

369. *Physical Properties and Chemical Constitution. Part XLI.*¹
Naphthalene Compounds

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Pure samples of 1- and 2-n-alkylnaphthalenes (methyl to n-octyl), n-alkyl 1- and 2-naphthoates (methyl to n-heptyl), n-alkyl 1- and 2-naphthylacetates (methyl to n-heptyl), n-alkyl 1-naphthylketones (methyl to n-heptyl), and a number of miscellaneous naphthalene compounds have been prepared and their physical properties (refractive indices at 20° and densities and surface tensions over a range of temperature) determined: the ultraviolet and infrared spectra were measured in detail for a number of representative compounds. The parachors, molecular refractions, and molecular refraction coefficients for the 1- and 2-naphthyl groups have been evaluated from the new experimental data.

THE present investigation was undertaken to secure trustworthy data on some physical properties of pure n-alkylnaphthalenes, n-alkyl naphthoates, n-alkyl naphthylacetates, n-alkyl 1-naphthyl ketones, and 1-halogenonaphthalenes, and to evaluate the refractions, molecular refraction coefficients, and parachors of the 1- and 2-naphthyl groups, and their dependence upon different substituents in the 1- and 2-positions.

¹ Part XL, Cumper, Leton, and Vogel, preceding Paper.

The mean values for the CH_2 increments of the refractions and of the molecular refraction coefficients are in good agreement with those previously found,² but the parachor increment (38.1 for 1-naphthyl compounds and 38.5 for 2-naphthyl compounds) is appreciably lower. The refraction and molecular refraction coefficient constants for the 1- and 2-naphthyl groups were calculated in the usual manner³ but the method of calculation of the parachor constants was modified so as to utilise the observed CH_2 increments for each particular series of compounds, *e.g.*:

$$(\text{C}_{10}\text{H}_7) = (\text{C}_{10}\text{H}_7) \cdot [\text{CH}_2]_n \cdot \text{CH}_3 - (n + 1)(\text{CH}_2)_{\text{obs}} - (\text{C}-\text{H}) - (\text{C}-\text{C}) \text{ (alkylnaphthalenes)}$$

$$(\text{C}_{10}\text{H}_7) = (\text{C}_{10}\text{H}_7) \text{CO}_2[\text{CH}_2]_n \cdot \text{CH}_3 - (n + 1)(\text{CH}_2)_{\text{obs}} - (\text{C}-\text{H}) - (\text{C}=\text{O}) - 2(\text{C}-\text{O}) - (\text{C}-\text{C}) \text{ (alkyl naphthoates)}$$

The constants for the 1- and 2-naphthyl groups are summarised in Table 1.

TABLE I
Mean constants for naphthyl groups

Compounds	<i>P</i>	$[R]_{\text{C}}$	$[R]_{\text{D}}$	$[R]_{\text{F}}$	$[R]_{\text{G}}$	Mn_{D}^{20}
<i>1-Naphthyl group</i>						
1-n-Alkylnaphthalenes	285.6	40.97	41.42	42.62	44.02	192.11
<i>s</i>	0.7	0.02	0.01	0.02	0.03	0.18
n-Alkyl 1-naphthoates	288.8	41.66	42.14	43.75	45.19	195.76
<i>s</i>	0.3	0.06	0.04	0.09	0.08	0.44
n-Alkyl 1-naphthylacetates	289.9	41.19	41.52	42.90	44.06	196.10
<i>s</i>	0.55	0.01	0.01	0.01	0.03	0.01
n-Alkyl 1-naphthyl ketones	289.2	41.47	41.96	43.60	45.04	195.72
<i>s</i>	0.3	0.04	0.03	0.04	0.05	0.38
Mean values	288.4	41.32	41.78	43.22	44.57	194.92
1-Halogenonaphthalenes	290.4	41.76	42.01	43.44	44.59	208.77
1-Methoxynaphthalene	291.2	42.27	42.79	44.28	45.54	209.72
1-Chloromethylnaphthalene	291.8	42.08	42.57	43.95	45.19	211.94
<i>2-Naphthyl group</i>						
2-n-Alkylnaphthalenes	287.5	41.42	41.87	43.29	44.47	191.55
<i>s</i>	0.8	0.05	0.03	0.05	0.06	0.10
n-Alkyl 2-naphthoates	292.8	42.14	42.71	44.33	45.84	196.13
<i>s</i>	0.6	0.06	0.04	0.06	0.07	0.5
n-Alkyl 2-naphthylacetates	292.4	41.33	41.76	43.17	44.25	193.88
<i>s</i>	0.47	0.02	0.02	0.02	0.03	0.54
Mean values	290.9	41.63	42.11	43.66	44.85	193.85
2-Isopropylnaphthalene	287.2	42.39	42.87	44.21	45.38	204.15
2-t-Butyl naphthalene	283.1	42.57	43.06	45.24	45.64	203.89

s = standard deviation.

