

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN A LOW-TEMPERATURE COAL TAR

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INTRODUCTION

In a previous publication¹ the Bureau of Mines reported the results of a detailed gas-liquid chromatographic analysis of aromatic hydrocarbons boiling up to 218° in a low-temperature bituminous coal tar. The present work extends this detailed characterization to include compounds boiling up to 280°, specifically, compounds in the range 202° to 280°.

Previously, only about 10 aromatic hydrocarbons boiling between 202° and 280°, including naphthalene and 5 alkylnaphthalenes, were found in low-temperature tars and in all instances by older techniques²⁻⁶. Quantitative results were essentially non-existent.

In the present work, employment of the eminently effective combination of gas-liquid chromatography and spectrophotometry enabled this laboratory to identify 48 compounds, including 9 mentioned in the previous publication. Of these identified compounds 20 are alkylnaphthalenes, including all isomeric dimethylnaphthalenes, except the 1,8-isomer. The rest of the compounds identified include methylated indans, tetralins, indenenes and biphenyls, and some oxygenated aromatic hydrocarbons. Cyclohexylbenzene and 2a,3,4,5-tetrahydroacenaphthene, which had never been reported in any low-temperature tar, were also found. Quantitative determinations were made on nearly all compounds.

A correlation between logarithm of relative retention at 220° and boiling point for some alkylbenzenes and some alkylnaphthalenes was established; this made it possible to identify several additional constituents of the tar. This correlation is similar to the one for alkylbenzenes at 150°¹.

EXPERIMENTAL WORK AND RESULTS

1. Preparation of aromatic concentrates from the coal tar for gas-liquid chromatography

The same neutral oil from a West Virginia bituminous coal tar that was used in the earlier part of this work was used for the present analysis. The neutral oil was distilled to the equivalent of 260° in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus at 50 mm., with the results shown in Table I of the previous publication. The residue left from this distillation was further fractionated at 10 mm. in a Fisher Unitized distillation apparatus with a 12 mm. I.D. column, using a reflux ratio of 20 to 1. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

The distillate fractions were each separated into saturates, unsaturates, and aromatics by means of displacement chromatography with silica gel, as previously described. The data on displacement chromatography are summarized in Table II.

TABLE I
FRACTIONATION OF NEUTRAL OILS IN FISHER STILL

Charge:	8.35 wt.-% of the tar		
	338.0 g.		
Distillate:	131.4 g. = 38.9 %		
Residue:	201.8 g. = 59.7 %		
Loss and holdup:	4.8 g. = 1.4 %		
Fraction No.	Head temperature, °C., 10 mm.	Estimated b.p., °C., 760 mm.	Weight, g.
1	122 - 124	257 - 259	2.9
2	124 - 127	259 - 262	9.0
3	127 - 129	262 - 265	9.0
4	129 - 132	265 - 268	9.3
5	132 - 134	268 - 270	8.5
6	134 - 135	270 - 272	6.2
7	135 - 137	272 - 274	9.2
8	137 - 138	274 - 275	9.6
9	138 - 139	275 - 276	9.0
10	139 - 141	276 - 278	9.0
11	141 - 143	278 - 280	8.6
12	143 - 144	280 - 282	9.4
13	144 - 146	282 - 284	9.2
14	146 - 148	284 - 286	9.3
15	148 - 149	286 - 287	9.6
16	149	287	3.6
Total			131.4

TABLE II

DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No. ^a	Weight of charge, g.	Column temperature, °C.	Saturates + some olefins			Aromatics + some olefins and some O, S compounds			Material retained on column, g.	Weight of aromatics identified by GLC, g.
			²⁰ n _D range	Total weight, g.	Number of fractions	²⁰ n _D range	Total weight, g.	Number of fractions		
7 + 8 ^b	21	70	1.4025-1.4894	9.98	22	1.4915-1.5658	9.03	11	1.99	5.828
9 ^b	4.29	70	1.4281-1.4705	1.77	8	1.4995-1.5867	1.94	7	0.58	1.329
10 + 11 ^b	14.93	room temp.	1.4383-1.4938	7.04	18	1.4985-1.5640	6.36	13	1.53	3.152
12 + 13 ^c	12.58	room temp.	1.4321-1.4900	5.00	14	1.4990-1.5790	5.87	13	1.71	3.089
14 ^c	11.16	room temp.	1.4285-1.4769	5.17	13	1.4991-1.5864	5.24	13	0.75	2.314
15 ^c	15.15	room temp.	1.4294-1.4839	6.80	17	1.4971-1.5947	7.31	18	1.04	5.419
16 ^c	13.90	room temp.	1.4400-1.4830	4.11	11	1.5027-1.6039	7.81	18	1.98	5.771
17 ^c	12.70	room temp.	1.4442-1.4843	2.96	9	1.5001-1.6047	6.97	15	2.77	4.322
18 ^c	10.61	room temp.	1.4478-1.5059	3.40	8	1.5331-1.6050	6.14	12	1.07	4.665
19 ^c	15.90	room temp.	1.4378-1.4971	6.05	13	1.5083-1.6005	7.13	13	2.72	4.647
20 ^c	12.20	70	1.4317-1.5050	5.12	13	1.5219-1.5951	5.06	11	2.02	3.672
21 ^c	16.36	70	1.4361-1.5079	6.02	14	1.5179-1.5968	9.11	16	1.23	5.989

