (w), 7.75 (w), 7.46 (w), 7.22 (w).

5, 6 - BENZOQUINOLINE
(BENZO [f] QUINOLINE)



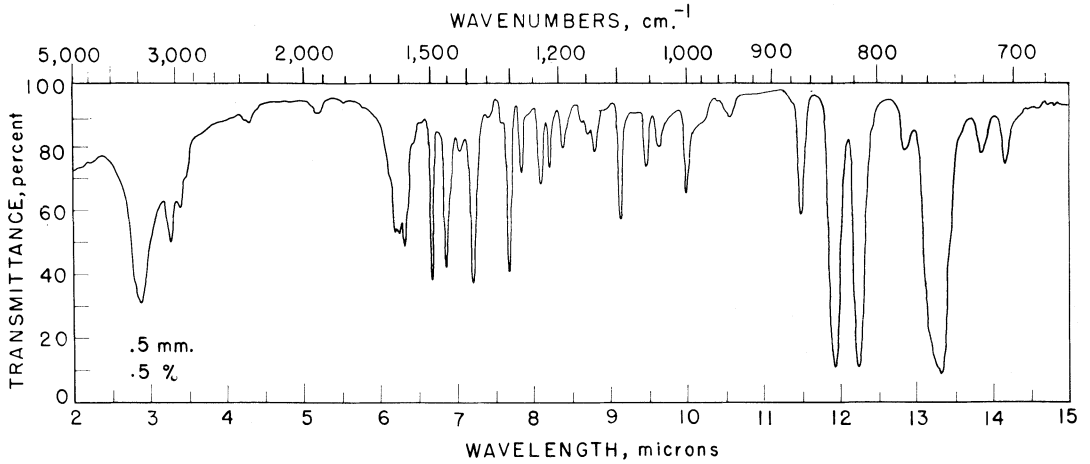


B.p. 350°/721 mm. (43)

158

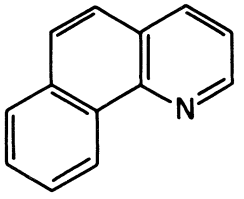
λ max, mμ (EtOH)	log ε
344.0	3.53
329.0	3.43
315.0	3.17
267.0	4.30
233.5	4.58

(53)



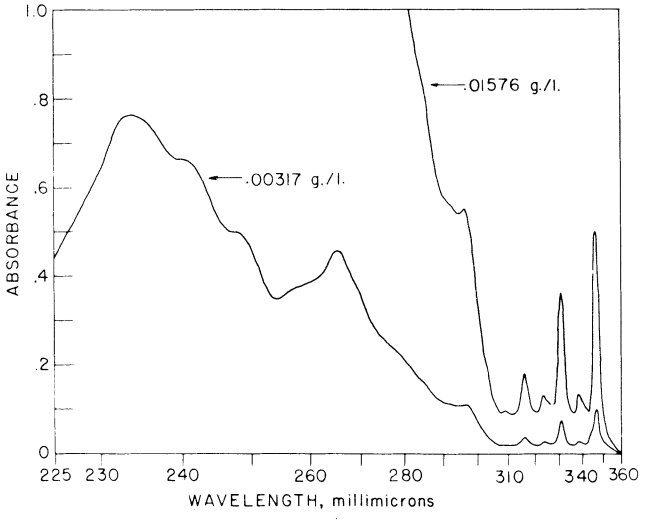
λ_{max}^{KBr}: 14.17 (w), 13.85 (w), 13.33 (s), 12.87 (w), 12.25 (s), 11.93 (s), 11.59 (m), 10.58 (w), 10.00 (w), 9.63 (w), 9.46 (w), 9.14 (m), 8.80 (w), 8.72 (w), 8.64 (w), 8.39 (w), 8.20 (w), 8.10 (w), 7.84 (w), 7.67 (m), 7.60 (w), 7.40 (w), 7.21 (m), 7.03 (w). (99)

7, 8 - BENZOQUINOLINE
(BENZO [h] QUINOLINE)

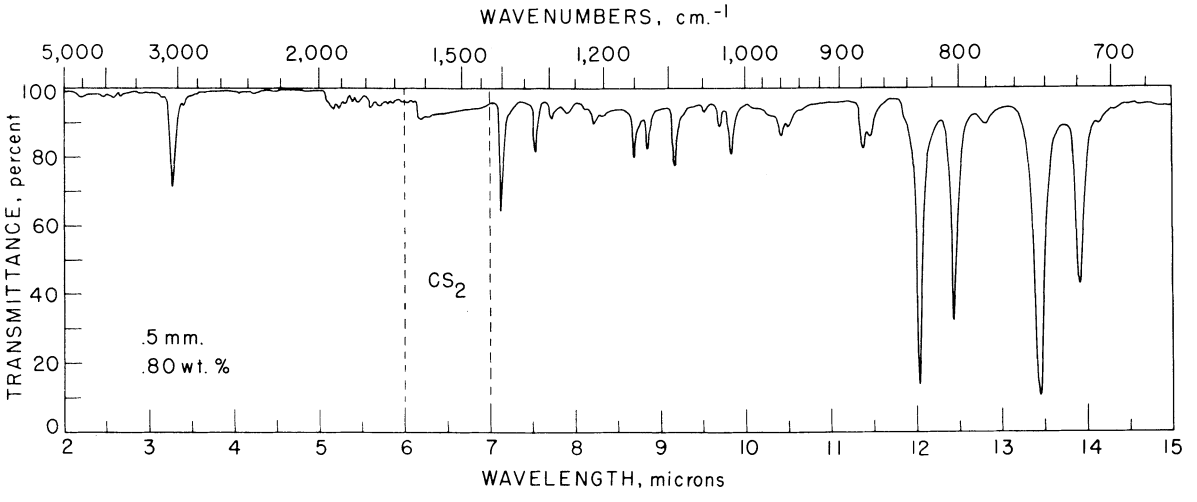


B.p. 335° (65)

159

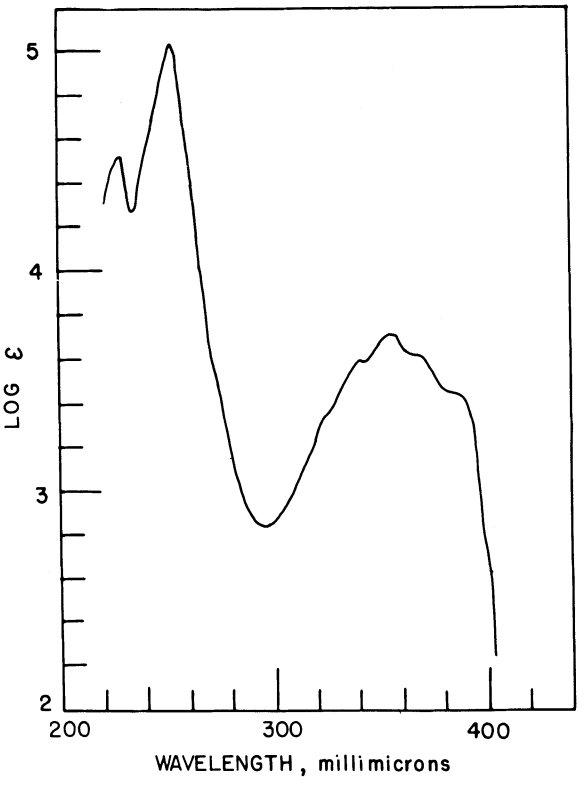


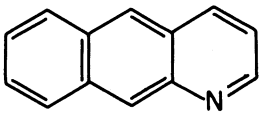
λ cyclohexane max, mμ	log ε
346.4	3.75
338.7	3.14
330.5	3.61
326.0	3.06
323.4	3.13
316.0	3.28
309.0	2.97
296.0	3.79
285.0	3.95
277.0	4.14
265.2	4.41
258.0	4.33
248.0	4.45
240.7	4.57
233.6	4.63



λ^{CS_2}: 13.91 (m), 13.44 (s), 12.80 (w), 12.43 (m), 12.03 (s), 11.46 (w), 11.37 (w), 10.50 (w), 10.42 (w), 9.83 (w), 9.16 (w), 8.85 (w), 8.68 (w), 8.21 (w), 7.91 (w), 7.72 (w), 7.53 (w), 7.13 (w).

6, 7 - BENZOQUINOLINE
(BENZO [g] QUINOLINE)





B.p. 200-205°/14 mm. (43)
[est. 345°]

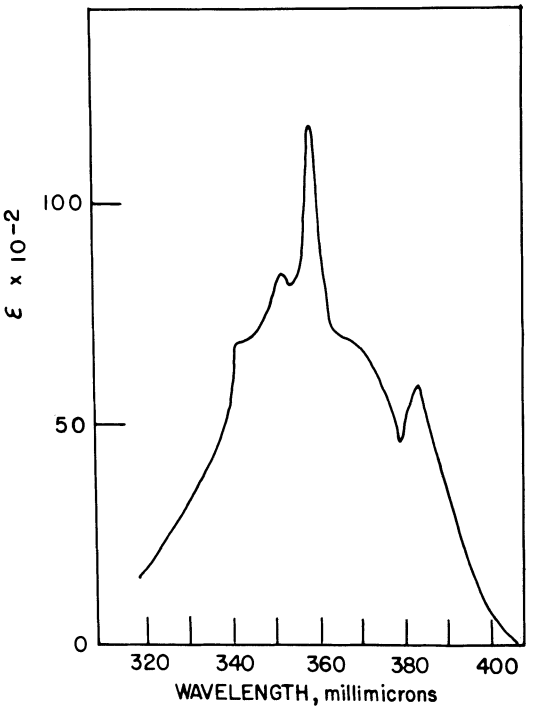
λ max, mμ	log ε
384.0	3.46
366.5	3.63
356.5	3.73
340.0	3.60
326.0	3.35
252.5	5.10
228.0	4.55

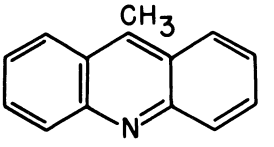
(33)

160

161

9 - METHYLACRIDINE



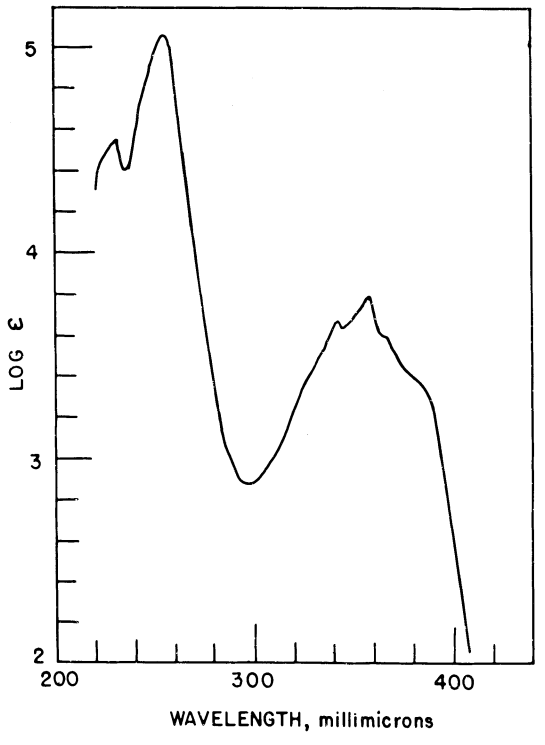


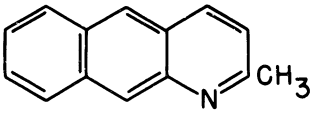
B.p. 359-360°/740 mm. (8)

λ max, mμ	log ε
383.0	3.78
368.7	3.85
357.8	4.07
351.1	3.93
340.4	3.85

(87)

2-METHYLBENZO[g]QUINOLINE





B.p. [est. 360°]

λ max, mμ	log ε
381.0	3.38
356.5	3.77
347.5	3.69
340.0	3.66
330.0	3.55
253.5	5.05
229.0	4.54

(33)

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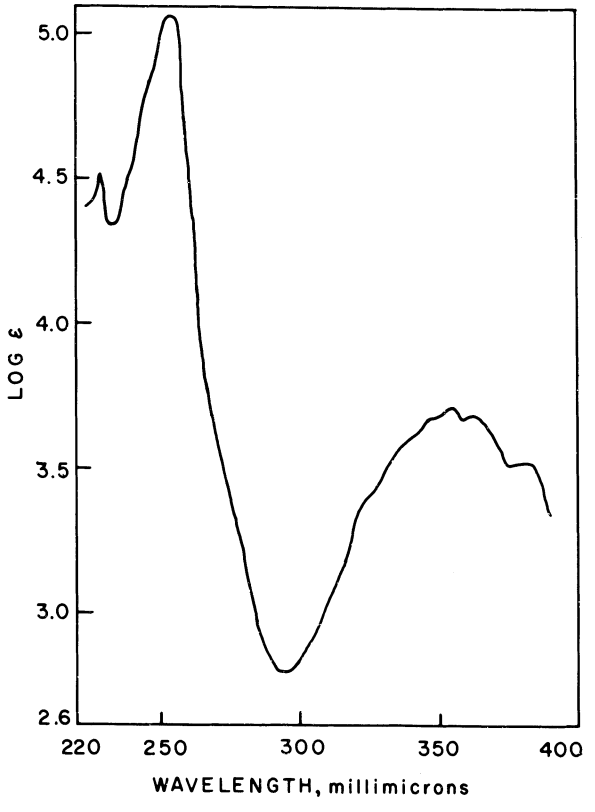
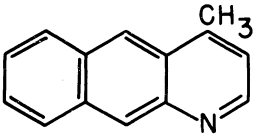
4-METHYLBENZO[g]QUINOLINE



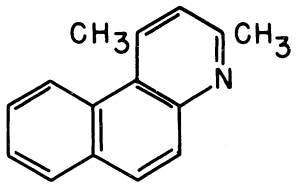


B.p. [est. 360°]

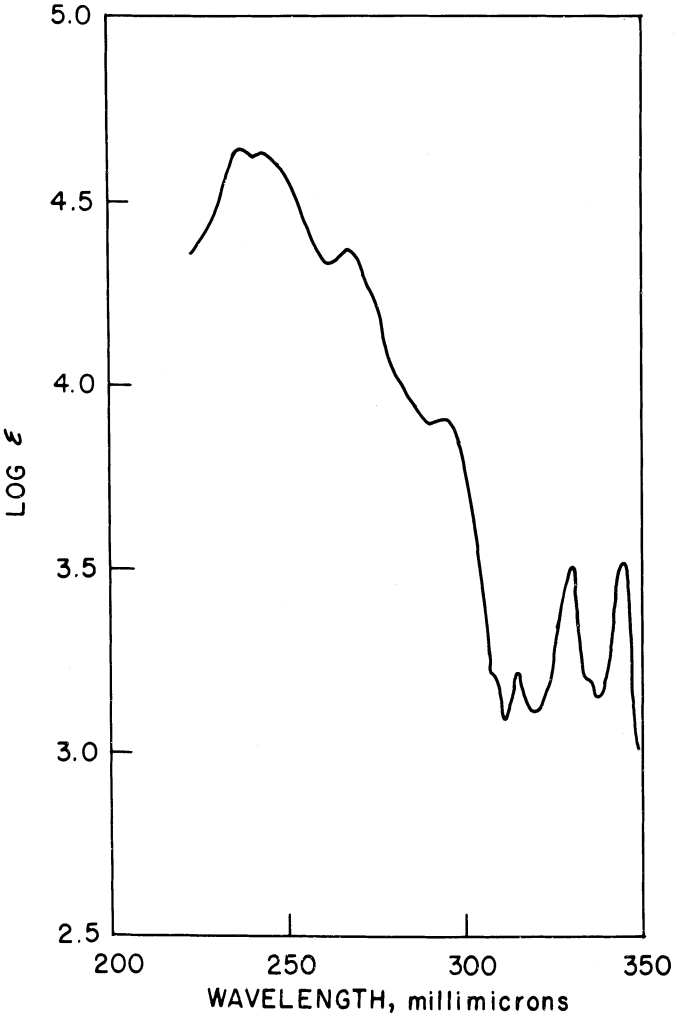
λ max, mμ	log ε
382.0	3.52
363.0	3.69
355.0	3.72
253.5	5.07
228.0	4.49