Theoretical values for the constants of the naphthyl groups can be calculated from the known³ bond constants, and it is interesting that, whereas the observed molecular refractions and molecular refraction coefficients are in moderate agreement with the values

TABLE 2
Constants for naphthyl groups

	<i>P</i>	$[R]_{\text{D}}$	Mn_{D}^{20}		<i>P</i>	$[R]_{\text{D}}$	Mn_{D}^{20}
		<i>Calculated</i>				<i>Observed</i>	
Aliphatic bond constants	293.3	40.36	151.20	1-Naphthyl...	288.4	41.78	194.92
Aromatic bond constants	306.45	41.30	199.46	2-Naphthyl...	290.9	42.11	193.85

calculated using the aromatic C-C bond constants, the observed parachor is in better agreement with the value calculated using the aliphatic C-C and C=C bond constants (Table 2).

² Part XXIII, Vogel, *J.*, 1948, 1842.

³ Part XXIV, Vogel, Cresswell Jeffery, and Leicester, *J.*, 1952, 531.

EXPERIMENTAL

Physical Measurements.—Details of experimental methods are given in Part XXVIII.⁴ Unless otherwise stated, b. p.s are corrected. The compounds were refractionated immediately before the measurements were made; they were examined for impurities by vapour-phase chromatography (a Griffin and George apparatus, Mark II, was used), and by ultraviolet and infrared spectroscopy, but none was found.

Materials.—*n-Alkyl naphthoates.* 1-Naphthoic acid and 2-naphthoic acid were prepared by oxidation of the corresponding methyl naphthyl ketone with potassium hypochlorite,⁵ and recrystallised from toluene (1-naphthoic acid, m. p. 162°), or benzene (2-naphthoic acid, m. p. 187.5°). The acids were converted into the esters by refluxing with the pure alcohols in presence of benzene and sulphuric acid, and these were isolated in the usual manner.^{6a}

n-Alkyl naphthylacetates. 1-Naphthylacetic acid was prepared from naphthalene by chloromethylation,⁷ treatment of the 1-chloromethylnaphthalene with potassium cyanide in aqueous ethyl alcohol solution, and hydrolysis of the resulting 1-naphthylacetonitrile with sulphuric acid in aqueous acetic acid solution.^{6b}

2-Naphthylacetic acid was prepared from pure methyl 2-naphthyl ketone (Fluka) by heating with sulphur in presence of morpholine, and hydrolysing the thiomorpholide thus obtained with sulphuric acid in aqueous acetic acid solution.⁸

Both acids were purified by recrystallisation of the sodium salt from aqueous solution, precipitation of the acid with hydrochloric acid, and recrystallisation from benzene (1-naphthylacetic acid, m. p. 132°), or benzene–light petroleum (b. p. 60–80°) (2-naphthylacetic acid, m. p. 144°). The esters were prepared as described for the naphthoates.

n-Alkyl 1-naphthyl ketones. Commercially pure methyl 1-naphthyl ketone (Fluka) was converted to the picrate which was recrystallised twice from ethanol (m. p. 120°) and the ketone regenerated by treatment with dilute aqueous ammonia; traces of picric acid were removed by passing a dry benzene solution of the ketone down a column packed with alumina. The remaining ketones (ethyl to n-heptyl) were prepared from pure 1-bromonaphthalene by forming the Grignard reagent, treating with anhydrous cadmium chloride to give di-1-naphthylcadmium, and reacting this in benzene solution with the appropriate acid chloride (propionyl to n-octanoyl).⁹ In every case the ketone was purified by conversion into the semicarbazone, which was recrystallised and then decomposed by refluxing with dilute sulphuric acid (30%).

1- and 2-n-Alkyl naphthalenes. 1-Methylnaphthalene was a high-grade commercial product (Light) which was fractionally distilled, converted into the picrate, and, after two recrystallisations from ethanol (m. p. 140°), decomposed with dilute aqueous ammonia; the recovered hydrocarbon was heated with sodium for 2 hr. at 150° before distilling under reduced pressure. The remaining hydrocarbons were prepared from the appropriate alkyl naphthyl ketone by Huang-Minlon's modification of the Wolff–Kishner reduction;¹⁰ the alkyl 2-naphthyl ketones required were prepared by interaction of 2-naphthoyl chloride with the appropriate dialkylcadmium. The hydrocarbons were all purified by way of the picrate and by heating with sodium before the final distillation.

1-Halogenonaphthalenes. 1-Fluoro-, 1-chloro-, and 1-iodo-naphthalene were prepared from pure 1-naphthylamine, whilst 1-bromonaphthalene was prepared by bromination of naphthalene.¹¹

1-Cyanonaphthalene. Pure 1-bromonaphthalene was heated with cuprous cyanide in presence of pyridine;¹² after fractionation the product was recrystallised from light petroleum (b. p. 40–60°) giving a white solid, m. p. 38°.

1-Chloromethylnaphthalene. A middle fraction of the product from the chloromethylation

⁴ Part XXVIII, Kyte, Jeffery, and Vogel, *J.*, 1960, 4454.

⁵ (a) Newman and Holmes, *Org. Synth.*, Coll. Vol. II, Wiley, New York, 1943, p. 428; (b) Hartough and Conley, *J. Amer. Chem. Soc.*, 1947, **69**, 3096; (c) Bassilios, *Bull. Soc. chim. France*, 1954, **21**, 72.