(Table II, continued)

22 ^c	17.75	70	1.4386-1.5087	5.17	14	1.5218-1.5989	11.22	22	1.36	8.048
23 ^c	17.14	70	1.4462-1.4988	3.89	9	1.5283-1.5916	12.24	20	1.01	8.516
24 ^c	5.45	70	1.4480-1.5044	1.53	6	1.5449-1.5953	3.52	10	0.40	2.863
25 ^d	16.42	85	1.4375-1.4769	2.20	6	1.5115-1.5970	12.73	23	1.49	11.502
26 ^d	17.48	85	1.4395-1.4941	2.36	6	1.5228-1.5983	13.50	28	1.62	11.874
27 ^d	17.55	85	1.4390-1.5000	2.25	6	1.5195-1.6014	13.59	23	1.71	10.691
28 ^d	19.23	90	1.4349-1.4857	2.96	7	1.5100-1.6025	14.58	25	1.69	10.057
29 ^d	10.19	90	1.4375-1.4941	2.03	5	1.5251-1.6040	7.00	12	1.16	5.414
1*d	2.90	95	1.4698	0.40	1	1.5489-1.6015	2.30	6	0.20	1.436
2*d	7.88	95	1.4572-1.4743	0.93	2	1.5359-1.6027	5.98	11	0.97	4.991
3*d	5.96	95	1.4509-1.4888	1.42	3	1.5421-1.5998	3.76	7	0.78	2.931
4*d	7.66	95	1.4537-1.5048	2.01	4	1.5232-1.5978	4.84	8	0.81	2.870
5*d	8.33	95	1.4591-1.4916	1.13	3	1.5172-1.5960	6.17	11	1.03	3.739
6*d	6.00	95	1.4587-1.4895	1.40	3	1.5189-1.5903	3.93	6	0.67	2.865
7*d	5.99	95	1.4555-1.5136	1.64	4	1.5460-1.6009	3.88	8	0.47	2.773
8*d	8.74	95	1.4565-1.5171	1.66	4	1.5340-1.5982	6.07	12	1.01	3.622

a Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report.

b Desorbent - butyl alcohol.

c Desorbent - isobutyl alcohol.

d Desorbent - cyclohexanol.

II. Analysis of aromatic hydrocarbons by gas-liquid chromatography

Apparatus and operating conditions. A Perkin-Elmer model 154C Vapor Fractometer equipped with thermistor detectors was used. The response range of the recorder was from 0 to 2.5 mv, and the chart speed varied from 4 to 20 inches per hour, depending on the retention times of the components. The peak areas on the chromatogram were measured with a planimeter.

Two columns were used, each made from a 20-ft. x 1/4-in. O.D. copper tubing filled with approximately 75 g. of packing made of 25% Apiezon L grease on 30- to 60-mesh firebrick. One of the columns was used at 200°, which was the temperature chosen for the analysis of the fractions boiling between 202° and 233°. The other column was used at 220°, which was the temperature for the analysis of the fractions boiling between 233° and 275°. The samples varied in size from 5 μ l to 15 μ l and were injected into the column with a 50- μ l syringe. The carrier gas was helium, admitted to the column at a pressure of 30 lb./in.², corresponding to a flow rate of 100 ml./min.; the outlet pressure was atmospheric. The potential for the detector was 8 V. Throughout the work the temperature stayed within $\pm 0.1^\circ$ and the helium pressure and the voltage of the detector stayed constant.

The efficiency of the column was calculated by using the equation: No. of theoretical plates = $16(x/y)^2$, where y = length of peak baseline (as defined) and x = length from start of the run to middle of baseline section. Referring to 1,3,5-triethylbenzene and to 1-methylnaphthalene, the efficiency of the column at 200° was 2393 and 3948 theoretical plates, respectively, and for the column at 220° was 3364 and 4356.

General approach for identification. The retention times of 58 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained. Their calculated relative retentions (either time or volume) referred to 1,3,5-triethylbenzene at 200° and 220°, and their boiling points are shown in Table III. The aromatic fractions obtained by displacement chromatography were each examined by GLC under the same conditions as for the known compounds.