(53)

1, 3-DIMETHYLBENZO[f]QUINOLINE



B.p. 240°/35 mm. (20)
[est. 358°]



EtOH λ_{max}, mμ	log ε
345.0	3.53
330.0	3.51
315.0	3.22
293.5	3.91
266.0	4.37
241.0	4.63
235.5	4.63

(53)

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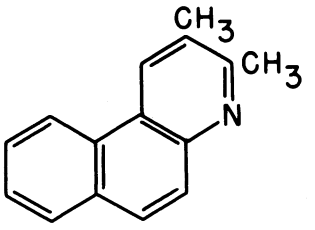
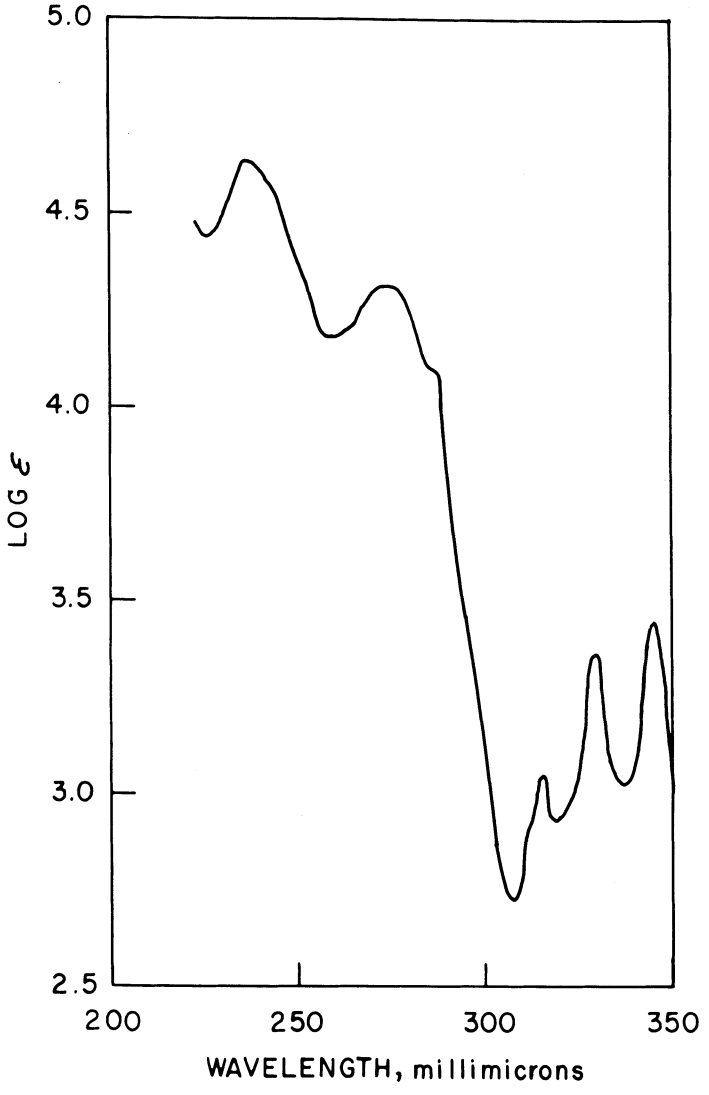
2, 3 - DIMETHYLBENZO [f] QUINOLINE



B.p. [est. 360°]

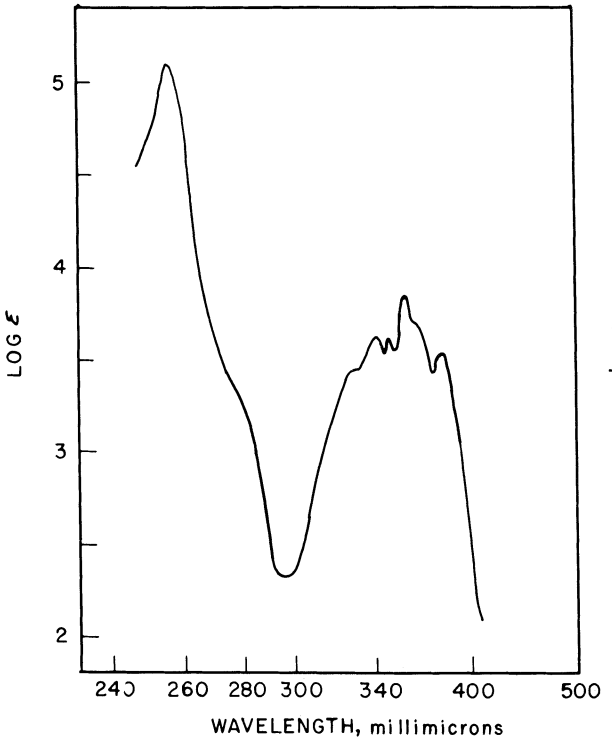
165

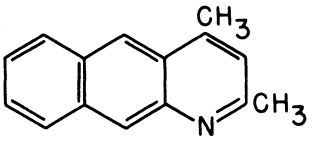


λ max, mμ (EtOH)	log ε
346.0	3.44
330.0	3.37
316.0	3.05
274.0	4.31
235.5	4.64

(53)

2, 4 - DIMETHYLBENZO[g]QUINOLINE





B.p. [est. 370°]

λ EtOH max, mμ	log ε
380.0	3.45
364.0	3.70
357.5	3.85
347.0	3.62
338.0	3.62
329.0	3.45
256.5	5.10

(52)

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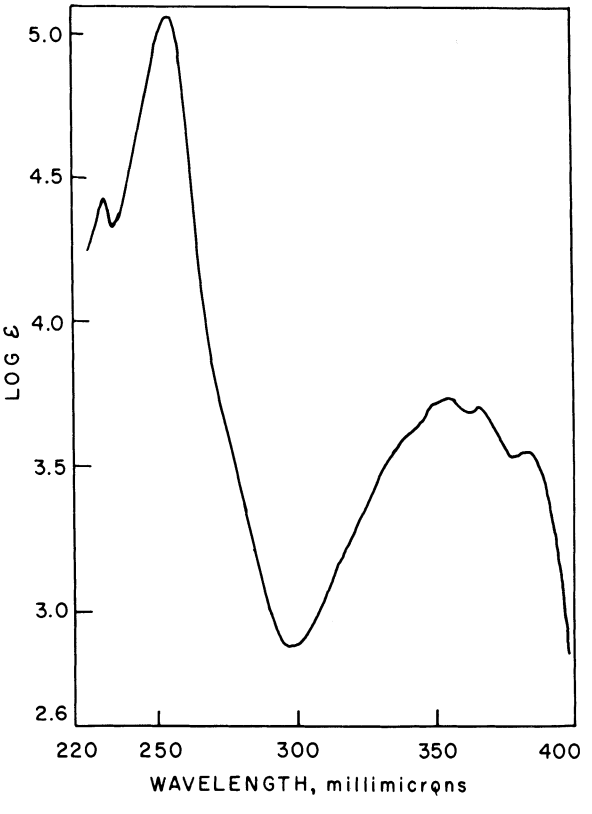
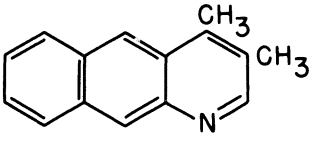
3, 4 - DIMETHYLBENZO[g]QUINOLINE



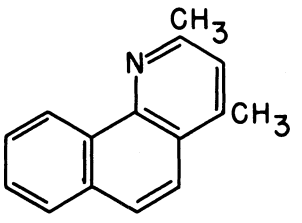


B.p. [est. 370°]

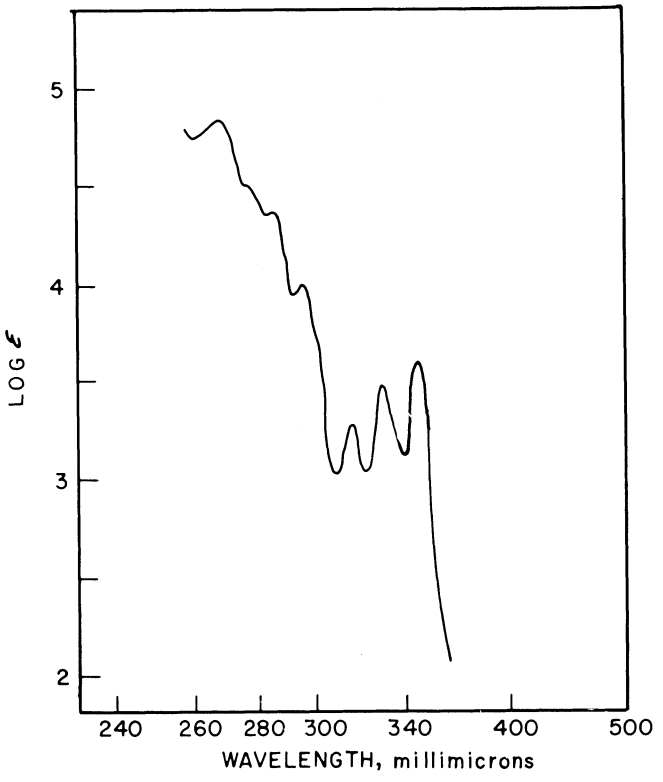
λ EtOH max, mμ	log ε
383.5	3.55
365.5	3.72
355.5	3.74
254.5	5.07
231.0	4.43

(53)

2, 4 - DIMETHYLBENZO[h]QUINOLINE



B.p. 355° (102)



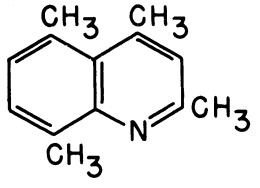
λ max, mμ (EtOH)	log ε
348.0	3.60
331.0	3.50
316.0	3.30
298.0	4.00
287.0	4.35
279.0	4.50
270.0	4.85

(52)

168

2, 4, 5, 8 - TETRAMETHYLQUINOLINE

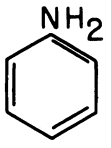
169



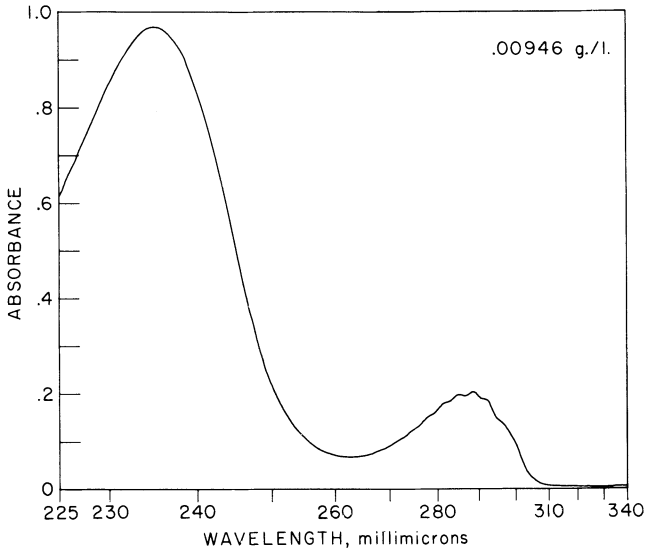
B.p. 168-172°/12 mm. (15)
[est. 310°]

Infrared bands, μ (CS_2): 14.25 (m), 12.77 (m), 12.68 (m), 12.23 (s), 11.67 (m).

ANILINE

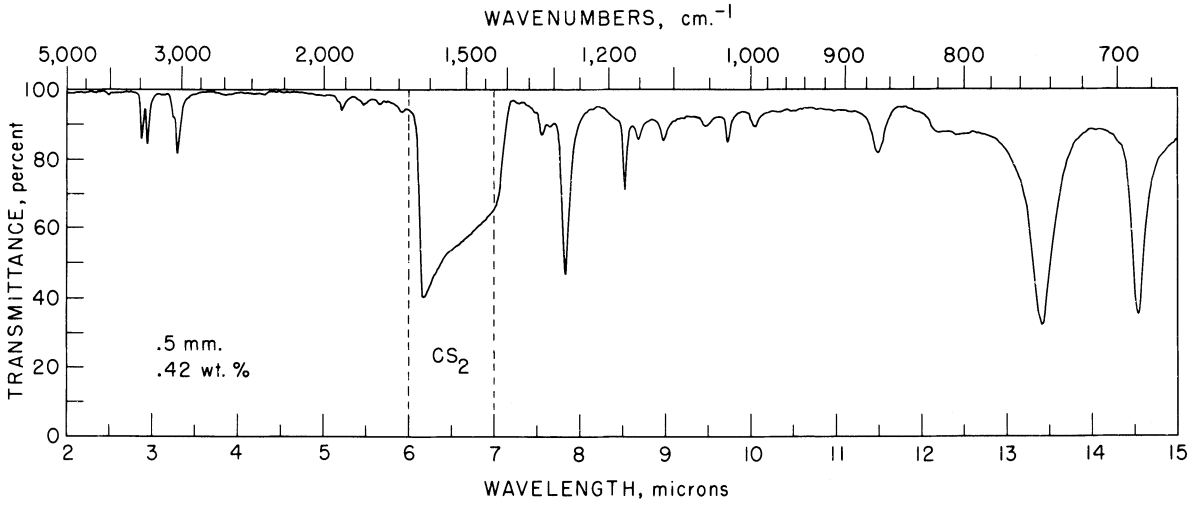


B.p. 183.93° (24)



λ max, mμ (cyclohexane)	log ε
300.0	2.99
296.0	3.15
291.5	3.27
288.3	3.20
284.8	3.29
281.4	3.25
278.2	3.18
235.0	3.98

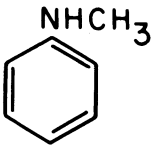
170



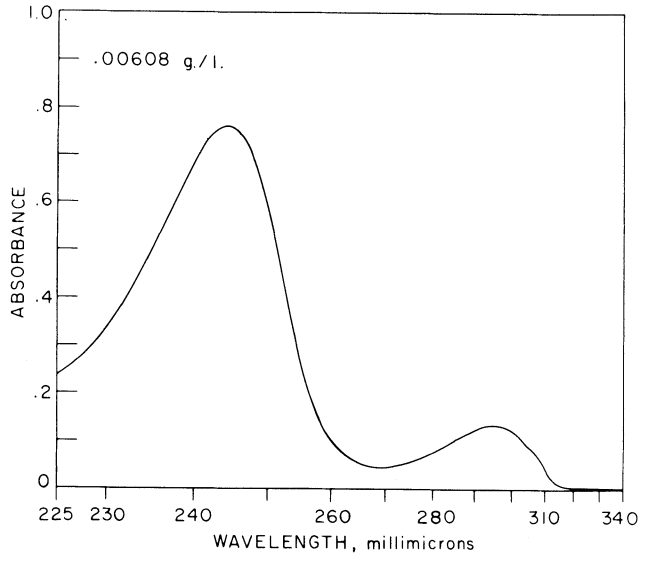
λ^{CS_2}: 14.54 (s), 13.42 (s), 12.40 (w), 12.20 (w), 11.47 (m), 10.05 (w), 9.72 (w), 9.47 (w), 8.97 (w), 8.68 (w), 8.52 (m), 8.40 (w), 7.84 (s), 7.67 (w), 7.57 (w).