⁶ Vogel, "Practical Organic Chemistry," 3rd edn., Longmans, Green & Co., London, 1956, (a) p. 387; (b) p. 763.

⁷ Cambron, *Canad. J. Res.*, 1939, **17B**, 10.

⁸ Carmack and Spielman, *Org. Reactions*, 1947, **3**, 97.

⁹ Cason and Prout, *Org. Synth.*, Coll. Vol. III, Wiley, New York, 1955, p. 601.

¹⁰ Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

¹¹ Vogel, ref. 5, pp. 609, 600, 598, 537.

¹² Vogel, ref. 5, p. 764.

of naphthalene ⁷ was twice redistilled under reduced pressure through a 4 in. column packed with Fenske helices.

1-Cyanomethylnaphthalene. The redistilled product from the interaction of 1-chloromethylnaphthalene and potassium cyanide was purified by way of the picrate, m. p. 107.5° (from ethanol). The nitrile, regenerated by treatment of the picrate with aqueous ammonia, was redistilled under reduced pressure.

TABLE 3

No.	Compound	B. p./mm.	d_4^{20}	d_4^{40}	d_4^{60}	d_4^{85}	γ^{20}	γ^{40}	γ^{60}	γ^{85}	P	Note
<i>Alkyl 1-naphthoates</i>												
841	Methyl	116°/0.9	1.1626	1.1472	1.1320	1.1123	44.14	41.95	39.81	37.34	413.3	<i>a</i>
842	Ethyl	124/0.3	1.1278	1.1123	1.0971	1.0776	41.34	39.21	37.03	34.25	450.2	<i>b</i>
843	n-Propyl	146.5/0.4	1.0978	1.0827	1.0675	1.0487	39.73	37.57	35.76	33.51	489.0	
844	n-Butyl	151/0.4	1.0778	1.0634	1.0488	1.0302	38.13	36.44	34.84	32.42	527.5	
845	n-Pentyl	172/0.2	1.0611	1.0472	1.0326	1.0143	37.22	35.45	33.62	31.51	565.0	
846	n-Hexyl	161/0.5	1.0467	1.0333	1.0186	1.0006	36.63	34.90	33.14	31.25	604.0	
847	n-Heptyl	182.5/0.4	1.0336	1.0195	1.0054	0.9874	35.83	34.32	32.72	30.69	641.9	
<i>Alkyl 2-naphthoates</i>												
848	Ethyl	128/0.2	1.1166	1.1015	1.0862	1.0667	41.56	39.61	37.14	34.47	455.1	<i>c</i>
849	n-Propyl	141/0.1	1.0902	1.0759	1.0607	1.0421	38.21	37.48	35.38	33.10	493.1	<i>d</i>
850	n-Butyl	160.5/0.2	—	1.0566	1.0418	1.0235	—	36.16	34.48	32.14	530.5	<i>e</i>
851	n-Pentyl	162/0.1	1.0554	1.0419	1.0263	1.0088	37.26	35.43	33.85	31.70	569.6	
852	n-Hexyl	172/0.2	1.0419	1.0280	1.0137	0.9975	36.79	35.18	33.45	31.46	608.3	
853	n-Heptyl	179/0.3	—	1.0135	0.9995	0.9815	—	34.49	33.37	30.98	647.3	<i>f</i>
<i>Alkyl 1-naphthylacetates</i>												
854	Methyl	130/0.5	1.1423	1.1277	1.1127	1.0933	45.11	43.09	40.78	38.20	455.1	<i>g</i>
855	Ethyl	139/0.5	1.1070	1.0921	1.0765	1.0574	41.14	38.96	36.87	34.37	490.4	<i>g</i>
856	n-Propyl	147/0.5	1.0831	1.0682	1.0537	1.0346	38.91	36.94	35.03	32.67	527.2	
857	n-Butyl	143/0.3	1.0644	1.0499	1.0353	1.0170	37.66	35.76	33.92	31.78	564.9	
858	n-Pentyl	160/0.2	1.0500	1.0357	1.0206	1.0022	36.39	34.57	32.90	30.81	601.1	
859	n-Hexyl	161.5/0.3	1.0393	1.0249	1.0107	0.9928	35.83	34.21	32.31	30.57	639.1	
860	n-Heptyl	169.5/0.2	1.0246	1.0102	0.9962	0.9785	35.24	33.51	32.04	30.04	677.2	