The approach for identification was principally the same as that described in the previous paper, except that ultraviolet spectrophotometry was included in addition to infrared. Components producing peaks were collected in the previously described manner. The ultraviolet spectra were obtained in cyclohexane solutions.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (a) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (b) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. In some instances, two components were found to have been eluted together. The infrared spectrum of the material producing a single peak served not only for qualitative identification but also for quantitative estimation of the components. The chromatograms for two different aromatic cuts shown in Figure 1 illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table IV shows the results of the identifications, the peak numbers in this table corresponding to the peak numbers in Figure 1.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available. These correlation curves are shown in Figure 2 and are discussed more fully in a later section. Boiling points of the components producing various peaks were obtained from their

TABLE III

BOILING POINTS, RELATIVE RETENTIONS, AND CALIBRATION FACTORS (f_C)
OF SOME AROMATIC HYDROCARBONS

Compound	Boiling point		At 200°		At 220°	
	°C./760 mm.	Source	Relative retention ^a	f_C ^b	Relative retention ^a	f_C ^b
n-Propyl benzene	159.217	c	0.37	0.86	0.40	0.85
1-Methyl-2-n-propyl benzene	184.80	c	0.62	0.95	0.64	0.93
1,4-Diethyl benzene	183.752	c	0.58	0.93	0.61	0.93
1,3-Dimethyl-5-ethyl benzene	183.75	c	0.58	0.91	0.60	0.89
1,2-Dimethyl-4-ethyl benzene	189.75	c	0.67	0.94	0.70	0.92
1-Methyl-3,5-diethyl benzene	200.70	c	0.77	1.00	0.79	0.97
1,2,4,5-Tetramethyl benzene	196.80	c	0.82	0.98	0.84	0.98
1,2,3,5-Tetramethyl benzene	198.00	c	0.85	1.02	0.87	0.99
1,3,5-Triethyl benzene	216.2	c	1.00	1.00	1.00	1.00
Pentamethyl benzene	231.8	c	1.72	1.01	1.75	1.00
Hexamethyl benzene	263.8	d	3.58	1.01	3.47	1.01
Cyclohexyl benzene	240.13	e	2.09	1.03	2.05	1.02
1,2,3,4-Tetrahydronaphthalene	207.57	c	1.14	1.54	1.16	1.52
Indan	177.82	c	0.59	1.42	--	--
Naphthalene	217.96	c	1.35	1.02	1.37	1.03
2-Methylnaphthalene	241.14	f	2.12	1.04	2.10	1.02
1-Methylnaphthalene	244.78	f	2.32	1.01	2.28	1.02
2-Ethyl naphthalene	257.9	c	3.01	1.08	2.93	1.07
1-Ethyl naphthalene	258.67	c	3.04	1.05	2.96	1.05
2,7-Dimethylnaphthalene	262	c	3.21	1.07	3.13	1.05
2,6-Dimethylnaphthalene	261	f	3.28	1.03	3.17	1.04
1,7-Dimethylnaphthalene	262.9	e	3.41	1.03	3.29	1.03
1,6-Dimethylnaphthalene	265.5	e	3.54	1.04	3.43	1.02
1,3-Dimethylnaphthalene	265	c	--	--	3.43	--
2,3-Dimethylnaphthalene	268	f	3.80	1.05	3.68	1.03
1,5-Dimethylnaphthalene	270.1	e	3.99	1.03	3.83	1.03
1,2-Dimethylnaphthalene	271.1	g	4.10	--	3.93	--
1,3,7-Trimethylnaphthalene	281.7	e	--	--	4.88	1.09
2,3,6-Trimethylnaphthalene	288.1	g	--	--	5.51	1.09
2,3,5-Trimethylnaphthalene	289	e	--	--	5.66	1.07
2a,3,4,5-Tetrahydroace- naphthene	252	e	2.88	1.20	2.80	1.20
Acenaphthylene	270	d	--	--	4.05	--
Acenaphthene	277.2	f	--	--	4.53	1.12
Biphenyl	255.0	c	2.66	1.01	2.60	1.00
3-Methylbiphenyl	272.70	c	--	--	3.82	1.04
2-Methylbiphenyl	260	d	2.46	--	2.51	1.06
4-Methylbiphenyl	267	d	--	--	3.10	--
2-Methylindene	204.1	e	1.05	1.08	1.08	1.06
2-Ethyl indene	222.5	e	1.64	1.10	1.63	1.09
3-Ethyl indene	218.1	e	1.58	1.08	1.57	1.09
1,3-Dimethylindene	207.5	e	1.09	--	1.10	--
2,3-Dimethylindene	224.5	e	1.70	--	1.69	--
2,6-Dimethylindene	226.8	e	1.63	1.09	1.62	1.07
1-Methyl-3-ethylindene	64-5/1.3	e	1.62	--	1.60	--
3-Methyl-2-ethylindene	74-6/1.25	e	2.40	--	2.34	--
2,3,6-Trimethylindene	242.6	e	2.57	--	2.51	--
Benzofuran	171.38	f	0.52	0.99	0.55	1.02
Dibenzofuran	287	f	--	--	5.02	1.18