569705 O—61——14

N-METHYLANILINE

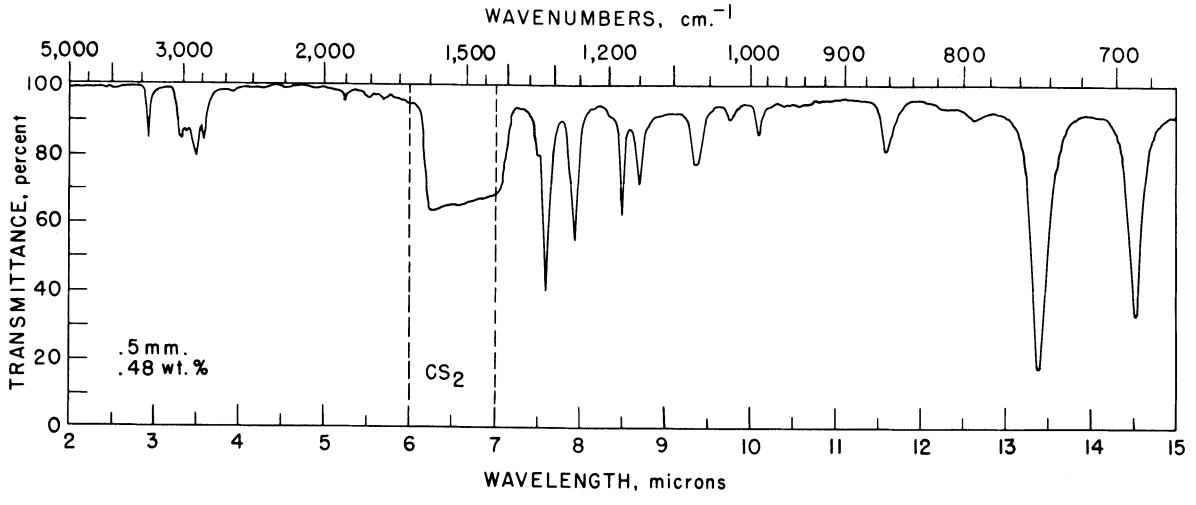


B.p. 196.1° (43)



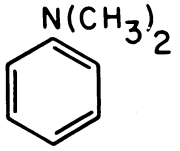
λ cyclohexane max, mμ	log ε
307.0	3.13
295.0	3.37
244.3	4.13

171

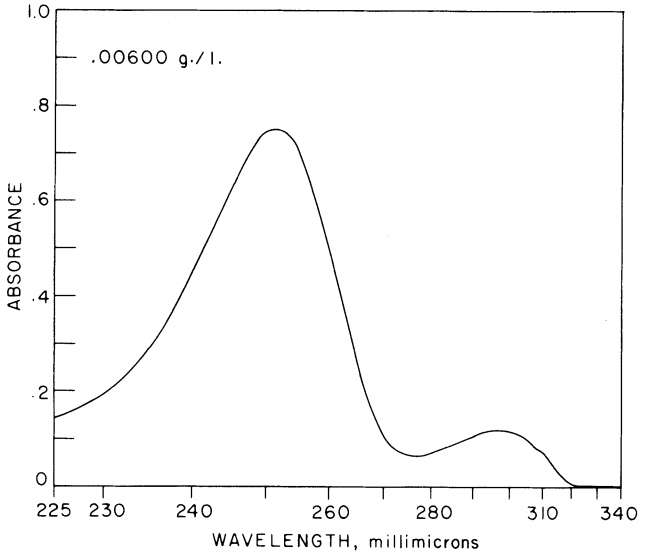


λ^{CS_2}: 14.52 (s), 13.39 (s), 12.62 (w), 11.59 (w), 10.09 (w), 9.77 (w), 9.36 (w), 8.69 (w), 8.49 (m), 8.35 (w), 7.94 (m), 7.87 (w), 7.60 (m), 7.50 (w).

N, N-DIMETHYLANILINE

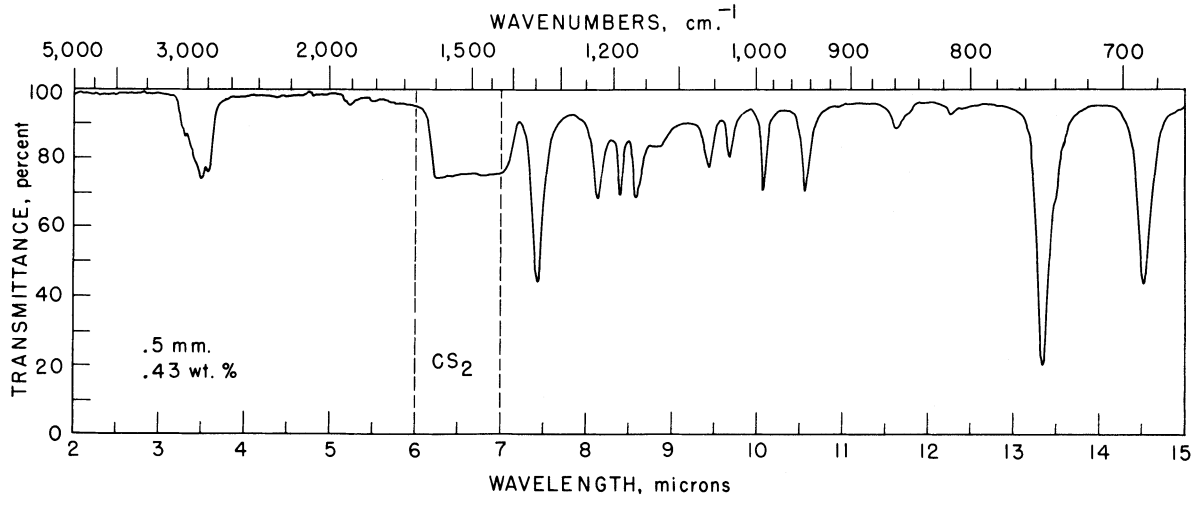


B.p. 192.5-193.5° (43)



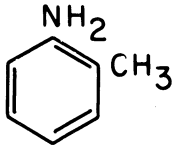
λ max, mμ (cyclohexane)	log ε
308.8	3.24
297.5	3.42
251.5	4.18

172

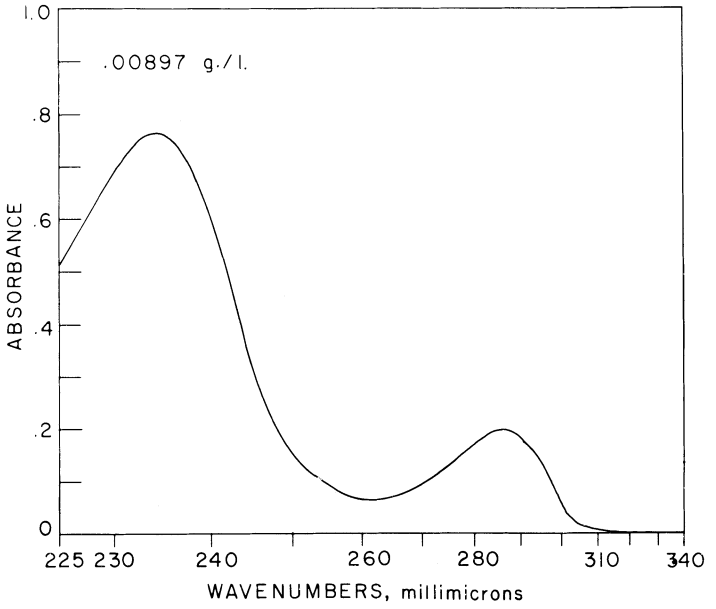


λ^{CS_2}: 14.52 (s), 13.48 (w), 13.35 (s), 12.26 (w), 11.64 (w), 10.57 (m), 10.07 (m), 9.67 (w), 9.44 (w), 8.85 (w), 8.63 (w), 8.58 (m), 8.40 (m), 8.13 (m), 7.44 (s).

2-METHYLANILINE

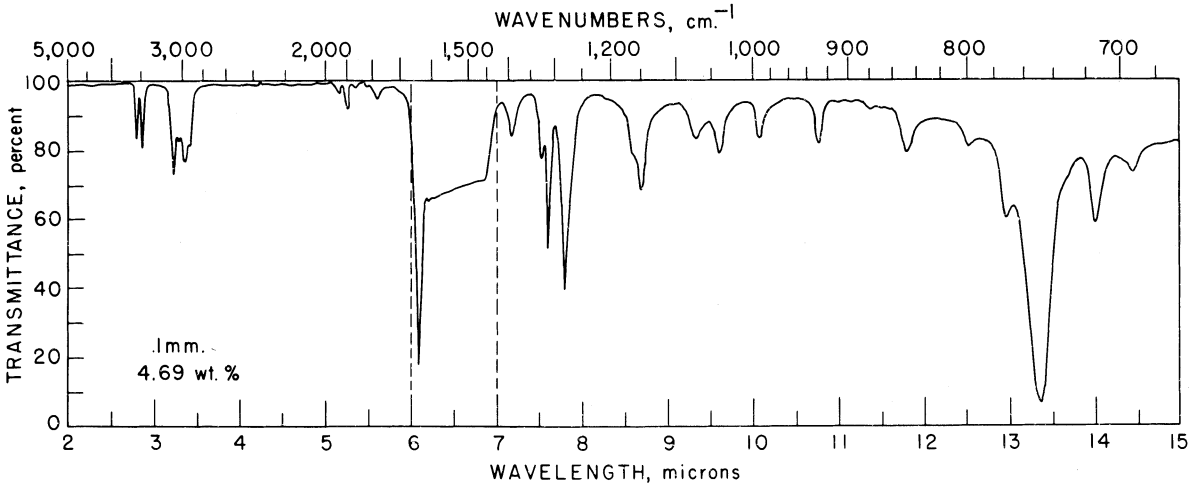


B.p. 200.3° (24)



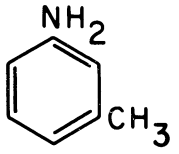
λ max, mμ (cyclohexane)	log ε
293.0	3.28
285.5	3.39
234.0	3.96

173

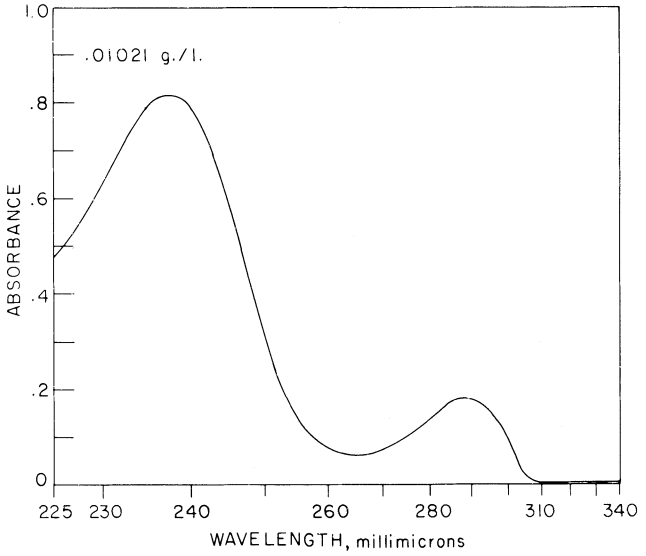


λ^{CS_2}: 14.47 (w), 14.02 (m), 13.70(w), 13.38 (s), 12.98 (w), 12.55 (w), 11.82 (w), 11.40 (w), 10.80 (w), 10.10 (w), 9.64 (w), 9.37 (w), 8.72 (m), 8.65 (w), 7.82 (m), 7.63 (m), 7.56 (w), 7.20 (w).

3-METHYLANILINE

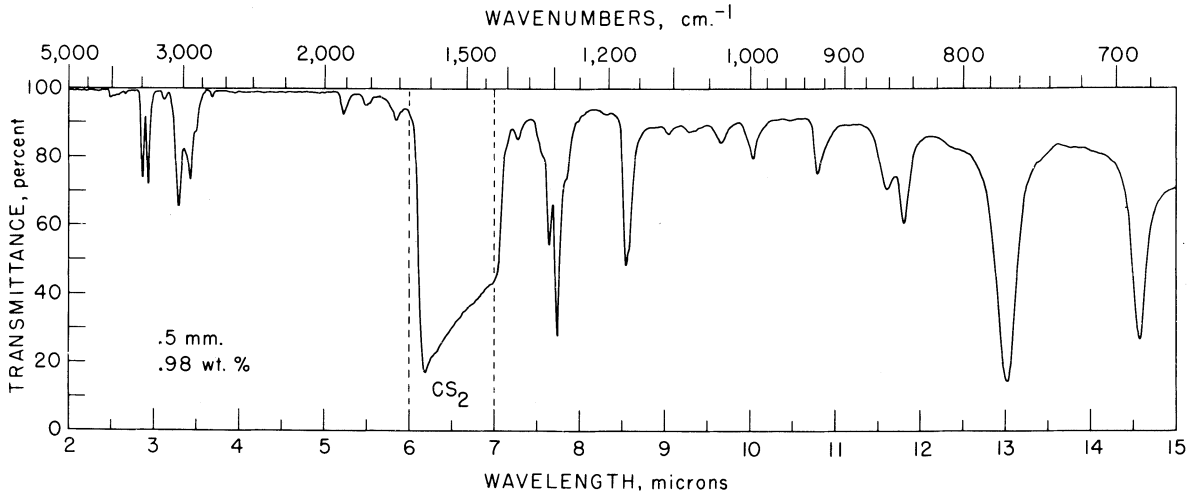


B.p. 203.34° (24)



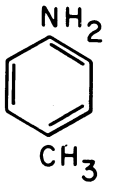
λ max, mμ (cyclohexane)	log ε
297.0	3.17
289.0	3.33
237.5	3.93

174

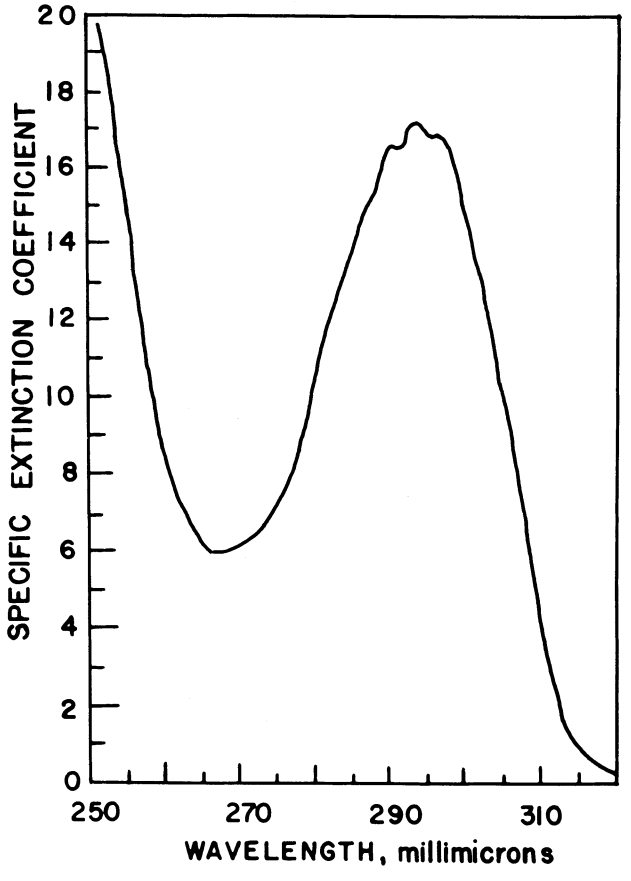


λ^{CS_2}: 14.57 (s), 13.02 (s), 11.80 (m), 11.60 (s), 10.78 (w), 10.02 (w), 9.65 (w), 9.29 (w), 9.04 (w), 8.57 (w), 8.54 (m), 7.85 (w), 7.74 (m), 7.64 (w), 7.57 (w), 7.52 (w), 7.27 (w).