<i>Alkyl 2-naphthylacetates</i>												
861	Methyl	136/0.3	1.1299	1.1145	1.0992	1.0800	43.76	41.42	39.34	35.86	455.9	
862	Ethyl	129/0.2	1.0967	1.0812	1.0654	1.0454	40.66	38.71	36.59	34.16	494.4	
863	n-Propyl	135.5/0.1	1.0740	1.0591	1.0443	1.0250	38.86	36.81	34.98	32.61	531.5	
864	n-Butyl	143.5/0.2	1.0567	1.0420	1.0271	1.0088	37.86	35.90	34.03	32.06	569.6	
865	n-Pentyl	152/0.2	1.0441	1.0294	1.0147	0.9966	37.12	35.15	33.90	31.56	608.6	
866	n-Hexyl	162/0.3	1.0299	1.0166	1.0013	0.9833	36.29	34.58	32.98	31.14	646.6	
867	n-Heptyl	170.5/0.3	1.0180	1.0041	0.9894	0.9722	35.75	34.01	32.48	30.51	685.3	
<i>Alkyl 1-naphthyl ketones</i>												
868	Methyl	124/1.0	1.1193	1.1042	1.0898	1.0721	46.29	43.83	41.70	39.16	396.7	<i>h</i>
869	Ethyl	116.5/0.4	1.0953	1.0807	1.0662	1.0479	43.56	41.37	39.25	36.81	432.6	<i>h</i>
870	n-Propyl	129.5/0.6	1.0718	1.0566	1.0427	1.0254	41.55	39.60	37.65	35.71	470.2	<i>h</i>
871	n-Butyl	146.5/0.7	1.0515	1.0375	1.0233	1.0061	39.37	37.76	35.96	34.31	508.0	<i>h</i>
872	n-Pentyl	148/0.5	1.0368	1.0222	1.0087	0.9912	38.70	36.83	35.15	33.45	546.0	<i>h</i>
873	n-Hexyl	160/0.2	1.0240	1.0101	0.9964	0.9791	36.47	34.81	33.43	31.32	584.6	<i>h</i>
874	n-Heptyl	178.5/0.3	1.0103	0.9969	0.9831	0.9660	36.74	35.37	33.90	31.95	623.0	
<i>1-n-Alkyl naphthalenes</i>												
875	Methyl	108.5/0.8	1.0221	1.0079	0.9941	0.9762	39.80	38.02	35.32	33.06	349.6	<i>i</i>
876	Ethyl	80.5/0.6	1.0078	0.9938	0.9798	0.9619	38.52	36.40	34.38	31.92	386.2	<i>i</i>
877	n-Propyl	99/0.3	0.9899	0.9760	0.9630	0.9446	36.80	34.75	32.88	30.77	423.8	<i>i</i>
878	n-Butyl	110/0.2	0.9759	0.9626	0.9492	0.9331	35.67	33.94	32.11	29.89	462.1	<i>j</i>
879	n-Pentyl	115.5/0.2	0.9661	0.9528	0.9394	0.9227	35.11	33.42	31.55	29.16	500.6	<i>j</i>
880	n-Hexyl	139/0.8	0.9578	0.9443	0.9309	0.9142	34.98	33.22	31.48	28.85	539.6	<i>j</i>
881	n-Heptyl	128/0.3	0.9500	0.9368	0.9234	0.9073	34.59	32.95	31.30	29.23	578.9	<i>k</i>
882	n-Octyl	144.5/0.2	0.9432	0.9304	0.9174	0.9012	34.27	32.65	31.07	29.18	618.3	<i>k</i>
<i>2-n-Alkyl naphthalenes</i>												
883	Ethyl	98.5/2.0	0.9917	0.9772	0.9631	0.9466	37.18	35.08	32.80	30.66	389.1	<i>l</i>
884	n-Propyl	99/0.6	0.9767	0.9626	0.9485	0.9311	35.69	33.87	32.00	29.66	426.6	<i>l</i>
885	n-Butyl	107/0.4	0.9652	0.9515	0.9376	0.9196	35.38	33.53	31.75	29.72	466.5	<i>l</i>
886	n-Pentyl	116.5/0.3	0.9557	0.9422	0.9284	0.9115	34.55	32.98	31.24	29.21	504.6	<i>l</i>
887	n-Hexyl	124/0.7	0.9475	0.9345	0.9210	0.9043	33.94	32.37	30.69	28.71	542.3	<i>l</i>
888	n-Heptyl	140/0.3	0.9413	0.9283	0.9150	0.8986	33.89	32.15	30.54	28.54	581.2	<i>m</i>
889	n-Octyl	151.5/1.0	0.9353	0.9220	0.9090	0.8930	33.68	32.08	30.51	28.50	620.9	<i>m</i>

TABLE 3 (Continued)