(Table III, continued)

Diphenyl ether	258.14	e	2.53	1.06	2.47	1.05
5-Methylindan	202.0	c	0.97 ^h	--	0.96 ^h	--
4-Methylindan	205.5	c	1.05 ^h	--	1.07 ^h	--
3-Methylindene	205	c	1.07 ^h	--	1.09 ^h	--
1,2,3,4-Tetramethylbenzene	205.04	c	1.01 ^h	--	1.07 ^h	--
1,6-Dimethylindan	210.9/740.0	i	1.09 ^h	--	1.07 ^h	--
4,7-Dimethylindan	227.6/745.5	j	1.67 ^h	--	1.64 ^h	--
2-Methyl-1,2,3,4-tetrahydro- naphthalene	220.2	k	1.38 ^h	--	1.35 ^h	--
6-Methyl-1,2,3,4-tetrahydro- naphthalene	229.03	c	1.75 ^h	--	1.72 ^h	--
1,4-Dimethylnaphthalene	268.5	c	--	--	3.70 ^h	--

a Dead volume corrected.

b Defined in eq. 1.

c API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh, Pa.

d G. Egloff, Physical Constants of Hydrocarbons, Reinhold Publishing Corp., New York, 1957.

e Determined in this laboratory.

f From Coal Tar Research Assoc., "Coal Tar Data Book," Gomersal, near Leeds, England (1953).

g From Gesellschaft für Teerverwertung mbH, "GfT-Aromaten," Duisburg-Meiderich, Germany.

h The relative retentions of these compounds were determined from tar components identified by I. R.

i J. Entel, C. H. Ruof, and H. C. Howard, Anal. Chem. **25** (1953) 1303.

j J. Entel, Anal. Chem. **26** (1954) 612.

k A. S. Bailey and C. M. Staveley, J. Inst. Petroleum **42** (1956) 97.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF TWO AROMATIC CUTS FROM DISTILLATE FRACTIONS 10 + 11 AND 26

Peak No.	Relative retention at 220°	Compound identified by I. R.	Relative retention of authentic specimen at 220°
1	1.98	Not identified	--
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethyl naphthalene	2.93
7	3.18	2,7-Dimethylnaphthalene	3.13
		2,6-Dimethylnaphthalene	3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	1,3-Dimethylnaphthalene	3.43
		1,6-Dimethylnaphthalene	3.43

D-8126

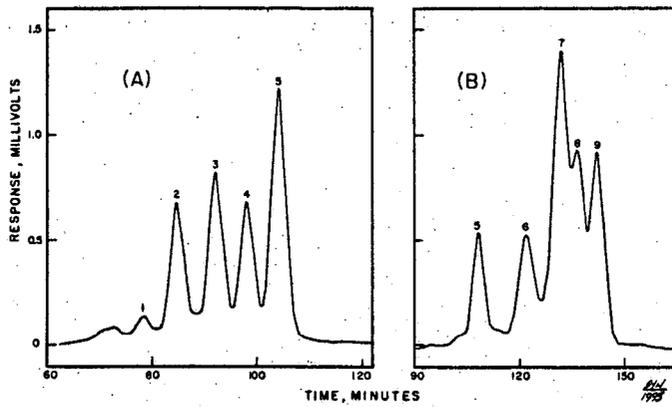


Fig. 1. Chromatograms of two aromatic cuts obtained from distillate fractions 10 + 11 (A) and 26 (B).

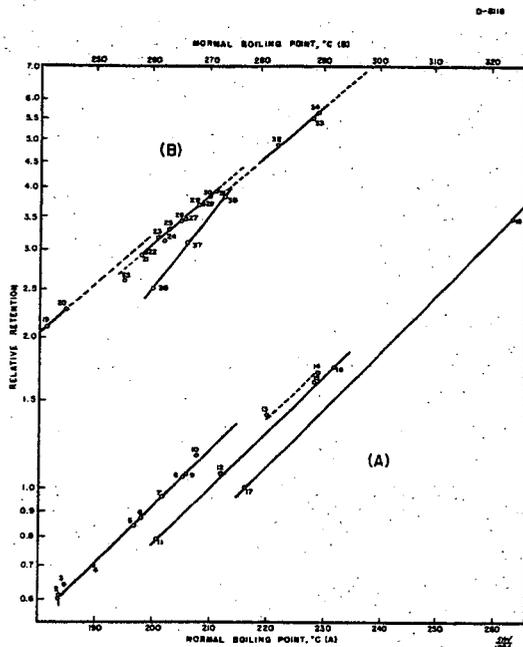


Fig. 2. Correlation between relative retentions and boiling points of some alkybenzenes (A) and alkylnaphthalenes (B) at 220° on Apiezon L grease.