4-METHYLANILINE



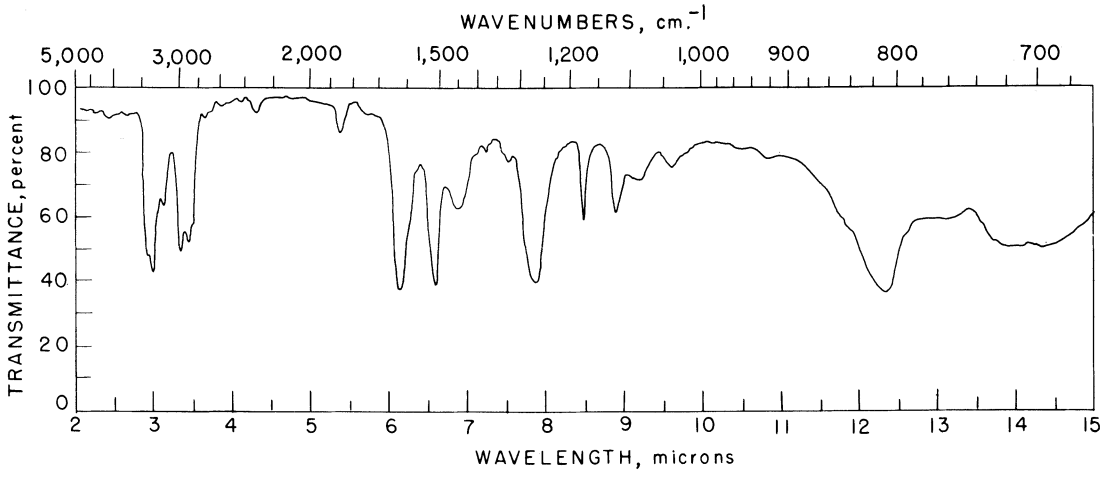
B.p. 200.55° (24)



λ max, mμ (iso-octane)	log ε
297	3.25
293	3.27
290	3.25

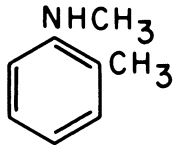
(109)

175

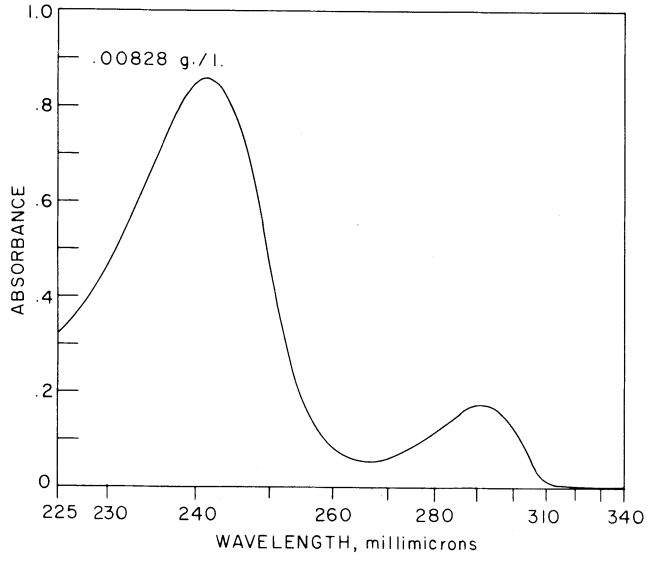


λ_{max}^{melt}: 13.20 (w), 12.35 (s), 10.85 (w), 9.62 (w), 9.20 (w), 8.90 (m), 8.48 (m), 7.85 (s), 7.54 (w), 7.46 (w), 7.25 (w). (99)

N-METHYL-2-METHYLANILINE

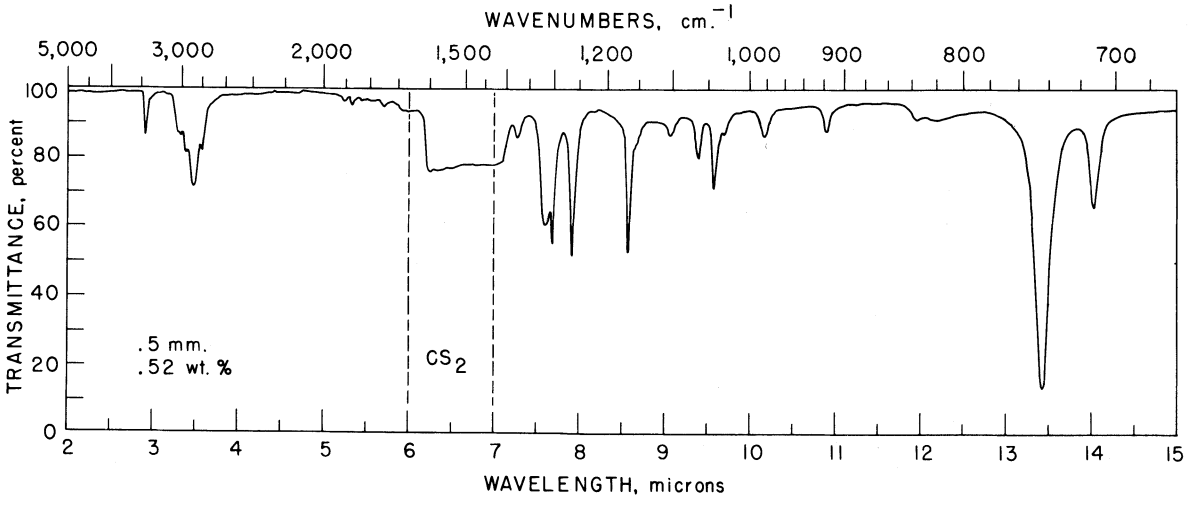


B.p. 207-208° (43)



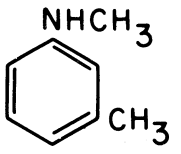
λ cyclohexane max, mμ	log ε
301.0	3.24
291.5	3.41
241.5	4.09

176

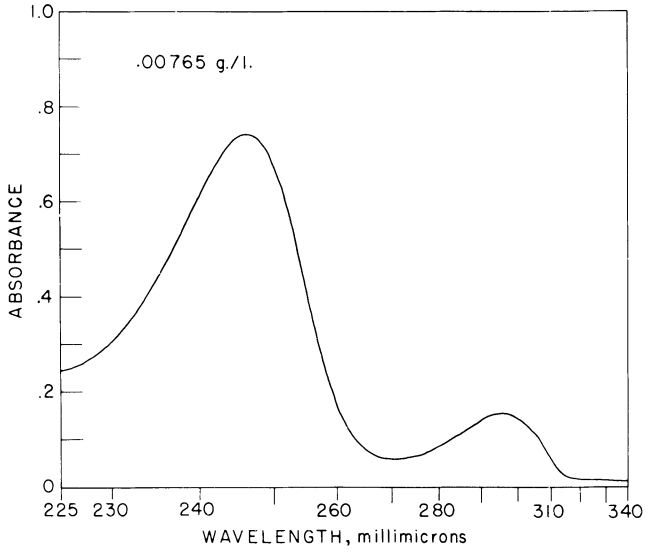


λ^{CS_2}: 14.03 (m), 13.43 (s), 12.15 (w), 11.97 (w), 10.90 (w), 10.16 (w), 9.70 (w), 9.57 (m), 9.40 (w), 9.07 (w), 8.58 (m), 7.92 (m), 7.68 (m), 7.60 (m), 7.27 (w).

N-METHYL-3-METHYLANILINE

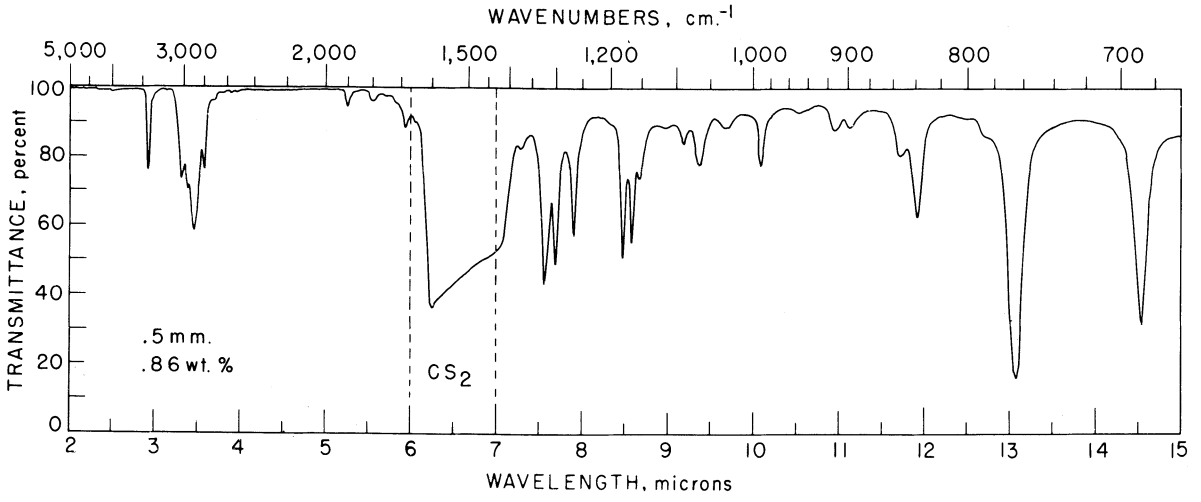


B.p. 206-207° (43)



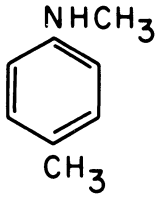
λ max, mμ (cyclohexane)	log ε
306.0	3.24
296.5	3.44
246.5	4.07

177

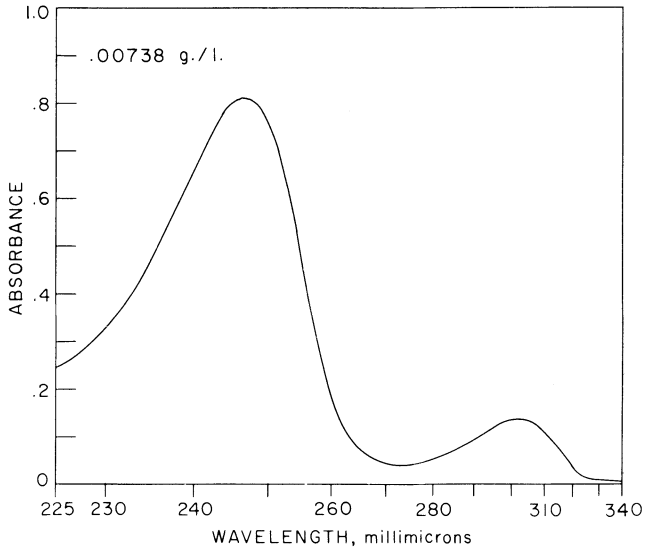


λ^{CS_2}: 14.52 (s), 13.06 (s), 11.90 (s), 11.70 (w), 11.62 (w), 10.93 (w), 10.52 (w), 10.08 (w), 9.67 (w), 9.37 (w), 9.18 (w), 8.66 (w), 8.57 (m), 8.47 (m), 7.89 (m), 7.68 (m), 7.55 (m), 7.29 (w).

N-METHYL-4-METHYLANILINE

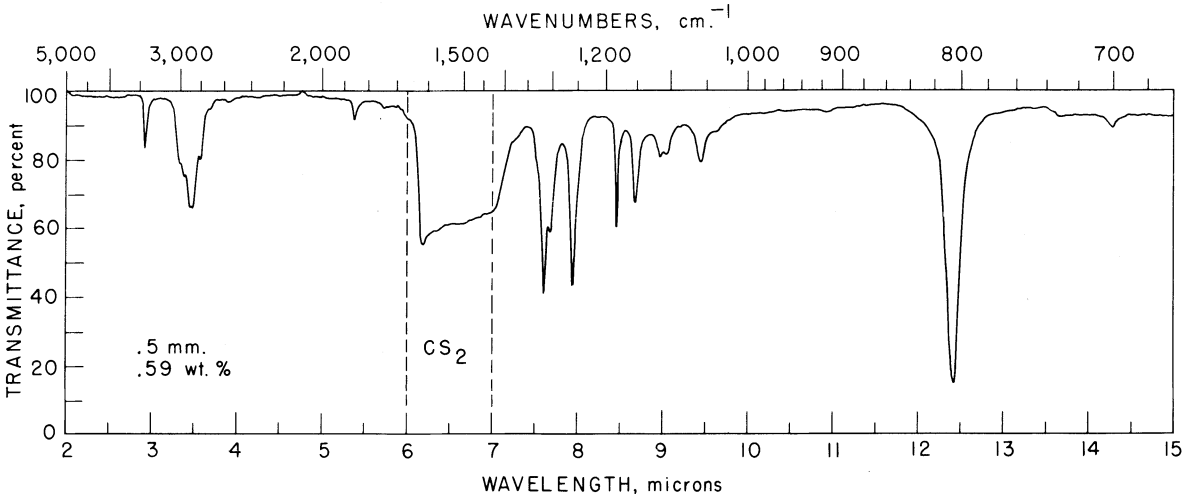


B.p. 209-211°/761 mm. (43)



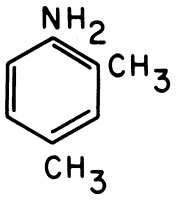
λ max, mμ (cyclohexane)	log ε
303.0	3.31
246.7	4.12

178

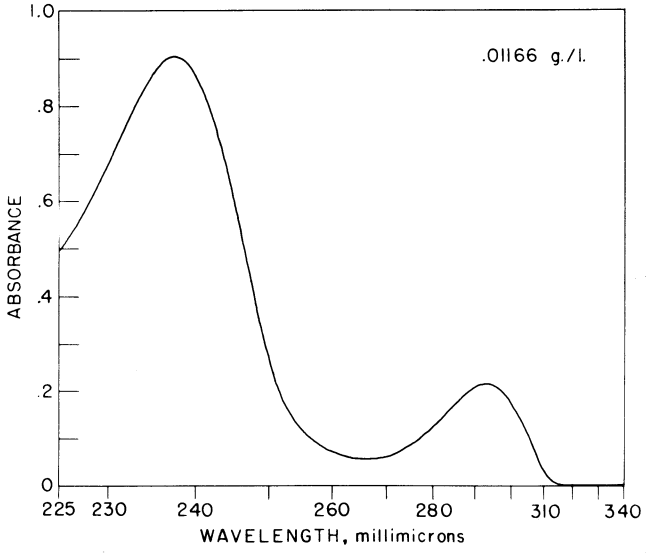


λ^{CS_2}: 14.28 (w), 12.42 (s), 9.64 (w), 9.45 (w), 9.05 (w), 8.97 (w), 8.68 (m), 8.47 (m), 7.95 (m), 7.68 (w), 7.62 (m), 7.55 (w), 7.25 (w).

2, 4 - DIMETHYLANILINE

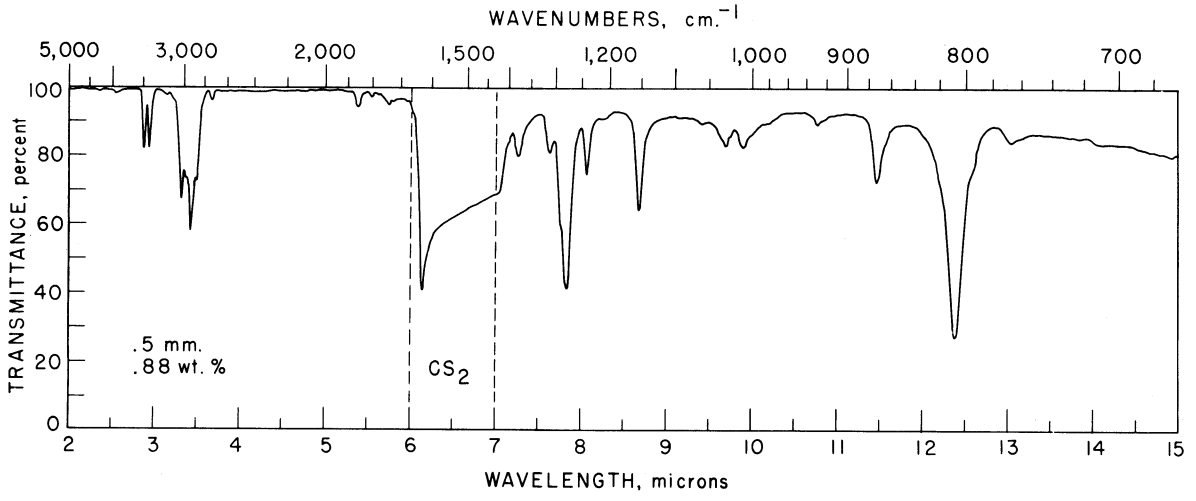


B.p. 215.8-216.0°/728 mm. (43)



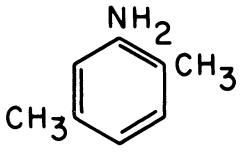
λ cyclohexane max, mμ	log ε
302.0	3.19
293.0	3.37
237.5	3.97

179

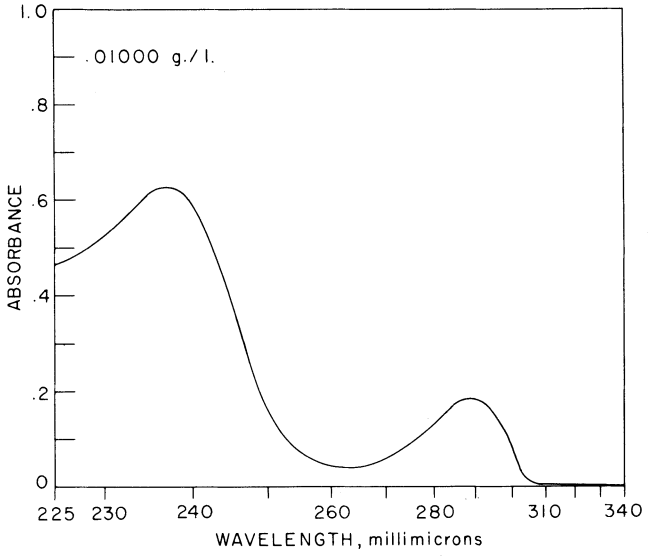


λ^{CS_2}: 13.04 (w), 12.38 (s), 11.47 (m), 10.77 (w), 9.80 (w), 9.69 (w), 9.40 (w), 8.68 (m), 8.07 (w), 7.83 (s), 7.76 (w), 7.63 (w), 7.25 (w).