No.	Compound	B. p./mm.	d_4^{20}	d_4^{40}	d_4^{60}	d_4^{85}	γ^{20}	γ^{40}	γ^{60}	γ^{85}	P	Note
<i>Miscellaneous naphthalene compounds</i>												
890	1-Fluoro-	96/18-0	1.1341	1.1176	1.1014	1.0800	38.26	36.01	33.80	31.24	320.4	<i>n</i>
891	1-Chloro-	108/4-0	1.1932	1.1778	1.1621	1.1424	42.05	39.97	37.91	35.32	347.2	<i>n</i>
892	1-Bromo-	140.5/18-0	1.4835	1.4648	1.4464	1.4228	44.44	42.34	40.27	37.83	360.7	<i>n</i>
893	1-Iodo-	121/0.5	1.7396	1.7188	1.6980	1.6716	47.30	44.79	42.67	40.12	382.3	<i>o</i>
894	1-Cyano-	112.5/0.3	1.1121	1.0976	1.0836	1.0653	46.46	44.16	42.33	39.61	360.2	<i>p</i>
895	1,2-Dimethyl	100/2.5	1.0179	1.0039	0.9906	0.9734	39.31	37.17	35.28	32.84	384.5	<i>q</i>
896	1,6-Dimethyl	91.5/1.0	1.0021	0.9886	0.9746	0.9574	37.42	35.40	33.59	31.35	386.0	<i>q</i>
897	1-Cyanomethyl	185/12.0	1.1197	1.1068	1.0930	1.0767	48.96	46.85	44.89	42.25	395.6	<i>r</i>
898	1-Chloromethyl	144.5/12.5	1.1813	1.1661	1.1509	1.1320	45.42	43.48	41.50	38.89	389.2	
899	1-Methoxy	92/1.0	1.0960	1.0813	1.0662	1.0475	42.90	40.68	38.47	35.98	369.6	<i>s</i>
900	2-Isopropyl	90/1.5	0.9753	0.9617	0.9476	0.9303	35.00	33.19	31.88	29.37	425.1	<i>t</i>
901	2-t-Butyl	113/4.0	0.9683	0.9547	0.9411	0.9241	34.27	32.47	30.62	28.84	461.0	<i>u</i>

For footnotes see under Table 4.

TABLE 4

No.	n_D^{20}	n_D^{20}	n_F^{20}	n_G^{20}	$[R]_G$	$[R]_D$	$[R]_F$	$[R]_G$	Mn_D^{20}	Note
<i>Alkyl 1-naphthoates</i>										
841	1.60363	1.61184	1.63367	1.65581	55.06	55.67	57.25	58.83	299.87	<i>a</i>
842	1.58660	1.59416	1.61495	1.63476	59.61	60.23	61.93	62.02	319.07	<i>b</i>
843	1.57598	1.58313	1.60271	1.62127	64.59	65.24	67.02	68.67	339.21	
844	1.56761	1.57437	1.59288	1.61034	69.26	69.93	71.77	73.47	359.42	
845	1.56073	1.56724	1.58481	1.60146	73.92	74.63	76.52	78.28	379.77	
846	1.55477	1.56098	1.57796	1.59370	78.58	79.31	81.27	83.07	400.13	
847	1.54924	1.55517	1.57134	1.58643	83.24	83.90	85.99	87.84	420.48	
<i>Alkyl 2-naphthoates</i>										
848	1.58853	1.59630	1.61748	1.63731	60.37	61.02	62.75	64.37	319.64	<i>c</i>
849	1.57778	1.58514	1.60508	1.62374	65.19	65.88	67.68	69.36	339.64	<i>d</i>
850	—	—	—	—	69.82	70.53	72.39	74.12	359.75	<i>e</i>
851	1.56234	1.56893	1.58687	1.60363	74.52	75.22	77.14	78.94	380.13	
852	1.55630	1.56269	1.57983	1.59588	79.12	79.90	81.87	83.71	400.59	
853	—	—	—	—	83.78	84.56	86.57	88.47	420.72	<i>f</i>
<i>Alkyl 1-naphthylacetates</i>										
854	1.59051	1.59753	1.61632	1.63354	59.20	59.77	61.28	62.65	319.89	<i>g</i>
855	1.57476	1.58132	1.59884	1.61482	63.94	64.54	66.11	67.53	338.82	<i>g</i>
856	1.56470	1.57088	1.58745	1.60253	68.63	69.24	70.88	72.35	358.62	
857	1.55656	1.56245	1.57822	1.59244	73.24	73.88	75.56	77.09	378.61	
858	1.55036	1.55601	1.57110	1.58472	77.82	78.48	80.23	81.78	398.88	
859	1.54457	1.55005	1.56446	1.57753	82.41	83.10	84.89	86.50	419.09	
860	1.53952	1.54471	1.55870	1.56976	87.02	87.72	89.58	91.14	439.32	
<i>Alkyl 2-naphthylacetates</i>										
861	1.58578	1.59265	1.61101	1.62774	59.45	60.02	61.52	62.87	318.91	
862	1.57130	1.57790	1.59492	1.61048	64.22	64.83	66.38	67.78	338.09	
863	1.56212	1.56830	1.58455	1.59937	68.95	69.57	71.19	72.66	358.03	
864	1.55482	1.56070	1.57628	1.59028	73.58	74.23	75.92	77.42	378.19	
865	1.54904	1.55470	1.56936	1.58309	78.20	78.87	80.61	82.17	398.54	
866	1.54357	1.54900	1.56333	1.56715	82.82	83.51	85.30	86.89	418.81	
867	1.53887	1.54269	1.55793	1.57033	87.50	88.15	90.06	91.70	439.02	
<i>Alkyl 1-naphthyl ketones</i>										
868	1.61978	1.62868	1.65321	1.67734	53.72	54.02	56.01	57.63	277.22	<i>h</i>
869	1.60512	1.61322	1.63546	1.65494	57.94	58.57	60.26	61.92	297.22	<i>h</i>
870	1.59284	1.60045	1.62084	1.64142	62.67	63.32	65.05	66.77	317.31	<i>h</i>
871	1.58258	1.58978	1.60950	1.62834	67.44	68.11	69.95	71.68	337.50	<i>h</i>
872	1.57452	1.58131	1.60003	1.61790	72.08	72.78	74.68	76.47	357.88	<i>h</i>
873	1.56715	1.57374	1.59181	1.60901	76.74	77.46	79.40	81.25	378.24	<i>h</i>
874	1.56012	1.56609	1.58306	1.59910	81.40	82.14	84.13	86.03	398.37	
<i>1-n-Alkyl-naphthalenes</i>										
875	1.60991	1.61800	1.63987	1.65995	48.23	48.74	50.12	51.36	230.08	<i>i</i>
876	1.59887	1.60645	1.62628	1.64563	52.95	53.39	54.93	56.24	250.97	<i>i</i>
877	1.58554	1.59263	1.61170	1.62930	57.69	58.25	59.76	61.14	271.15	<i>j</i>
878	1.57491	1.58166	1.59948	1.61588	62.39	62.99	64.56	65.98	291.47	<i>j</i>
879	1.56662	1.57291	1.58984	1.60532	67.02	67.63	69.26	70.73	311.92	<i>j</i>
880	1.55969	1.56583	1.58203	1.59674	71.65	72.30	73.99	75.51	332.48	<i>j</i>
881	1.55330	1.55912	1.57455	1.58859	76.29	76.95	78.69	80.26	352.93	<i>k</i>
882	1.54773	1.55330	1.56808	1.58143	80.91	81.60	83.39	84.99	373.40	<i>k</i>