Legend:

- | | |
|---|-------------------------------|
| 1 1,3-Dimethyl-5-ethylbenzene | 20 1-Methylnaphthalene |
| 2 1,4-Diethylbenzene | 21 2-Ethylnaphthalene |
| 3 1-Methyl-2-n-propylbenzene | 22 1-Ethylnaphthalene |
| 4 1,2-Dimethyl-4-ethylbenzene | 23 2,6-Dimethylnaphthalene |
| 5 1,2,4,5-Tetramethylbenzene | 24 2,7-Dimethylnaphthalene |
| 6 1,2,3,5-Tetramethylbenzene | 25 1,7-Dimethylnaphthalene |
| 7 5-Methylindan | 26 1,3-Dimethylnaphthalene |
| 8 4-Methylindan | 27 1,6-Dimethylnaphthalene |
| 9 1,2,3,4-Tetramethylbenzene | 28 2,3-Dimethylnaphthalene |
| 10 1,2,3,4-Tetrahydronaphthalene | 29 1,4-Dimethylnaphthalene |
| 11 1-Methyl-3,5-diethylbenzene | 30 1,5-Dimethylnaphthalene |
| 12 1,6-Dimethylindan | 31 1,2-Dimethylnaphthalene |
| 13 2-Methyl-1,2,3,4-tetrahydronaphthalene | 32 1,3,7-Trimethylnaphthalene |
| 14 6-Methyl-1,2,3,4-tetrahydronaphthalene | 33 2,3,6-Trimethylnaphthalene |
| 15 4,7-Dimethylindan | 34 2,3,5-Trimethylnaphthalene |
| 16 Pentamethylbenzene | 35 Biphenyl |
| 17 1,3,5-Triethylbenzene | 36 2-Methylbiphenyl |
| 18 Hexamethylbenzene | 37 4-Methylbiphenyl |
| 19 2-Methylnaphthalene | 38 3-Methylbiphenyl |

relative retention by these curves and were used as a preliminary means of identification. Since relative retention or boiling point could not be depended on entirely for identification, confirmation of identity depended on the comparison of the infrared or ultraviolet spectra of the collected samples with published spectra of the pure compounds. However, not all of the spectra of the probable constituents could be found in the literature; to substantiate the preliminary identification, spectral-structural correlations became necessary. Table V shows eight alkyl-naphthalenes identified by the second method. The details of these identifications are as follows:

(1) Constituent having a relative retention of 3.70: The boiling point of the constituent, obtained from its relative retention by the correlation curve for dimethylnaphthalenes, agreed very well with that of 1,4-dimethylnaphthalene. The identity of this naphthalene was confirmed by comparing the infrared spectrum of the constituent with that of 1,4-dimethylnaphthalene, published by the American Petroleum Institute (see Table VI).

(2) Constituents having relative retentions of 4.80 and 5.20: According to the correlation curve for trimethylnaphthalenes, the boiling points for these constituents were 281.5° and 285°, respectively. They are somewhat higher than the literature values for 1,3,6-, 1,2,6-, and 1,2,7-trimethylnaphthalene. However, the ultraviolet spectrum of the sample having a relative retention of 4.80 matched well with the literature spectrum of 1,3,6-trimethylnaphthalene. The material having a relative retention of 5.20 was found to have more than one constituent and was collected as two individual samples, one corresponding to the first half of the peak and the other the second half. By comparing the ultraviolet spectra of the two samples with the published spectra of 1,2,6- and 1,2,7-trimethylnaphthalene, the first sample was found to contain principally 1,2,6-, and the second to contain 1,2,7- as a major and 1,2,6- as a minor component.

(3) Constituents having a relative retention of 4.39: The boiling point obtained for this material from the trimethylnaphthalene correlation curve was 277.3°, a few degrees higher than any of the literature values for the four possible 1,6- and 1,7-methylethyl- and ethylmethylnaphthalenes. The identification of the material therefore depended mainly on spectral-structural correlations, as follows: An examination of the ultraviolet spectra of 1-methyl-, 1-ethyl-, 2-methyl-, and 2-ethylnaphthalene showed that the two 1-alkylnaphthalenes absorb at nearly identical maxima in the region of 300 m μ to 320 m μ but differ in absorptivities; the same is true for the two 2-alkylnaphthalenes. A similar situation was also observed in the 300 m μ to 330 m μ region for 1,4,5-trimethyl- and 1,4-dimethyl-5-ethylnaphthalene and for 1,3,5-trimethyl- and 1,3-dimethyl-5-ethylnaphthalene upon examining the ultraviolet spectral data of these compounds reported by Evans, Smith, and Straus⁸. This indicates that for absorption in the 300 m μ to 330 m μ region methyl groups and ethyl groups can be interchanged without significantly changing the position of the absorption peak; however, the absorptivities are usually altered. Therefore, naphthalene substituted with one methyl group and one ethyl group could be expected to show nearly identical absorption maxima in the 300 m μ to 330 m μ region as the naphthalenes substituted with two methyl groups in the same positions. The constituents had absorption bands at 307.8 m μ , 314.7 m μ , and 322 m μ which are also exhibited by 1,6- and 1,7-dimethylnaphthalene, both of which had already been accounted for in much lower boiling fractions. It therefore appeared likely that one or more of the four possible 1,6- or 1,7-methylethyl- or ethylmethylnaphthalenes were present. The infrared spectrum of the material was in agreement with this conclusion. According to Werner, Kennard, and Rayson⁹, the two strong bands shown in the sample spectrum at 783 cm.⁻¹ and 810 cm.⁻¹ could be due to 3H and 2H out-of-plane deformation vibrations of 1,6-disubstituted naphthalene, and the other two strong bands at 760 cm.⁻¹ and 835 cm.⁻¹ could be due to the same vibrations of 1,7-disubstituted naphthalene.