2, 5 - DIMETHYLANILINE

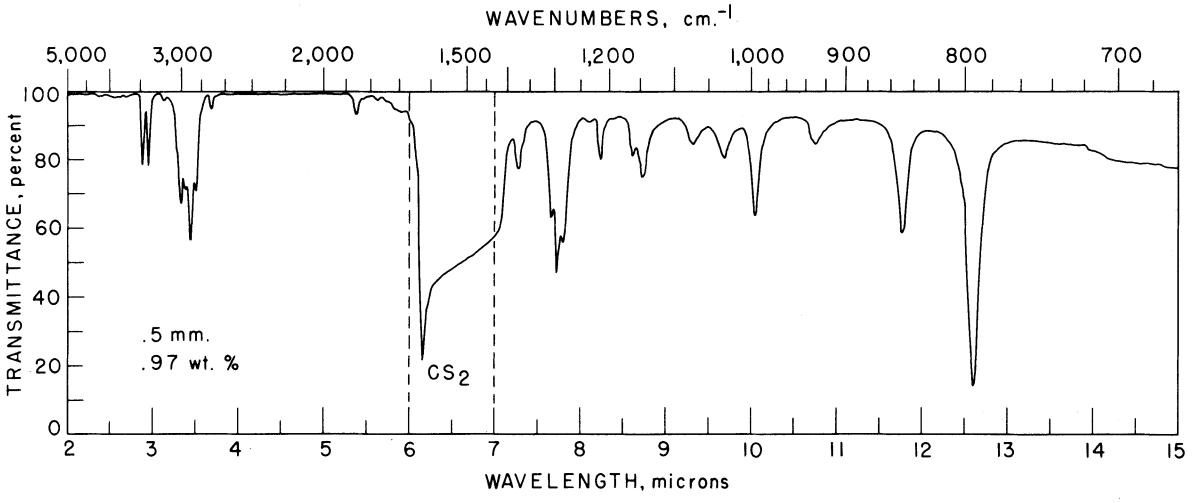


B.p. 213.5° (43)



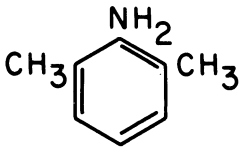
λ max, mμ (cyclohexane)	log ε
296.0	3.24
288.8	3.35
237.0	3.88

180

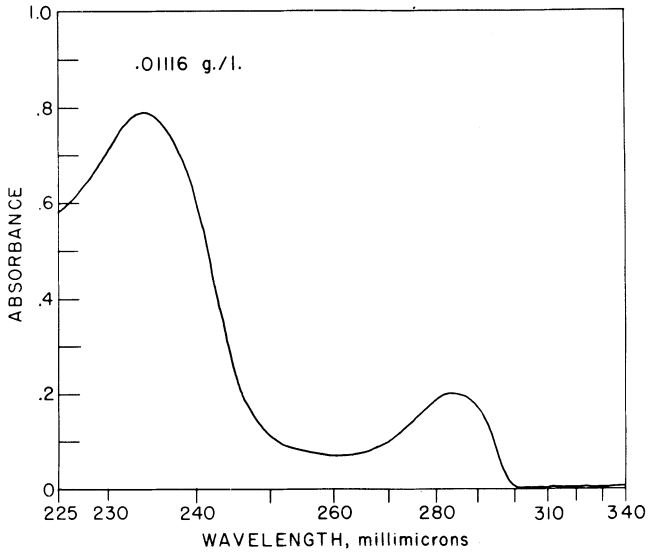


λ^{CS_2}: 12.61 (s), 11.77 (m), 10.75 (w), 10.04 (m), 9.68 (w), 9.32 (w), 8.74 (w), 8.62 (w), 8.24 (w), 8.10 (w), 7.80 (w), 7.73 (m), 7.65 (w), 7.27 (w).

2, 6 - DIMETHYLANILINE

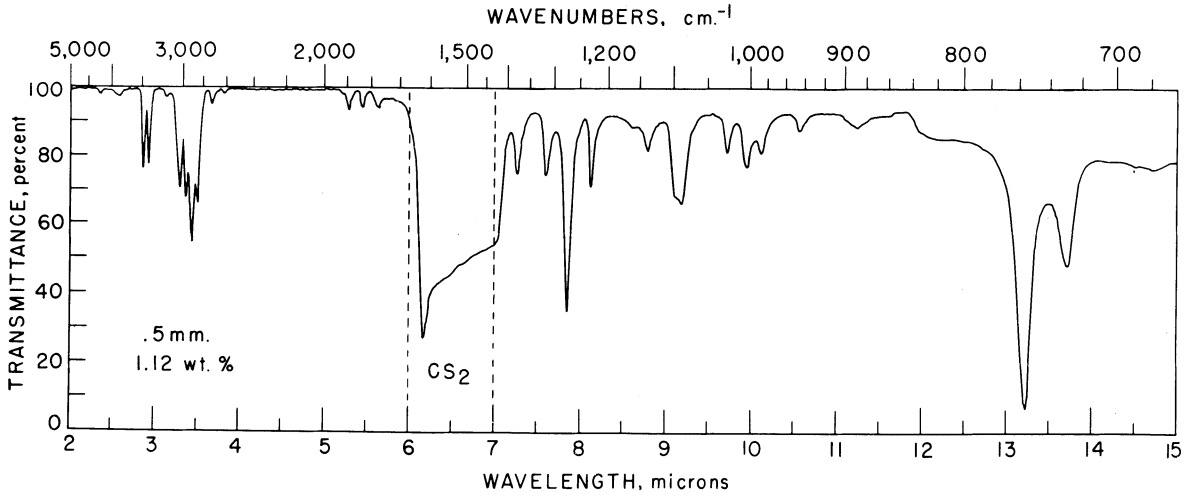


B.p. 214°/739 mm. (43)



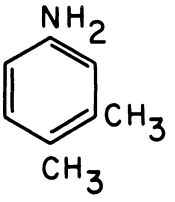
λ max, mμ (cyclohexane)	log ε
290.0	3.27
284.5	3.34
234.0	3.93

181

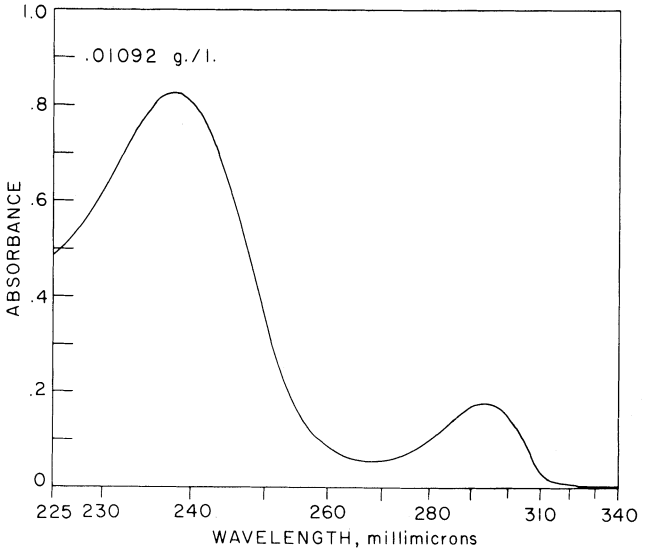


λ^{CS_2}: 13.71 (m), 13.22 (s), 11.23 (w), 10.57 (w), 10.12 (w), 9.95 (w), 9.72 (w), 9.19 (m), 9.12 (m), 8.78 (w), 8.62 (w), 8.12 (m), 7.85 (s), 7.69 (m), 7.26 (m).

3, 4 - DIMETHYLANILINE

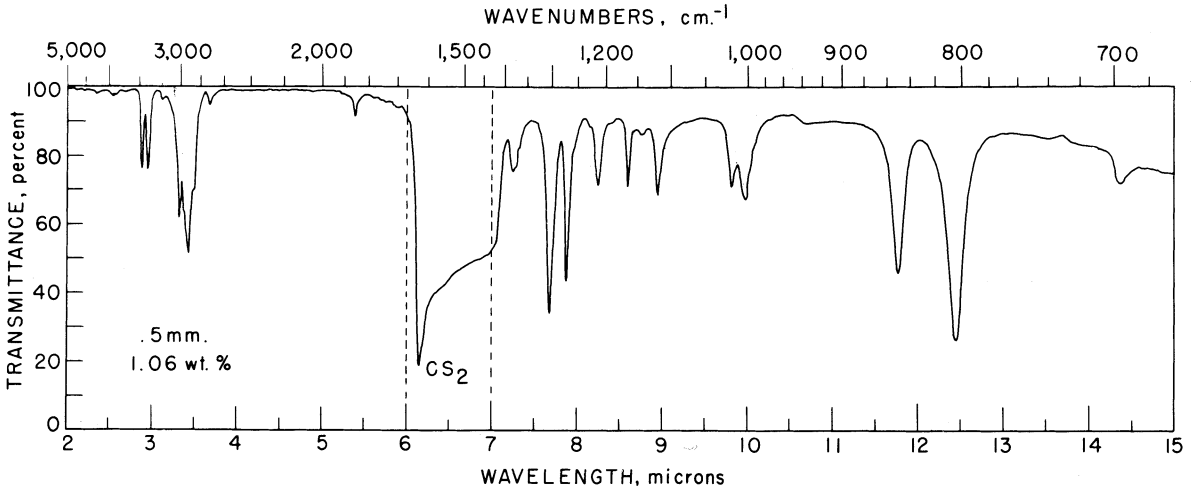


B.p. 226° (43)



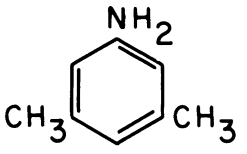
λ max, mμ (cyclohexane)	log ε
304.0	3.10
293.5	3.31
238.0	3.96

182

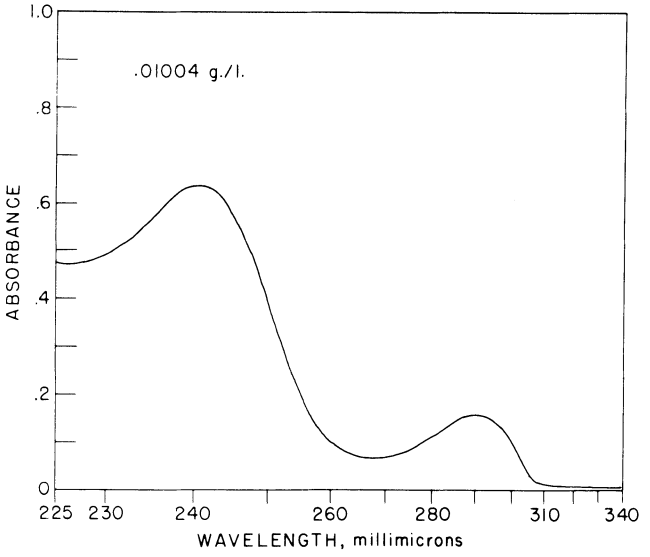


λ^{CS_2}: 14.35 (w), 12.44 (s), 11.76 (m), 10.67 (w), 9.98 (m), 9.81 (w), 8.94 (w), 8.77 (w), 8.59 (w), 7.87 (m), 7.67 (m), 7.25 (w).

3, 5 - DIMETHYLANILINE

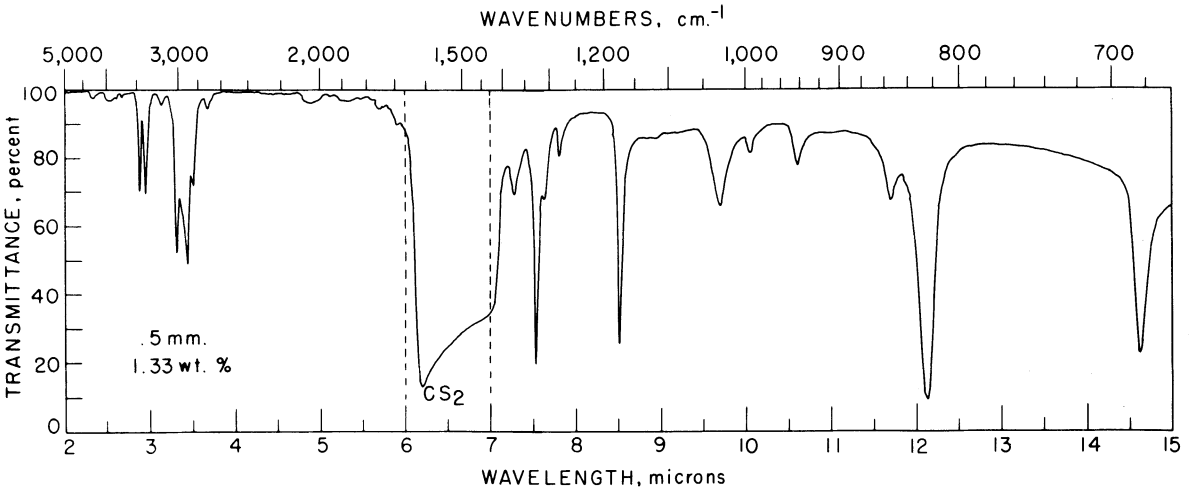


B.p. 220-221° (43)



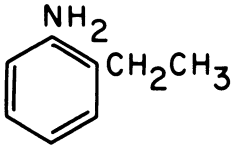
λ cyclohexane max, mμ	log ε
298.0	3.15
290.0	3.27
240.5	3.89

183

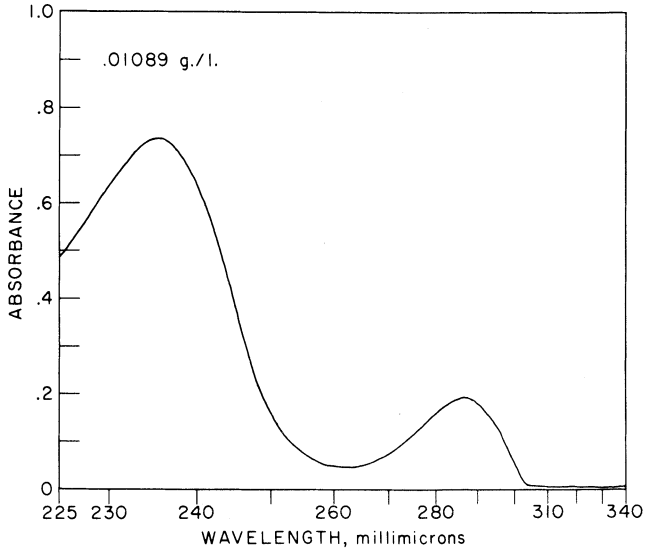


λ^{CS_2}: 14.62 (s), 12.13 (s), 11.70 (w), 10.60 (w), 10.05 (w), 9.70 (m), 8.92 (w), 8.52 (s), 7.82 (w), 7.63 (w), 7.53 (s), 7.29 (w).