TABLE 4 (Continued)

No.	n_{C}^{20}	n_{D}^{20}	n_{F}^{20}	n_{G}^{20}	[R] _G	[R] _D	[R] _F	[R] _G	Mn_{D}^{20}	Note
<i>2-n-Alkyl-naphthalenes</i>										
883	1.59241	1.59981	1.61983	1.63805	53.34	53.88	55.32	56.62	249.94	
884	1.58101	1.58806	1.60682	1.62390	58.10	58.67	60.18	61.54	270.38	l
885	1.57155	1.57815	1.59587	1.61194	62.78	63.37	64.95	66.36	290.82	l
886	1.56377	1.57009	1.58667	1.60201	67.47	68.09	69.70	71.19	311.36	l
887	1.55669	1.56272	1.57872	1.59318	72.11	72.75	74.45	75.96	331.82	l
888	1.55115	1.55692	1.57226	1.58603	76.74	77.41	79.93	80.71	352.43	m
889	1.54598	1.55157	1.56618	1.67950	81.38	82.07	83.88	85.47	372.98	m
<i>Miscellaneous naphthalene compounds</i>										
890	1.59011	1.59383	1.61461	1.63377	43.50	43.72	44.96	46.07	232.96	n
891	1.62482	1.63315	1.65557	1.67640	48.17	48.69	50.05	51.29	265.59	n
892	1.64927	1.65803	1.68173	1.70374	50.87	50.97	52.86	54.17	343.35	n
895	1.60862	1.61656	1.63800	1.65785	53.14	53.69	55.18	56.54	252.65	q
896	1.59859	1.60632	1.62698	1.64608	53.25	53.81	55.28	56.61	251.05	q
898	1.62966	1.63792	1.66018	1.68088	53.18	53.73	55.22	56.57	289.34	
899	1.61445	1.62294	1.64606	1.66801	50.34	50.90	52.40	53.79	256.75	s
900	1.57793	1.58482	1.60304	1.61963	57.93	58.49	59.96	61.29	269.82	t
901	1.57333	1.60653	1.57995	1.61356	62.74	63.33	65.68	66.29	291.16	u

Footnotes to Tables 3 and 4.