TABLE V

IDENTIFICATION OF EIGHT ALKYLNAPHTHALENES

Relative retention at 220°	Compound	Literature ^a b.p., °C. 760 mm.	B.P., °C. obtained from the correlation curve	Spectroscopic identification
3.70	1,4-Dimethylnaphthalene	268.5	268.4	Infrared
4.80	1,3,6-Trimethylnaphthalene	280	281.5	Ultraviolet
5.20	1,2,6-Trimethylnaphthalene	280	285	Ultraviolet
	1,2,7-Trimethylnaphthalene	278		Ultraviolet
4.39	1-Methyl-6-ethylnaphthalene, or 1-Ethyl-6-methylnaphthalene	273	277.3	Ultraviolet and infrared spectral-structural correlations
	1-Methyl-7-ethylnaphthalene, or 1-Ethyl-7-methylnaphthalene	270		
	1-Methyl-6-ethylnaphthalene	271		
	1-Ethyl-6-ethylnaphthalene	270		
	1-Ethyl-7-ethylnaphthalene	270		
4.15	2-Methyl-6-ethylnaphthalene	270	275.2	Ultraviolet and infrared spectral-structural correlations
	2-Methyl-7-ethylnaphthalene	270		

^a API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh, Pa.

TABLE VI

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280°
IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of spectrum	Total weight, g.	Wt. % in neutral oil ^a
1,2,3,4-Tetramethylbenzene ^b	6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.0681	0.153
1,2-Dimethyl-3-n-propylbenzene ^b	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.2976	0.042
1,4-Dimethyl-2-n-propylbenzene ^b	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.5874	0.084
1-Methyl-2,4-diethylbenzene ^b	6-13	Rel. retention-b.p. correlation, I.R.-structural correlation	-	0.9873	0.141
5-Methylindan ^b	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.7566	0.251
4-Methylindan ^{b,d}	5,6,7,8,9	Rel. retention-b.p. correlation, I.R.	c	1.7389	0.249
1,6-Dimethylindan	7-14	Rel. retention-b.p. correlation, I.R.	c	2.3746	0.340
4,7-Dimethylindan	7-16	Rel. retention-b.p. correlation, I.R.	c	1.3034	0.186
3-Methylindene ^b	5,6,7,8	I.R.	c	0.7141	0.102
3-Ethylindene	7-17	Rel. retention, I.R.	e	1.3126	0.188
2-Ethylindene	7-17	Rel. retention, I.R.	e	1.3032	0.186
2,3-Dimethylindene	7-17	Rel. retention, I.R.	e	1.7762	0.254
1,2,3,4-Tetrahydronaphthalene ^{b,d}	5,6,7,8	Rel. retention, I.R.	e	0.6170	0.088

(Table VI, continued)