2-ETHYLANILINE

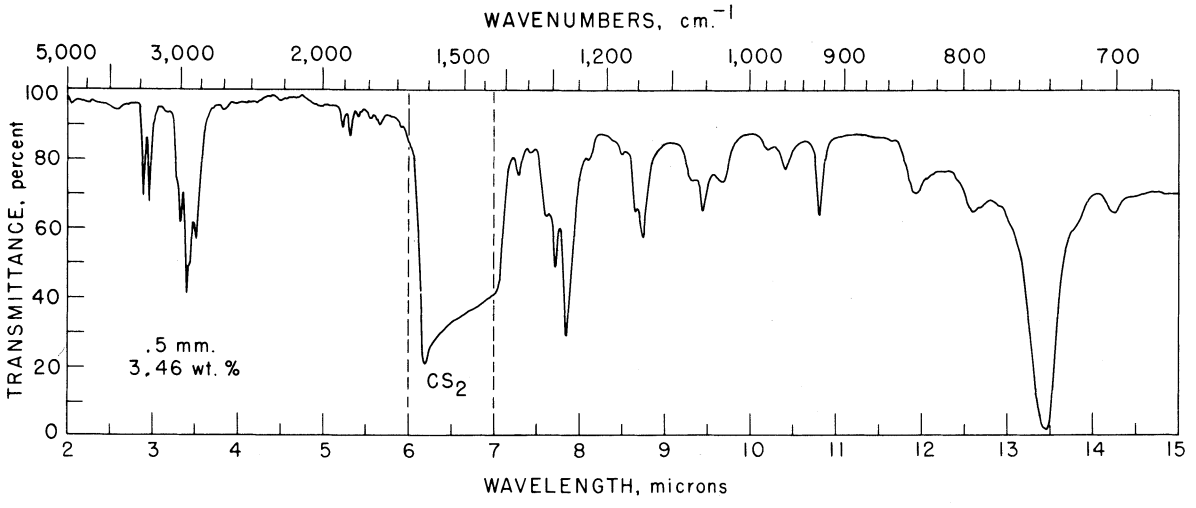


B.p. 215-216°/769 mm. (43)



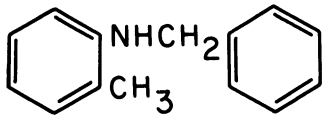
λ max, mμ (cyclohexane)	log ε
287.0	3.33
235.0	3.91

184

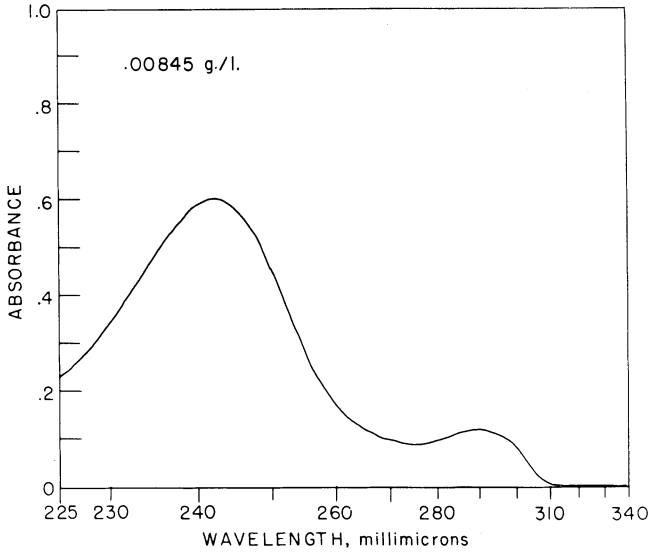


λ^{CS_2}: 14.25 (w), 13.80 (w), 13.45 (s), 12.60 (w), 11.93 (w), 10.82 (w), 10.42 (w), 10.20 (w), 9.69 (w), 9.45 (w), 9.32 (w), 8.75 (w), 8.67 (w), 8.50 (w), 8.12 (w), 7.85 (m), 7.72 (w), 7.62 (w), 7.44 (w), 7.29 (w).

N-BENZYL-2-METHYLANILINE

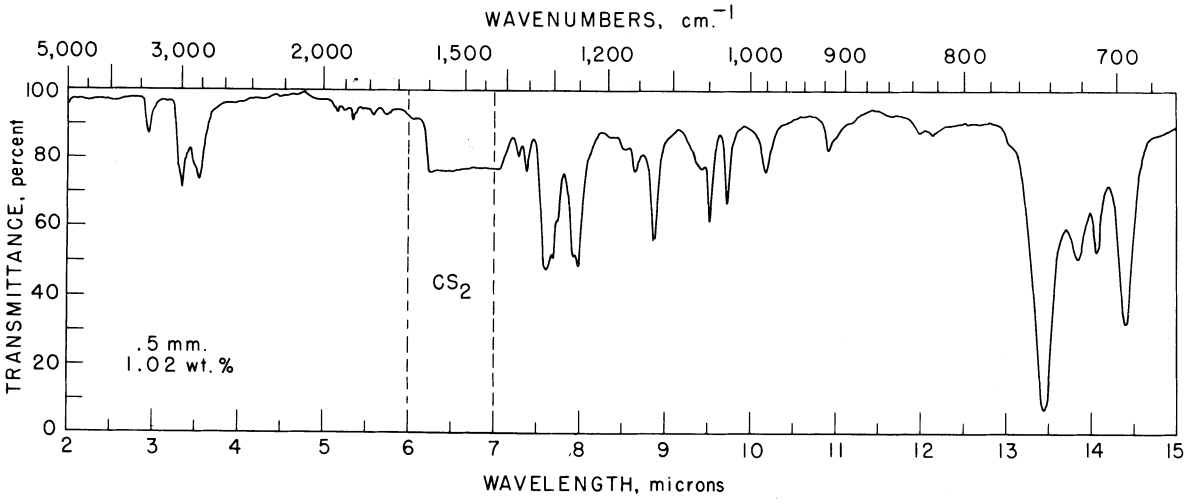


B.p. 176°/10 mm. (43)
[est. 310°]



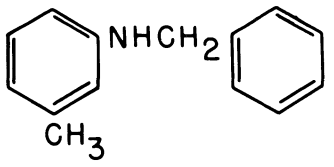
λ max, mμ (cyclohexane)	log ε
300.0	3.32
290.5	3.48
265.0	3.49
242.3	4.15

185

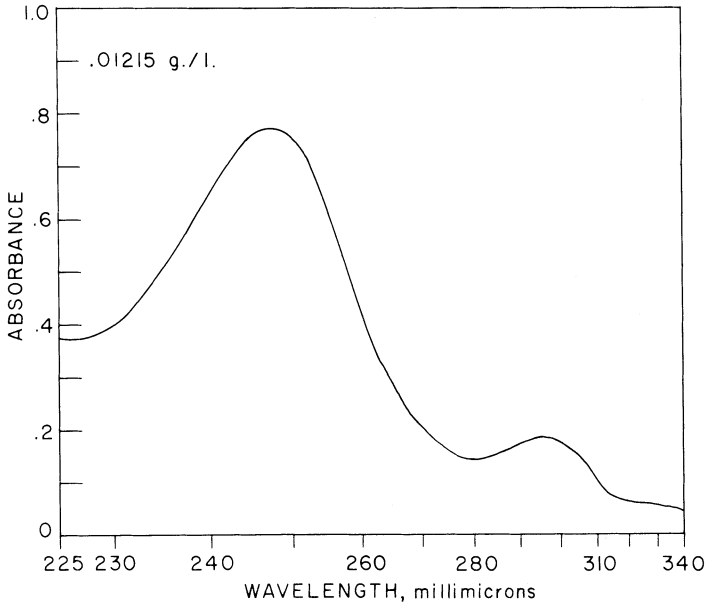


λ^{CS_2}: 14.40 (s), 14.06 (m), 13.85 (m), 13.45 (s), 13.05 (w), 12.15 (w), 12.00 (w), 10.92 (w), 10.18 (w), 9.74 (w), 9.52 (m), 9.43 (w), 8.87 (m), 8.65 (w), 8.54 (w), 7.98 (m), 7.93 (m), 7.74 (w), 7.69 (w), 7.62 (m), 7.37 (w), 7.29 (w).

N-BENZYL-3-METHYLANILINE

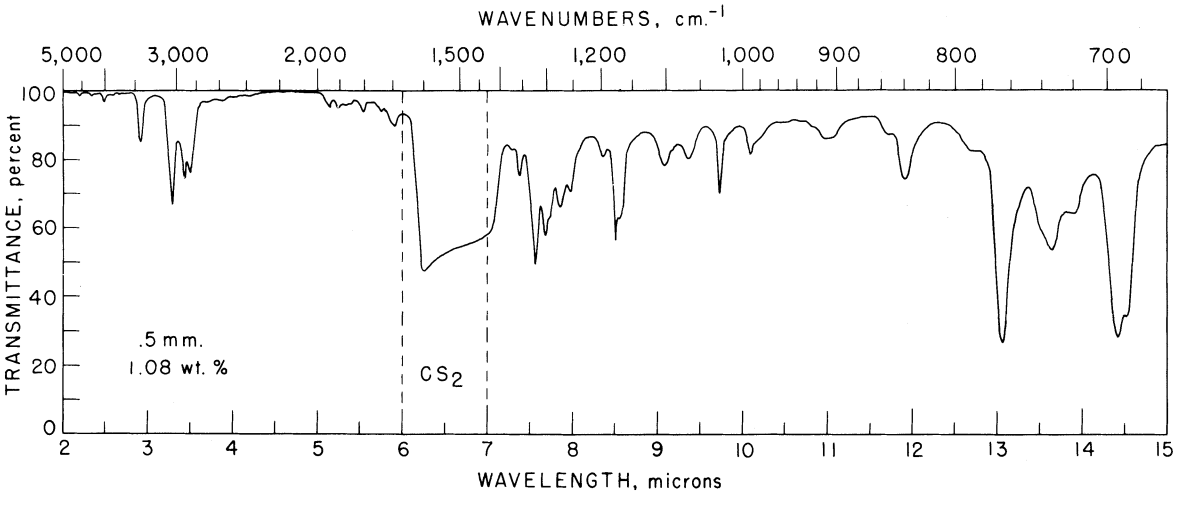


B.p. 312° (43)



λ max, mμ (cyclohexane)	log ε
305.2	3.37
296.0	3.48
247.5	4.10

186



CS_2

λ : 14.52 (s), 14.41 (s), 13.90 (w), 13.64 (m), 13.50 (m), 13.05 (s), 12.65 (w), 11.90 (m), 11.70 (w), 11.02 (w), 10.96 (w), 10.07 (w), 9.72 (m), 9.37 (w), 9.17 (w), 9.08 (w), 8.55 (w), 8.50 (m), 8.35 (w), 7.97 (w), 7.85 (w), 7.73 (w), 7.67 (m), 7.55 (m), 7.37 (w), 7.27 (w).

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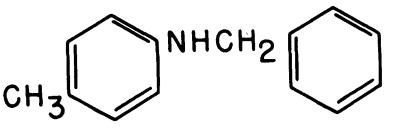
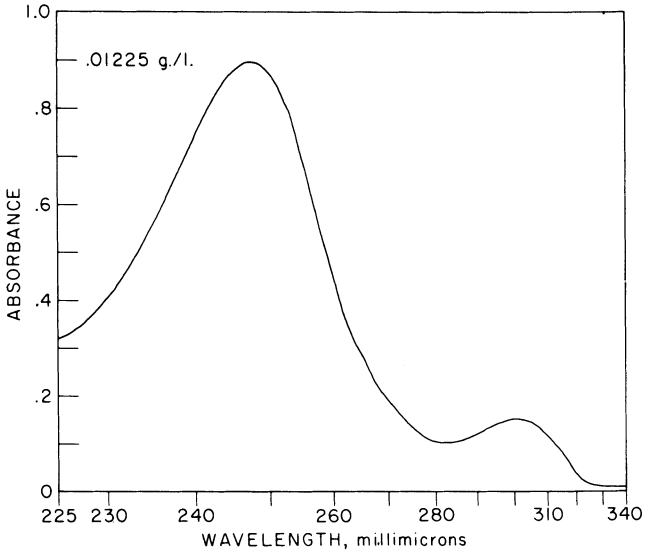
N-BENZYL-4-METHYLANILINE

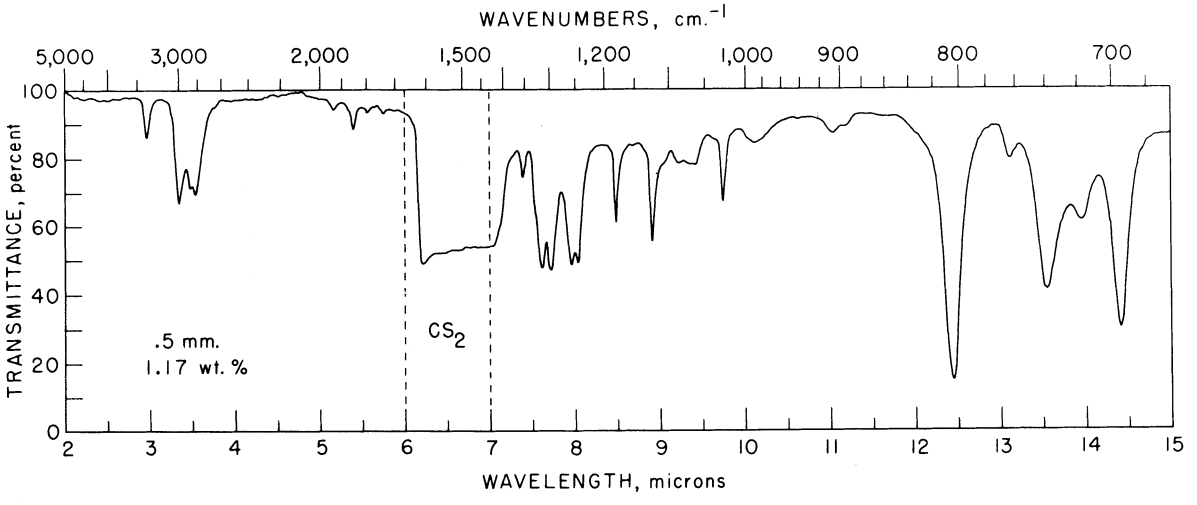


B.p. 312-313° (43)



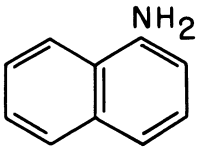
λ max, mμ (cyclohexane)	log ε
301.2	3.39
247.2	4.16

187

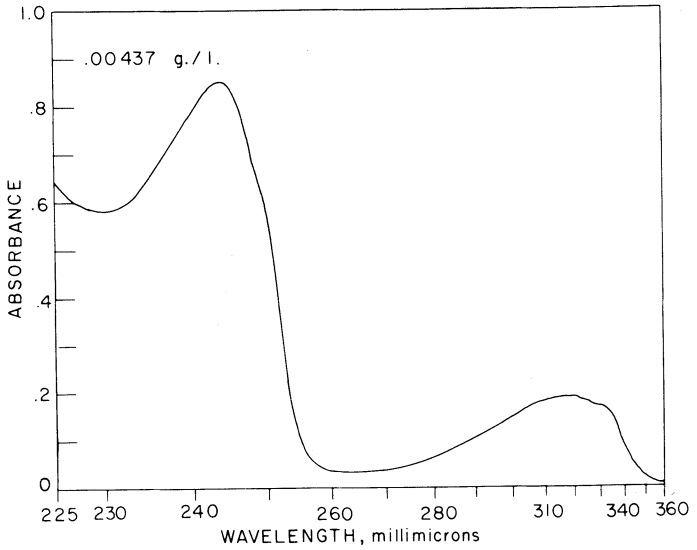


λ^{CS_2}: 14.40 (s), 13.95 (m), 13.54 (s), 13.10 (w), 12.45 (s), 11.18 (w), 11.02 (w), 9.74 (w), 9.40 (w), 9.22 (w), 9.04 (w), 8.92 (m), 8.48 (m), 8.04 (m), 7.95 (m), 7.72 (m), 7.61 (m), 7.55 (w), 7.39 (w).