(a) Price and Huber (*J. Amer. Chem. Soc.*, 1942, **64**, 2136) give b. p. 100—102°/0.04 mm., d_4^{20} 1.129, n_{D}^{20} 1.6068; Lauer (*Ber.*, 1937, **70**, 1288) gives m. p. 59.5°: our product could not be induced to solidify. (b) Perkin (*J.*, 1896, **69**, 1025) gives d_4^{20} 1.1244; Adkins and Burgoyne (*J. Amer. Chem. Soc.*, 1949, **71**, 3528) give n_{D}^{25} 1.5931. (c) Perkin (*J.*, 1896, **69**, 1025) gives d_4^{20} 1.1181; von Anwers and Fruhling (*Annalen*, 1921, **422**, 196) give $n_{\text{C}}^{22.7}$ 1.5876, $n_{\text{D}}^{22.7}$ 1.5951, $n_{\text{F}}^{22.7}$ 1.6165, $n_{\text{G}}^{22.7}$ 1.6354. (d) Solid, m. p. 37°; values recorded for supercooled liquid. (e) Solid, m. p. 41°; values for supercooled liquid (at 35°) n_{C} 1.56322, n_{D} 1.57009, n_{F} 1.58876, n_{G} 1.60621; (at 30°) n_{C} 1.56507, n_{D} 1.57200, n_{F} 1.59069, n_{G} 1.60819; molar refractivities and molar refraction coefficients calculated from extrapolated data. (f) Solid, m. p. 36°; values for supercooled liquid (at 35°) n_{C} 1.54436, n_{D} 1.55040, n_{F} 1.56660, n_{G} 1.58162; (at 30°) n_{C} 1.54620, n_{D} 1.55229, n_{F} 1.56861, n_{G} 1.58364; molar refractivities and molar refraction coefficients calculated from extrapolated data. (g) Adkins and Burgoyne (*J. Amer. Chem. Soc.*, 1949, **71**, 3528) give n_{D}^{25} 1.5952 (methyl), 1.5797 (ethyl). (h) Nunn and Henze (*J. Org. Chem.*, 1947, **12**, 541) give methyl d_4^{20} 1.1203, n_{D}^{20} 1.6257; ethyl d_4^{20} 1.0971, n_{D}^{20} 1.6108; n-propyl d_4^{20} 1.0722, n_{D}^{20} 1.5988; n-butyl d_4^{20} 1.0562, n_{D}^{20} 1.5894; n-pentyl d_4^{20} 1.0394, n_{D}^{20} 1.5808; n-hexyl d_4^{20} 1.0251, n_{D}^{20} 1.5728. (i) Morrell, Pickering, and Smith (*J. Inst. Petroleum*, 1948, **34**, 677) give methyl d_4^{20} 1.020, n_{D}^{20} 1.6174; ethyl d_4^{20} 1.008, n_{D}^{20} 1.6062; n-propyl d_4^{20} 0.990, n_{D}^{20} 1.5923; Levina [*J. Gen. Chem. (U.S.S.R.)*, 1940, **10**, 913] gives n-propyl d_4^{20} 0.9904, n_{D}^{20} 1.5928. (j) Bailey, Pickering, and Smith (*J. Inst. Petroleum*, 1949, **35**, 103) give n-butyl d_4^{20} 0.977, n_{D}^{20} 1.5811; n-pentyl d_4^{20} 0.966, n_{D}^{20} 1.5728; n-hexyl d_4^{20} 0.958, n_{D}^{20} 1.5652. (k) Anderson and Smith (*J. Inst. Petroleum*, 1952, **38**, 415) give n-heptyl d_4^{20} 0.9500, n_{D}^{20} 1.5583; n-octyl d_4^{20} 1.5532, n_{D}^{20} 0.9401. (l) Bailey, Pickering, and Smith (*loc. cit.*) give ethyl d_4^{20} 0.992, n_{D}^{20} 1.5999; n-propyl d_4^{20} 0.977, n_{D}^{20} 1.5872; n-butyl d_4^{20} 0.966, n_{D}^{20} 1.5776; n-pentyl d_4^{20} 0.956, n_{D}^{20} 1.5694; n-hexyl d_4^{20} 0.948, n_{D}^{20} 1.5620. (m) Anderson and Smith (*loc. cit.*) give n-heptyl d_4^{20} 0.9407; n_{D}^{20} 1.5565; n-octyl d_4^{20} 0.9390, n_{D}^{20} 1.5511; Petrov [*J. Gen. Chem. (U.S.S.R.)*, 1942, **12**, 87] gives n-octyl d_4^{20} 0.9366, n_{D}^{20} 1.5510. (n) Cf. Part XIV (*J.*, 1948, 645). (o) Pale yellow oil; light absorption too strong for measurements on Hilger-Chance refractometer, n_{D}^{20} 1.7028 (Abbe refractometer). Parts (*Z. Phys. Chem.*, 1930, **10**, 264) gives $d_4^{19.5}$ 1.7409; $n_4^{19.5}$ 1.70256. (p) Solid, m. p. 38°. (q) Schade and Kniber (*Ber.*, 1935, **68**, 11) give (1,2-) d_4^{20} 1.015, n_{D}^{20} 1.6135; (2,6-) d_4^{20} 1.0115, n_{D}^{20} 1.6083. (r) Solid, m. p. 33°. (s) Nasini (*Gazzetta*, 1885, **15**, 9) gives $d_4^{13.9}$ 1.0964; $n_{\text{D}}^{13.9}$ 1.6232. (t) Romadane (*Zhur. obskchei Khim.*, 1957, **27**, 1833) gives d_4^{20} 0.9773, n_{D}^{20} 1.5874. (u) Petrov [*J. Gen. Chem. (U.S.S.R.)*, 1942, **12**, 95] gives d_4^{20} 0.9674, n_{D}^{20} 1.5812.

1-Methoxynaphthalene. Pure 1-naphthol was treated with dimethyl sulphate in presence of 10% sodium hydroxide solution and the product, after fractional distillation, was converted to the picrate, m. p. 130.5° (from absolute ethanol). This was decomposed with ethanolamine and the regenerated ether distilled twice under reduced pressure.

2-Isopropyl-naphthalene. Pure isopropyl bromide was reacted with naphthalene in presence of aluminium chloride,¹³ and the product, after fractional distillation, converted into the picrate, m. p. 93° (from absolute ethanol). The regenerated hydrocarbon was heated with sodium and redistilled under reduced pressure.