2-Methyl-1,2,3,4-tetrahydro-naphthalene	7-15	I.R.	c	1.0426	0.149
6-Methyl-1,2,3,4-tetrahydro-naphthalene	12,13,14,15	I.R.	c	0.4958	0.071
Naphthalene ^{b,d}	6-15	Rel. retention, I.R.	e	6.3853	0.914
1-Methylnaphthalene ^d	14-24	Rel. retention, I.R.	e	12.0615	1.728
2-Methylnaphthalene ^d	12-24	Rel. retention, I.R.	e	16.1630	2.315
1-Ethylnaphthalene	20-29, 1* ^f	Rel. retention, I.R.	e	1.9777	0.283
2-Ethylnaphthalene	20-29, 1*	Rel. retention, I.R.	e	3.1184	0.456
2,7-Dimethylnaphthalene	21-29, 1*,2*	Rel. retention, I.R.	e	4.8187	0.690
1,7-Dimethylnaphthalene	23-29, 1*,2*	Rel. retention, I.R.	e	4.7915	0.686
2,6-Dimethylnaphthalene ^d	23-29, 1*,2*	Rel. retention, I.R.	e	4.1664	0.596
1,6-Dimethylnaphthalene ^d	25-29, 1*-5*	Rel. retention, I.R.	e	6.4648	0.926
1,3-Dimethylnaphthalene	25-29, 1*-5*	Rel. retention, I.R.	e	6.5617	0.940
2,3-Dimethylnaphthalene ^d	27,28,29, 1*-7*	Rel. retention, I.R.	e	3.8247	0.547
1,5-Dimethylnaphthalene	28,29, 1*-7*	Rel. retention, I.R.	e	3.6861	0.528
1,2-Dimethylnaphthalene	29, 1*-7*	Rel. retention, I.R.	e	3.5632	0.510
1,4-Dimethylnaphthalene	3*,4*	Rel. retention- b.p. correlation, I.R.	c	0.0979	0.014
2-Methyl-6-ethylnaphthalene } 2-Methyl-7-ethylnaphthalene }	4*-8*	{ Rel. retention- b.p. correlation, U.V. and I.R. structural correlations	-	3.9029	0.559
1-Methyl-7-ethylnaphthalene ^g and/or 1-Methyl-6-ethylnaphthalene ^g	4*-8*	Rel. retention- b.p. correlation, U.V. and I.R. structural correlations	-	3.2925	0.471
1,3,6-Trimethylnaphthalene	5*-7*	Rel. retention- b.p. correlation, U.V.	h	0.7338	0.105
1,3,7-Trimethylnaphthalene	5*-7*	Rel. retention, I.R.	e	0.452	0.064

(Table VI, continued)

1,2,6-Trimethylnaphthalene	6*-8*	Rel. retention- b.p. correlation, U.V.	h	0.8751	---
1,2,7-Trimethylnaphthalene			h		
Biphenyl ^d	18-29,1*	Rel. retention, I.R.	e	18.8235	2.696
4-Methylbiphenyl	28,29,1*,2*	Rel. retention, I.R.	e	0.7271	0.104
3-Methylbiphenyl	1*-7*	Rel. retention, I.R.	e	1.2431	0.178
Cyclohexyl benzene	12-15	Rel. retention, I.R.	e	0.2769	0.039
2a,3,4,5-Tetrahydroacenaphthene	20-26	Rel. retention, I.R.	e	1.1713	0.167
Acenaphthylene	4*-6*	Rel. retention, I.R.	e	0.6963	0.099
Acenaphthene ^d	2*-8*	Rel. retention, I.R.	e	2.336	---
Diphenyl ether	18-29,1*,2*	Rel. retention, I.R.	e	38.5897	5.528
2,3-Dimethylbenzofuran	14-16	I.R.-structural correlation	-	0.1778	0.025
Dimethylbenzofuran [I]	7-13	I.R.-structural correlation	-	1.7848	0.255
Dimethylbenzofuran [II]	9-15	I.R.-structural correlation	-	0.6451	0.092
Dibenzofuran	5*-8*	Rel. retention, I.R.	e	1.4718	---

a Total neutral oil distilling up to about 360°, representing 16.92 wt. % of the total tar.

b Identified in prior work by this laboratory¹.

c American Petroleum Institute, Research Project 44, Infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

d Previously identified by others²⁻⁶.

e This laboratory.

f Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report¹.

g The positions of the ethyl and methyl groups might be reversed.

h E. Heilbronner, U. Fröhlicher and P. A. Plattner, *Helv. Chim. Acta*, 32 (1949) 2479.

(4) Constituents having a relative retention of 4.15: This material appeared to consist of a mixture of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. The boiling point of the sample found by the trimethylnaphthalene curve was several degrees higher than the literature value for the two naphthalenes. However, the ultraviolet absorption maxima in the 300-330 m μ range for the constituent producing the first half of the peak were at 303 m μ , 310 m μ , 317 m μ , and 324.8 m μ , in close agreement with the much lower boiling 2,6-dimethylnaphthalene. The maxima shown by the second constituent were nearly identical to those for 2,7-dimethylnaphthalene at 307 m μ , 317 m μ , and 321 m μ . The presence of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene was thus indicated. The infrared bands at 800 cm.⁻¹ to 900 cm.⁻¹ substantiated these identifications. The strong bands shown by the first constituent at 823 cm.⁻¹ and 874 cm.⁻¹ and those shown by the second constituent at 835 cm.⁻¹ and 876 cm.⁻¹ could be due, respectively, to 2H and 1H out-of-plane deformation vibrations of 2,6- and 2,7-disubstituted naphthalenes⁹.

In addition to these alkyl naphthalenes, three dialkylbenzofurans, of which one might be the 2,3-dimethyl-isomer, were tentatively identified by the characteristic infrared bands of benzofurans, observed by examining the spectra of benzofuran and all its monomethyl derivatives¹⁰. A strong band between 1,250 cm.⁻¹ and 1,280 cm.⁻¹ and one or two between 1,090 cm.⁻¹ and 1,160 cm.⁻¹ could be characteristic of benzofurans. According to Bellamy¹¹, compounds containing the structure = C - O - may absorb near 1,250 cm.⁻¹ and in unsaturated cyclic compounds, with the structure = C - O - C =, a band may appear near 1,100 cm.⁻¹ or somewhat higher frequencies. Therefore, in the spectra of the benzofuran constituents, the bands between 1,250 cm.⁻¹ and 1,280 cm.⁻¹ and between 1,090 cm.⁻¹ and 1,160 cm.⁻¹ may be due to the furan structure in the molecule.