1-NAPHTHYLAMINE

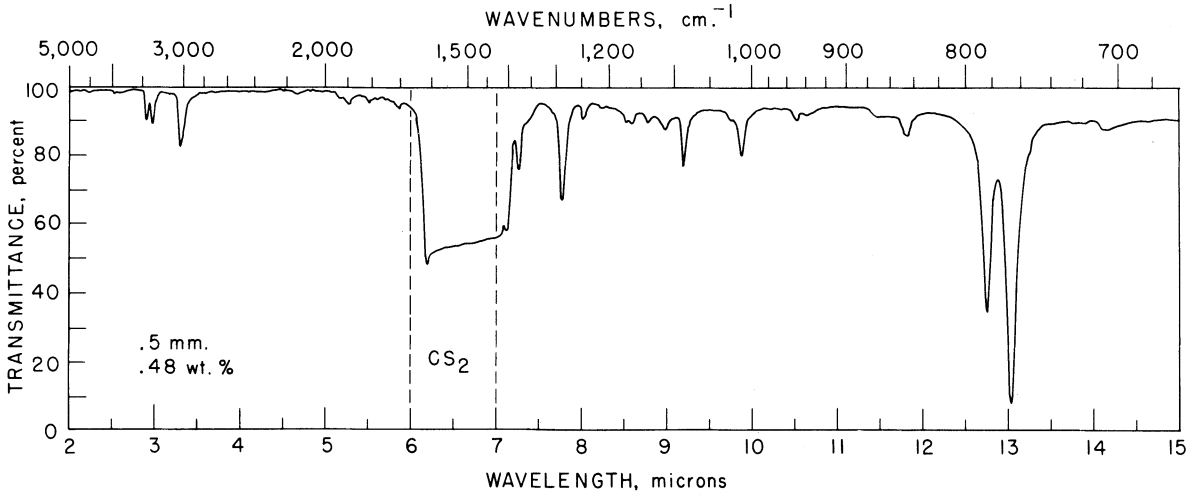


B.p. 300.8° (43)



λ max, mμ (cyclohexane)	log ε
330.0	3.73
324.0	3.76
319.0	3.78
311.0	3.76
249.5	4.30
243.7	4.45

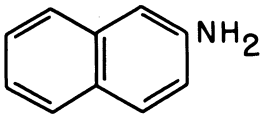
188



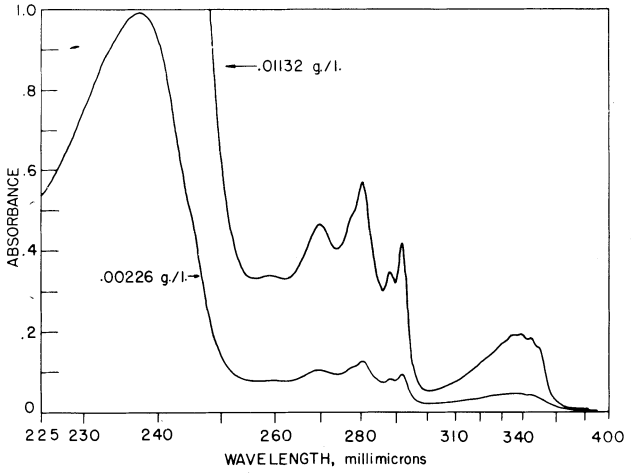
CS_2

λ : 14.14 (w), 13.04 (s), 12.75 (m), 11.80 (w), 10.64 (w), 10.52 (w), 9.88 (w), 9.75 (w), 9.20 (w), 8.97 (w), 8.78 (w), 8.60 (w), 8.52 (w), 8.23 (w), 8.02 (w), 7.77 (m), 7.40 (w), 7.26 (w), 7.12 (w).

2-NAPHTHYLAMINE

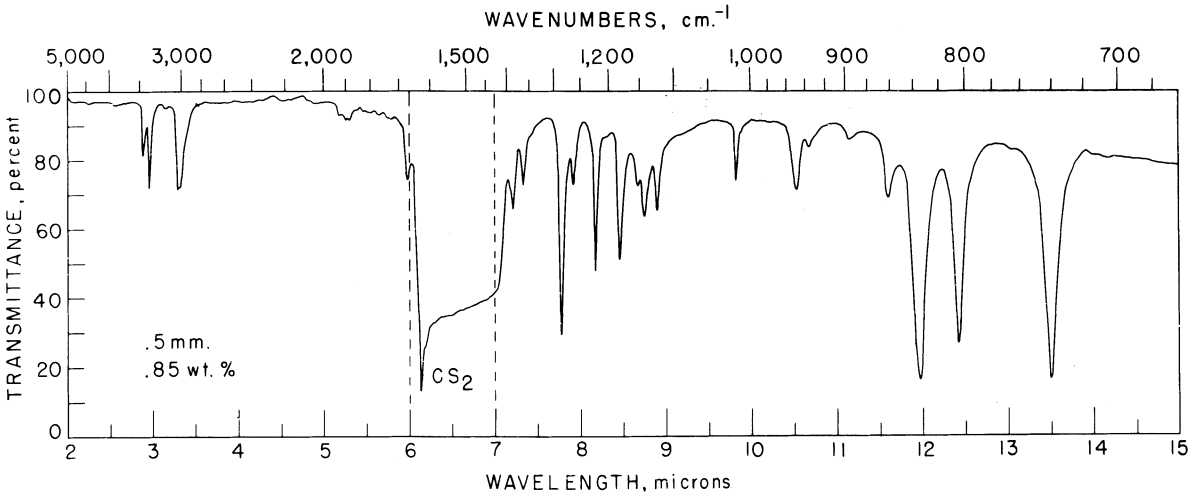


B.p. 294° (43)



λ max, mμ (cyclohexane)	log ε
348.8	3.30
344.8	3.36
339.3	3.38
335.0	3.38
330.0	3.32
325.0	3.25

189



λ^{CS_2}: 13.50 (s), 12.42 (s), 11.97 (s), 11.60 (w), 11.15 (w), 10.67 (w), 10.52 (w), 9.83 (w), 8.90 (w), 8.75 (w), 8.68 (w), 8.47 (m), 8.18 (m), 7.92 (w), 7.78 (s), 7.34 (w), 7.22 (w).

BIBLIOGRAPHY [8]

1. ADAMS, R., AND CAMPBELL, J. 2,4,5- and 2,4,7-Trimethylquinolines. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1021–1022.
2. AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 44. Catalog of Infrared Spectra. Carnegie Institute of Technology, Pittsburgh, Pa.[9]
3. ANCHEL, M., AND BLATT, A. H. The Cyclic Dehydration of Biphenyl Derivatives to Fluorenes. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 1948–1952.
4. ARDASHEV, B. I. [Quinoline Derivatives. IV. Synthesis of Quinaldine and Some Methyl Homologs from Aromatic Amines and Ethylene Glycol.] Zhur. Obshcheĭ Khim., vol. 19, 1949, pp. 550–555.
5. BADER, A. R. Cyclopentenylphenols. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 5967–5969.
6. ———. Unsaturated Phenols. III. Alkali Isomerization. Jour. Am. Chem. Soc., vol. 78, 1956, pp. 1709–1713.
7. BARKER, L., AND HOLLINGWORTH, N. W. The Composition of Ammoniacal Liquors. II. Analysis of the Phenolic Content by Chromatography. Jour. Appl. Chem. (London), vol. 9, 1959, pp. 16–25.
8. BEILSTEINS HANDBUCH DER ORGANISCHEN CHEMIE. Julius Springer, Berlin, Germany, vol. 6, 1923, 1285 pp.; vol. 6, 2d supp., 1944, 1245 pp.; vol. 20, 1935, 566 pp.
9. BELLAMY, L. J. The Infrared Spectra of Complex Molecules. John Wiley & Sons, Inc., New York, N.Y., 1956, 323 pp.
10. BERINGER, F. M., AND GEERING, E. J. The Aromatization and Rearrangement of Cyclic Ketones. III. 2,3,5- and 3,4,5-Trimethylphenol From Isophorone. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 2633–2635.
11. BLACKBURN, W. H., BARKER, L., AND CATCHPOLE, J. R. An Investigation Into the Composition of Ammoniacal Liquor. I. Continuous Vertical Retort Liquor. Gas Council Research Commun. GC 17, 1954, 47 pp.
12. BLACKBURN, W. H., BARKER, L., CATCHPOLE, J. R., AND HOLLINGWORTH, N. W. An Investigation Into the Composition of Ammoniacal Liquor. I (Continued). Continuous Vertical Retort Liquor. Gas Council Research Commun. GC 24, 1955, 101 pp.
13. BONNER, T. G., THORNE, M. P., AND WILKINS, J. M. The Cyclodehydration of Anils. I. Kinetics of Cyclodehydration of 2-Anilino- and 2-p-Toluidinopent-2-en-4-one in Sulfuric Acid. Jour. Chem. Soc., 1955, pp. 2351–2358.
14. BOWEN, D. M., BELFIT, R. W., JR., AND WALSER, R. A. The Synthesis and Nitration of 2,6- and 2,7-Dimethylquinoline and of 2,5,8-Trimethylquinoline. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 4307–4311.
15. BRAUN, J. VON, GMELIN, W., AND PETZOLD, A. [bz-Tetrahydroquinolines and Their Derivatives. IV.]. Ber. deut. chem. Gesell., vol. 57B, 1924, pp. 382–391.
16. BRAUNS, F. E. The Chemistry of Lignin. Academic Press, Inc., New York, N.Y., 1952, 808 pp.
17. BREWER, J., AND SMITH, C. D. Studies on Texas Lignite Tar. Analysis of Low Boiling Tar Acids by Infrared Spectroscopy. Am. Chem. Soc. 135th Meeting, Boston, Abs. of Papers, 1959, p. 3J.
18. BREWSTER, C. M., AND HARRIS, J. C. Some Halogen Derivatives of Acyl and Alkyl Resorcinols. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 4866–4872.
19. BROWNING, L. C., AND WATTS, J. O. Interpretation of Areas Used for Quantitative Analysis in Gas-Liquid Partition Chromatography. Anal. Chem., vol. 29, 1957, pp. 24–27.
20. BUU-HOĬ, NG. PH., AND GUETTIER, D. [Substituted Quinolines. V. Polyalkyl Quinolines and Polyalkyl Naphthoquinolines.] Rec. trav. chim., vol. 65, 1946, pp. 502–508.
21. CANNON, C. G., AND SUTHERLAND, G. B. B. M. The Infrared Absorption Spectra of Some Aromatic Compounds. Spectrochim. Acta, vol. 4, 1951, pp. 373–395.
22. CHANG, T.-C. L., AND KARR, C., JR. Spectrophotometric Determination of Small Quantities of Some Individual Pyridine Bases by Successive Extractions. Anal. Chem., vol. 29, 1957, pp. 1617–1619.
23. ———. Ultraviolet Spectrophotometric Determination of Total Pyridines and Quinolines in Low-Temperature Coal-Tar Distillates. Anal. Chem., vol. 30, 1958, pp. 971–972.
24. COAL TAR RESEARCH ASSOCIATION, THE. The Coal Tar Data Book, Oxford Road, Gomersal, nr. Leeds, England, 1953.[10]
25. COCKER, W., CROSS, B. E., FATEEN, A. K., LIPMAN, C., STUART, E. R., THOMPSON, W. H., AND WHYTE, D. R. A. The Constitution of ψ-Santonin. Part VII. Some Dimethylethylnaphthols. Jour. Chem. Soc., 1950, pp. 1781–1794.
26. COOK, G. L., AND CHURCH, F. M. Determination of Pyridines by Infrared Spectroscopy. Anal. Chem., vol. 28, 1956, pp. 993–995.
27. COULSON, E. A., COX, J. D., HERINGTON, E. F. G., AND MARTIN, J. F. The Preparation and Physical Properties of the Pure Lutidines. Jour. Chem. Soc., 1959, pp. 1934–1940.
28. DAVIES, D. W. Inclusion of Overlap in Molecular Orbital Calculations on Heterocyclic Molecules. Trans. Faraday Soc., vol. 51, 1955, pp. 449–457.
29. DREIDING, A. S., PUMMER, W. J., AND TOMASEWSKI, A. J. The Dienone-Phenol Rearrangement With Mineral Acids. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 3159–3161.
30. ELSNER, B. B., AND PARKER, K. J. Synthesis of Cyclic Hydrocarbons. Part IV. Alkylindanes. Jour. Chem. Soc., 1957, pp. 592–600.
31. ENTEL, J. Nuclear Structure of the Water-Soluble Polycarboxylic Acids From the Oxidation of Bituminous Coal: The Decarboxylation Reaction. Jour. Am. Chem. Soc., vol. 77, 1955, pp. 611–615.

[8] Titles enclosed in brackets are translations from the language in which the item was published.

[9] Continuing looseleaf series.

[10] Looseleaf notebook; additional and replacement sheets are separately dated and received periodically.