2-t-Butyl-naphthalene. This was prepared by reacting pure t-butyl chloride with naphthalene

¹³ Haworth, Letsky, and Mavin, *J.*, 1932, 1784.

in presence of zinc chloride,¹⁴ and purified in similar manner to 2-isopropylnaphthalene; the recrystallised picrate had m. p. 100.5°.

1,2- and 1,6-Dimethylnaphthalene. High-grade commercial samples (Fluka), were fractionated under reduced pressure and converted into the picrates, m. p.s 131.5° (1,2-) and 113° (1,6-) (from absolute ethanol). The picrates were decomposed by treatment with aqueous ethanolamine and the hydrocarbons fractionated under reduced pressure after heating with sodium.

Tables 3 and 4 summarise the physical properties of all the pure compounds investigated; the numbering of compounds in Clarendon type follows from Part XXXII.¹⁵ Table 3 contains the b. p. (at 760 mm., unless otherwise stated), rounded values of the density and surface tension at various temperatures, and the mean parachor, whilst Table 4 gives the refractive indices, molar refractivities, and the molar refraction coefficients. Compounds not previously reported in the literature were analysed for carbon and hydrogen, and in all cases gave satisfactory results.

Ultraviolet Spectra.—Measurements were made in matched 0.5 or 1 cm. silica cells on a Unicam S.P. 500 spectrophotometer. Solutions were prepared by dissolving 100–200 mg. of the sample, accurately weighed in 50.0 ml. of Burroughs's absolute ethanol: portions of this solution were then diluted in graduated flasks to give solutions containing 4–40 mg. of solute per litre. Some typical results are collected in Table 5; λ_{\max} is given in μ .

TABLE 5
Ultraviolet absorption data

Alkyl group	λ_{\max} .	ϵ_{\max} .	λ_{\max} .	ϵ_{\max} .	λ_{\max} .	ϵ_{\max} .	λ_{\max} .	ϵ_{\max} .	
		<i>1-n-Alkylnaphthalenes</i>				<i>2-n-Alkylnaphthalenes</i>			
Ethyl	224.5	8.436×10^4	282	12.83×10^3	225	1.392×10^5	276	4.903×10^3	
n-Propyl	225	8.570	282.5	12.97	225	1.218	276	5.012	
n-Butyl	225	9.733	282.5	9.443	225	1.107	276	4.823	
n-Pentyl	225	11.24	283	7.764	225	1.201	276	5.244	
n-Octyl	224.5	13.77	282.5	7.634	225	1.223	275	5.376	
		<i>n-Alkyl 1-naphthoates</i>				<i>n-Alkyl 2-naphthoates</i>			
Ethyl	220	4.205×10^5	296.5	6.471×10^3	237	7.819×10^4	279	7.879×10^3	
n-Propyl	220	4.635	295	6.398	237	8.291	280	7.536	
n-Butyl	220	4.504	296	6.279	237	8.203	280	7.677	
n-Pentyl	220	4.276	296.5	6.420	237.5	7.755	281	7.803	
n-Hexyl	220	4.422	296	6.511	238	7.563	280	7.867	
n-Heptyl	220	4.320	296	6.284	237	7.149	281	8.005	
		<i>n-Alkyl 1-naphthyl ketones</i>				<i>n-Alkyl 2-naphthyl ketones</i>			
Methyl	213	4.708×10^4	298	6.259×10^3	240	5.446×10^4	291	9.838×10^3	
Ethyl	213	5.030	299	6.226	240	5.142	292	9.360	
n-Butyl	215	5.427	298	6.054	240	5.079	291	9.324	
n-Pentyl	215	4.906	299	6.328	240	5.088	292	9.443	
n-Hexyl	216	4.721	298	6.448	240	5.107	291	9.225	
		<i>n-Alkyl 1-naphthylacetates</i>				<i>n-Alkyl 1-naphthylacetates</i>			
Methyl	224.5	8.696×10^4	281	7.062×10^3	224	10.73×10^4	275.5	5.389×10^3	
Ethyl	224.5	9.661	281	6.903	224	10.45	275	5.253	
n-Propyl	225	9.987	281	6.884	224	10.12	275.5	5.387	
n-Pentyl	224.5	9.166	281	7.183	224	10.74	275.5	5.402	
n-Heptyl	224	10.028	280.5	6.953	224	10.34	276	5.391	

Infrared Spectra.—The infrared absorption spectra (capillary film) were measured using a Perkin-Elmer Infracord spectrophotometer; typical spectra are incorporated in ref. 16. Where overlap occurs, our results agree well with previously published spectra for some alkyl- and halogeno-naphthalenes.¹⁷

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¹⁴ Bromby, Peters, and Rowe, *J.*, 1943, 144.

¹⁵ Part XXXII, *J.*, 1961, 570.

¹⁶ G. B. Arrowsmith, Ph.D. Thesis, University of London, 1962.

¹⁷ (a) Broomfield, *J. Inst. Petroleum*, 1952, **38**, 424; (b) Warner, Kennard, and Rayson, *Austral. J. Chem.*, 1955, **8**, 347.