One benzofuran sample, having a relative retention of 1.28 at 200°, showed a strong band at 1,251 cm.⁻¹ as in 2-methylbenzofuran and another strong band at 1,092 cm.⁻¹ as in 3-methylbenzofuran. This sample also absorbed strongly at 742 cm.⁻¹, similarly to 2-methyl- and 3-methylbenzofuran, both of which have a band at 746 cm.⁻¹ that is probably due to the 4H out-of-plane deformation vibration in the benzene ring. The boiling point of 2,3-dimethylbenzofuran from the literature¹² is approximately 220°, which falls in the boiling range of the distillate fractions containing this component. It is, therefore, very likely that this constituent is 2,3-dimethylbenzofuran. The other two samples showed the characteristic infrared bands of benzofurans in both regions. In addition, a few sharp bands also appeared between 1,000 cm.⁻¹ and 1,400 cm.⁻¹. These were considered to be dimethylbenzofurans, all of the isomers of which boil well within the range 210° to 230°.

Quantitative estimation of aromatic hydrocarbons.

The internal standard method, which was described in the previous paper¹, was employed for quantitative analysis of the samples, 1,2,3-triethylbenzene being selected as the standard. The equation used for the calculations is as follows:

$$f_C = A_S W_C / A_C W_S \dots \dots \dots (1)$$

where f_C is the calibration factor, as defined, A_S and A_C are the areas for the standard and component in the mixture, and W_C and W_S are the weight-percentages of the compound and the standard. The f_C values for a number of aromatic hydrocarbons were determined at 200° and 220° and are given in Table III. No significant difference was found between the values for each compound at these two temperatures. These values were used to determine the weight-percentages of the constituents in the fractions. For those compounds present in the tar for which authentic specimens were not available, the f_C values of their isomers or of structurally similar compounds were used. For example, an average f_C of 1.03 for six dimethylnaphthalenes was used to calculate the amounts of the 1,2- and 1,4-dimethyl isomers, an average of 1.08 for three trimethylnaphthalenes was used for other trimethyl and

methylethynaphthalenes, the f_C value of 0.99 for 1,2,3,5-tetramethylbenzene was used for 1,2,3,4-tetramethylbenzene, the value of 1.42 for indan was used for all indan derivatives, the value of 1.52 for tetralin was used for the two methyl-tetralins, and 1.05, an average of the values for 2-methyl- and 3-methylbiphenyl, was used for 4-methylbiphenyl.

The aromatic hydrocarbons boiling between 202° and 280° found in the low-temperature bituminous tar and their quantities are presented in Table VI. The values of weight-percentages in neutral oil of the three highest boiling components are not entered, since they are also expected to be present in the next higher boiling fraction.

DISCUSSION

Correlation between relative retentions and boiling points of alkylbenzenes and alkylnaphthalenes.

When the logarithms of relative retentions at 220° for alkylbenzenes and for alkylnaphthalenes, in either instance having an equal number of carbon atoms in the alkyl groups, were plotted against their boiling points, a straight line resulted. The relationship is similar to that established for a number of alkylbenzenes at 150°, as previously reported¹.

Figure 2 (A) shows three parallel lines corresponding to alkylbenzenes having 4, 5, and 6 carbon atoms in the alkyl groups. Indans, which have a benzene nucleus with a 1,2-trimethylene-type alkylation, fall closely on the correlation curves for alkylbenzenes having the corresponding number of carbon atoms in alkyl groups. However, tetralin (point 10 in Fig. 2), which has a 1,2-tetramethylene-type alkylation, does not fit so closely to the line for C_{10} -alkylbenzenes, and its 2-methyl- and 6-methyl-derivatives (points 13 and 14) are well off the line for C_{11} -alkylbenzenes. However, a line drawn between points 13 and 14 is essentially parallel to the line for the C_{11} -alkylbenzenes. No clear-cut relationship can be established between the indans and the tetralins with this limited data for alkyltetralins.

Figure 2 (B) shows three parallel straight lines corresponding to alkylnaphthalenes having 1, 2, and 3 carbon atoms in the alkyl groups. A fourth line representing three monomethylbiphenyls (points 36, 37, and 38) is not parallel to the naphthalene lines.

A difference in slope can be observed among the three groups--benzenes, naphthalenes, and biphenyls. The slope of the benzenes is 0.0113, that of the naphthalenes is 0.0098, and that of the biphenyls is 0.0164.

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