32. ERGUN, S. Graphitelike Layers in Coals and High Vacuum Distillation Products. Fuel, vol. 37, 1958, pp. 365–370.
33. ÉTIENNE, A., AND LEGRAND, M. [Ultraviolet Absorption Spectra of Some α- and β-Azanthracenes.] Bull. soc. chim. France, 1953, pp. 108–111.
34. FAIR, F. V., AND FRIEDRICH, R. J. Quantitative Infrared Analysis of Alkyl Phenol Mixtures. Anal. Chem., vol. 27, 1955, pp. 1886–1888.
35. FIESER, L. F. Experiments in Organic Chemistry. D. C. Heath and Co., Boston, Mass., 3d ed., 1955, 359 pp.
36. FISHER, C. H., AND EISNER, A. Extraction Methods for Determining Tar Acids and Bases, and Variables Affecting Their Accuracy. Ind. Eng. Chem., Anal. Ed., vol. 9, 1937, pp. 213–218.
37. FRIEDEL, R. A., AND ORCHIN, M. Ultraviolet Spectra of Aromatic Compounds. John Wiley & Sons, Inc., New York, N.Y., 1951.[11]
38. GIVEN, P. H. Reactions of Alkylphenols Over Cracking Catalysts. II. Isomeric Composition of the Products From a Series of Phenols. Jour. Appl. Chem., vol. 7, 1957, pp. 182–193.
39. GLASSTONE, S., LAIDLER, K. J., AND EYRING, H. The Theory of Rate Processes. McGraw-Hill Book Co., Inc., New York, N. Y., 1941, 611 pp.
40. GODAR, E., AND MARIELLA, R. P. An Investigation of the Mills-Nixon Effect in Pyridines. Jour. Am. Chem. Soc., vol. 79, 1957, pp. 1402–1406.
41. GOLUMBIC, C., WOOLFOLK, E. O., FRIEDEL, R. A., AND ORCHIN, M. Partition Studies on Phenols. IV. Isolation of Indanols From Coal Hydrogenation Oils. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1939–1942.
42. HAWTHORNE, M. F. Simple Procedure for the Conversion of Aryl Halides to the Corresponding Phenols. Jour. Org. Chem., vol. 22, 1957, p. 1001.
43. HEILBRON, I., AND BUNBURY, H. M. Dictionary of Organic Compounds. Oxford University Press, New York, N. Y., 1953, vol. I, 654 pp.; vol. II, 845 pp.: vol. III, 838 pp.; vol. IV, 694 pp.
44. HERINGTON, E. F. G. Applications of the Electronic Spectra of Pyridine Homologs to Quantitative Analysis and to the Measurement of Dissociation Constants. Discussions Faraday Soc., No. 9, 1950, pp. 26–34.
45. HEY, D. H., STIRLING, C. J. M., AND WILLIAMS, G. H. Homolytic Aromatic Substitution. X. Phenylation of Pyridine. Jour. Chem. Soc., 1955, pp. 3963–3969.
46. HODGMAN, C. D., editor. Handbook of Chemistry and Physics. Chemical Rubber Publishing Co., Cleveland, Ohio, 37th ed., 1954, 3156 pp.
47. IKEKAWA, N., AND SATO, Y. Studies on the Coal Tar Bases. XI. The Ultraviolet Absorption Spectra of Ethylpyridines. Pharm. Bull. (Japan), vol. 4, 1956, pp. 136–137.
48. INGOLD, C. K., AND SHAW, F. R. The Nature of the Alternating Effect in Carbon Chains. Part XXII. An Attempt Further to Define the Probable Mechanism of Orientation in Aromatic Substitution. Jour. Chem. Soc., 1927, pp. 2918–2926.
49. IRVINE, L., AND MITCHELL, T. J. Gas-Liquid Chromatography. II. Analysis of the Alkali Extract of a Low-Temperature Coal Tar. Jour. Appl. Chem. (London), vol. 8, 1958, pp. 425–432.
50. JÄGER, A., AND KATTWINKEL, G. [The Quantitative Determination of the Acid Oils in Low-Temperature Coal Tar With the Assistance of Fractionation. I. Aromatic Oxygen Compounds Boiling From 180 to 225°.] Brennstoff-Chem., vol. 31, 1950, pp. 65–79.
51. ———. [Identification of Some Hydrocarbons in Low-Temperature Coal Tar. II. Estimation.] Erdöl u. Kohle, vol. 8, 1955, pp. 706–711.
52. JOHNSON, W. S., AND MATHEWS, F. J. Cyclization Studies in the Benzoquinoline Series. Jour. Am. Chem. Soc., vol. 66, 1944, pp. 210–215.
53. JOHNSON, W. S., WOROCH, E., AND MATHEWS, F. J. Cyclization Studies in the Benzoquinoline and Naphthoquinoline Series. II. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 566–571.
54. KARR, C., JR. Physical Properties of Low-Boiling Phenols. A Literature Survey. Bureau of Mines Inf. Circ. 7802, 1957, 15 pp.
55. ———. Chemical Thermodynamic Equilibria and Free Valence Indices as Applied to a Low-Temperature Bituminous Coal Pyrolyzate. Jour. Phys. Chem., vol. 64, 1960, pp. 462–464.
56. KARR, C., JR., AND BROWN, P. M. Retention Volumes of Phenol, Methyl- and Dimethyl-Phenols in Gas-Liquid Partition Chromatography. Am. Chem. Soc. 130th Meeting, Atlantic City, Abs. of Papers, 1956, p. 4K.
57. KARR, C., JR., BROWN, P. M., ESTEP, P. A., AND HUMPHREY, G. L. Identification and Determination of Low-Boiling Phenols in Low-Temperature Coal Tar. Anal. Chem., vol. 30, 1958, pp. 1413–1416.
58. ———. Analysis of Low-Temperature Tar Phenols Boiling up to 234° C. Fuel, vol. 37, 1958, pp. 227–235.
59. KARR, C., JR., AND CHANG, T.-C. L. Spectrophotometric Analysis of the Distillable Low-Temperature Tar Bases. Jour. Inst. Fuel, vol. 31, 1958 pp. 522–527.
60. KARR, C., JR., ESTEP, P. A., AND HIRST, L. L., JR. Countercurrent Distribution of High-Boiling Phenols From a Low-Temperature Coal Tar. Anal. Chem., vol. 32, 1960, pp. 463–475.
61. KARR, C., JR., ESTEP, P. A., AND PAPA, A. J. Infrared Spectral-Structural Correlations of Quinolines. Jour. Am. Chem. Soc., vol. 81, 1959, pp. 152–156.
62. KNIGHT, S. B., WALLICK, R. H., and BALCH, C. The Ultraviolet Absorption Spectra and the Dissociation Constants of the Monochloroquinolines and the Monomethylquinolines. Jour. Am. Chem. Soc., vol. 77, 1955, pp. 2577–2579.
63. KOOYMAN, E. C., AND FARENHORST, E. The Relative Reactivities of Polycyclic Aromatics Towards Trichloromethyl Radicals. Trans. Faraday Soc., vol. 49, 1953, pp. 58–67.
64. KRUBER, O. [The Phenols of Anthracene Oil.] Ber. deut. chem. Gesell., vol. 69B, 1936, pp. 107–114.
65. KRUBER, O., AND RAEITHEL, A. [Coal-Tar Anthracene Oil.] Chem. Ber., vol. 85, 1952, pp. 327–333.
66. KRUBER, O., AND RAPPEN, L. [The Bases of Coal-Tar Heavy Oil. II.] Chem. Ber., vol. 81, 1948, pp. 483–488.
67. KRUMHOLZ, P. Structural Studies on Polynuclear Pyridine Compounds. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 3487–3492.
68. KUIVILA, H. G. Electrophilic Displacement Reactions. III. Kinetics of the Reaction Between Hydrogen Peroxide and Benzeneboronic Acid. Jour. Am. Chem. Soc., vol. 76, 1954, pp. 870–874.
69. LEFEBVRE, H., AND LEVAS, É. [The Direct Alkylation of Phenol by Cyclohexene in the Presence of Boron Trifluoride.] Compt. rend., vol. 220, 1945, pp. 782–784.
70. LEIBNITZ, E., BEHRENS, U., AND RINGPFEIL, M. [The Qualitative Paper Chromatographic De-

[11] Looseleaf sheets, mostly printed on one side only without page numbers.

termination of Polyphenols Occurring in Low-Temperature Carbonization Water With Consideration of Calculation of Unknown Structures by the R_f Value.] Wasserwirtsch.-Wassertech., vol. 6, 1956, pp. 299–304.

71. Le Rosen, H. D., and Wiley, J. T. Determination of Pyridine and Its Homologs in Hydrocarbons by Ultraviolet Spectrophotometry. Anal. Chem., vol. 21, 1949, pp. 1175–1177.
72. López-Vázquez, F. J. I. [Electronic Structure and Reactivity of Aromatic Hydroxy Compounds. I. Mono- and Dibasic Phenols.] Anales real soc. españ. fís. y quím., vol. 51B, 1955, pp. 203–212.
73. MacGregor, I. R., Neblett, R. F., and Cook, C. H. Aminoketones Derived From Fluorene. I. Derivatives of 2-Acyl-7-Hydroxyfluorene. Jour. Org. Chem., vol. 19, 1954, pp. 626–630.
74. Manske, R. H. F., Marion, L., and Leger, F. The Synthesis and Characterization of the Monomethyl and Dimethylquinolines. Can. Jour. Research, vol. 20B, 1942, pp. 133–152.
75. Matsumoto, K., and Ihara, I. [Tar Bases in Low-Temperature Coal Tar.] Kooru Taaru (Coal Tar) (Tokyo), vol. 3, 1951, pp. 224–227.
76. May, O. E., Berliner, J. F. T., and Lynch, D. F. J. Vapor Pressure. IV. The Naphthols. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 1012–1016.
77. Meissner, H. P., and French, F. E. Isomerization of the Cresols by Aluminum Chloride. Jour. Am. Chem. Soc., vol. 74. 1952, pp. 1000–1003.
78. Morrison, A., and Mulholland, T. P. C. Gibberellic Acid. Part X. 7-Hydroxy-1-methylfluorene. Jour. Chem. Soc., 1958, pp. 2702–2705.
79. Mosby, W. L. Friedel-Crafts Reaction With γ-Valerolactone. I. Synthesis of Various Polymethylnaphthalenes. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 2564–2569.
80. Murray, K. E. A Modified Spinning-Band Column for Low-Pressure Fractionation. Jour. Am. Oil Chemists' Soc., vol. 28, 1951, pp. 235–239.
81. Neuworth, M. B., Hofmann, V., and Kelly, T. E. Fractional Extraction Process for Recovery of Pure Tar Acids. Ind. Eng. Chem. vol. 43, 1951, pp. 1689–1694.
82. Nickels, J. E. Isomerization of Phenols. U.S. Patent 2,551,628, May 8, 1951.
83. Nisbet, H. B., and Pryde, A. M. Studies in the Higher Coal-Tar Bases. Jour. Inst. Fuel, vol. 27, 1954, pp. 58–66.
84. Ogata, Y., Okano, M., and Kitamura, Y. The Chemistry of 1–Naphthaleneacetic Acid Derivatives. Jour. Org. Chem., vol. 16, 1951, pp. 1588–1592.
85. Orchin, M., and Storch, H. H. Solvation and Hydrogenation of Coal. Ind. Eng. Chem., vol. 40, 1948, pp. 1385–1389.
86. Orning, A. A., and Greifer, B. Infrared Spectrum of the Solid Distillate From High Vacuum Pyrolysis of a Bituminous Coal. Fuel, vol. 35, 1956, pp. 381–383.
87. Pacault, A. [Ultraviolet Absorption of a Series of Benzacridines, Some of Which Have Carcinogenic Properties.] Bull. soc. chim., France, 1950, pp. 1270–1276.
88. Parant, A. [Azeotropes of Coal-Tar Phenols.] Chim. et ind., vol. 63, 1950, pp. 434–438.
89. ———. [Research on the Constituents of Low-Temperature Tar.] Compt. rend., Cong. ind. gaz., vol. 65, 1948, pp. 409–421.
90. Perez, S. S., Herráez, M. A., and Igea, F. J. [Molecular Diagrams of Aniline, Monomethylaniline, Dimethylaniline, Diphenyl- and Triphenylamine.] Anales real soc. españ. fís. y quím., vol. 50B, 1954, pp. 243–252.
91. Pigman, I., Del Bel, E., and Neuworth, M. B. Silica-Alumina Catalyzed Isomerization-Disproportionation of Cresols and Xylenols. Jour. Am. Chem. Soc., vol. 76, 1954, pp. 6169–6171.
92. Potts, W. J., Jr. Some Applications of Infrared Spectroscopy to Chemical Analysis. Soc. Appl. Spectroscopy, 11th Meeting, New York, 1956.
93. Pound, G. S. The Production of Chemicals From Low-Temperature Tar. I. and II. Coke and Gas, vol. 14, 1952, pp. 355–362, 401–407.
94. Prelog, V., Barman, P., and Zimmermann, M. [Carbon rings. LIII. 3,4-Dimethyl-2,6-polymethylenephenols.] Helv. Chim. Acta, vol. 33, 1950, pp. 356–364.
95. Prelog, V., Metzler, O., and Jeger, O. [Synthesis of Substituted Phenols.] Helv. Chim. Acta, vol. 30, 1947, pp. 675–689.
96. Rapoport, H., King, T. P., and Lavigne, J. B. The Preparation of Some Acenaphthoxyacetic Acids. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2718–2721.
97. Roberts, E., and Turner, E. E. Factors Controlling the Formation of Some Derivatives of Quinoline and a New Aspect of the Problem of Substitution in the Quinoline Series. Jour. Chem. Soc., 1927, pp. 1832–1857.
98. Rossini, F. D., Mair, B. J., and Streiff, A. J. Hydrocarbons From Petroleum. Reinhold Publishing Corporation, New York, N.Y., 1953, 556 pp.
99. Sadtler Standard Spectra. S. P. Sadtler and Son, Inc., 1517 Vine Street, Philadelphia 2, Pa.[12]
100. Sah, P. P. T. [Synthesis of Compounds Related to the Antihemorrhagic Vitamin K. IV. 1-Naphthol as a Starting Material for the Preparation of 4-Amino-2-methyl-1-naphthol Hydrochloride or Vitamin K_5.] Rec. trav. chim., vol. 60, 1941, pp. 373–377.
101. Sándorfy, C., and Yvan, P. [Comparison of Reactivity Parameters in the Case of Quinoline.] Compt. rend., vol. 229, 1949, pp. 715–717.
102. Schenck, L. M., and Bailey, J. R. Nitrogen Compounds in Petroleum Distillates. XXIII. Isolation of 2,3-Dimethylbenzo[h]quinoline and 2,4-Dimethylbenzo[h]quinoline From California Petroleum. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 2331–2333.
103. Seaman, W., and Johnson, J. R. Derivatives of Phenylboric Acid, Their Preparation and Action upon Bacteria. Jour. Am. Chem. Soc., vol. 53, 1931, pp. 711–723.
104. Shindo, H., and Tamura, S. Infrared Spectra of Heterocyclic Compounds. II. Infrared Spectra of Methyl Quinolines. Pharm. Bull. (Japan), vol. 4, 1956, pp. 292–297.
105. Silverman, M., and Bogert, M. T. The Synthesis of Some Indene and Dihydronaphthalene Derivatives Related to Stilbestrol. Jour. Org. Chem., vol. 11, 1946, pp. 34–49.
106. Smith, L. I., and Opie, J. W. The Chemistry of Vitamin E. XXVIII. (1) Synthesis of the Three Dimethylethylquinones. Jour. Org. Chem., vol. 6, 1941, pp. 427–436.
107. Taylor, W. J., Wagman, D. D., Williams, M. G., Pitzer, K. S., and Rossini, F. D. Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes. Jour. Research Nat. Bur. Standards, vol. 37, 1946, pp. 95–122.
108. Terres, E., Gebert, F., Hülsemann, H., Petereit, H., Toepsch, H., and Ruppert, W. [Information on Physico-Chemical Principles for the Recovery and Analysis of the Phenol

[12] Individual spectra available by purchase.

Fraction From Bituminous Tar and Brown-Coal Low-Temperature Tar. V. Distillate Analysis of the Phenol Fraction From Bituminous Tar and the Chromatographic Identification of Individual Components.] Brennstoff-Chem., vol. 36, 1955, pp. 275–280.

109. Tischler, A. O., and Howard, J. N. Ultraviolet Absorption Spectra of Aromatic Amines in Isooctane and in Water. Nat. Advisory Comm. Aeronautics, A.R.R. No. E5H27a, 1945, 14 pp.
110. U.S. Bureau of Mines Staff. Review and Status of Low-Temperature Tar Investigations of the Bureau of Mines. Inf. Circ. 7893, 1959, 32 pp.
111. Vahrman, M. Resinous Acid Esters in Low-Temperature Coal Tars. Chem. & Ind. (London), 1958, pp. 462–463.
112. ———. Origin of the Phenols in Coal Tar—Structure of the Resinols. Fuel, vol. 30, 1951, pp. 288–290.
113. Van Meter, R. A., Bailey, C. W., Smith, J. R., Moore, R. T., Allbright, C. S., Jacobson, I. A., Jr., Hylton, V. M., and Ball, J. S. Oxygen and Nitrogen Compounds in Shale-Oil Naphtha. Anal. Chem., vol. 24, 1952, pp. 1758–1762.
114. Weisburger, E. K., and Weisburger, J. H. A New Route to 3- and 2,6-Substituted Fluorenes. Jour. Org. Chem., vol. 23, 1958, pp. 1193–1198.
115. Wiebe, A. K. Elution Time and Resolution in Vapor Chromatography. Jour. Phys. Chem., vol. 60, 1956, pp. 685–688.
116. Williamson, B., and Craig, L. C. Identification of Small Amounts of Organic Compounds by Distribution Studies. V. Calculation of Theoretical Curves. Jour. Biol. Chem., vol. 168, 1947, pp. 687–697.
117. Woods, G. F., Reed, F. T., Arthur, T. E., and Ezekiel, H. m-Diarylbenzenes. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 3854–3858.
118. Woolfolk, E. O., Golumbic, C., Friedel, R. A., Orchin, M., and Storch, H. H. Characterization of Tar Acids From Coal-Hydrogenation Oils. Bureau of Mines Bull. 487, 1950, 56 pp.
119. Yarboro, T. L., and Karr, C., Jr. A Procedure for Converting Aryl Halides to High Molecular Weight Phenols. Jour. Org. Chem., vol. 24, 1959, pp. 1141–1143.
120. Yeh, T.-H., and Kalechits, I. V. [Conversion of the Nitrogen Bases Under Conditions of Destructive Hydrogenation. I. Raw Material for Hydrogenation. Separation and Identification of Lower Pyridine Bases From Low-Temperature Coal Tars.] Jan Liao Hsüeh Pao (Peking), vol. 2, 1957, pp. 146–155.
121. Yohe, G. R. Oxidation of Coal. Illinois State Geol. Survey, Rept. of Investigations 207, 1958, 51 pp.

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