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TECHNICAL NOTE 2430

SYNTHESIS, PURIFICATION, AND PHYSICAL PROPERTIES OF HYDROCARBONS OF THE NAPHTHALENE SERIES

I - 1-METHYLNAPHTHALENE, 1-ETHYLNAPHTHALENE, 1-BUTYLNAPHTHALENE, AND 1-ISOBUTYLNAPHTHALENE

By Harold F. Hipsher and Paul H. Wise

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SUMMARY

The synthesis, the purification, and several physical properties of four 1-alkylnaphthalenes, 1-methylnaphthalene, 1-ethylnaphthalene, 1-butylnaphthalene, and 1-isobutylnaphthalene, are described. In each case, the hydrocarbon was synthesized from 1-naphthylmagnesium bromide by well-known methods. The final hydrocarbons (a minimum of 2000 ml each) were purified by fractional distillation through 6-foot Podbielniak columns to obtain 500 milliliters of each hydrocarbon with a calculated purity higher than 99 mole percent. The physical properties, determined for material having a calculated purity of 99.8 mole percent or higher, include melting point, boiling points at 760 millimeters of mercury, index of refraction, density at 20° C, kinematic viscosity at four temperatures, heat of fusion, and heat of combustion. Time-temperature melting curves and infrared spectra are presented for the four 1-alkylnaphthalenes.

INTRODUCTION

As part of an investigation of the effect of molecular structure on the physical properties of hydrocarbons, a series of alkylnaphthalenes and their hydrogenated derivatives is being prepared at the NACA Lewis laboratory. The synthesis program was necessary because of the relative scarcity of complete and reliable data in the literature.

Almost all the literature on the alkylnaphthalenes describes attempts to separate the individual hydrocarbons from mixtures of isomers or from natural products such as petroleum (reference 1) or coal-tar distillates (references 2 and 3). In order to obtain products of known structure and purity, direct synthesis of the desired hydrocarbons appeared to be a preferable approach.

The synthesis of 1-methylnaphthalene by the hydrolysis of 1-naphthylmethylmagnesium chloride has been reported (reference 4). The condensation of dimethyl sulfate with 1-naphthylmagnesium bromide, as suggested in reference 5, was chosen for this preparation.

2206

1-Ethylnaphthalene has been prepared by the reduction of methyl-1-naphthyl ketone (references 6 to 9), by the condensation of 1-naphthylmagnesium bromide with diethyl sulfate (reference 5) or ethyl-p-toluenesulfonate (reference 10), and by the reaction of 1-naphthylmethylmagnesium chloride with dimethyl sulfate (reference 11). The reaction of diethyl sulfate with 1-naphthylmagnesium bromide was used herein.

Three methods for the synthesis of 1-butylnaphthalene are reported in the literature: a Wurtz-type reaction of 1-bromonaphthalene with butyl chloride (reference 12), the reduction of propyl-1-naphthyl ketone made by the Friedel-Crafts synthesis (reference 13), and the reaction of butylmagnesium bromide with α-tetralone and the dehydration and dehydrogenation of the resulting tetralol (reference 9).

The following three methods, not previously reported, were used in this research to prepare 1-butylnaphthalene: (1) condensation of butyraldehyde with 1-naphthyl Grignard reagent, dehydration of the resulting carbinol to 1(1-naphthyl)1-butene, and hydrogenation of that olefin with copper chromite catalyst; (2) Wolff-Kishner reduction of 1(1-naphthyl)1-butanone obtained by the condensation of butyronitrile with 1-naphthylmagnesium bromide; and (3) directly, by the reaction of butyl-p-toluenesulfonate with the 1-naphthyl Grignard reagent.

The only mention of 1-isobutylnaphthalene in the literature is the synthesis of the intermediate isopropyl-1-naphthyl ketone by the Friedel-Crafts reaction and reduction of the ketone with nickel catalyst (reference 14). 1-Isobutylnaphthalene was prepared in this investigation by the hydrogenation of the olefin synthesized by the reaction of methallyl chloride with 1-naphthylmagnesium bromide.

DISCUSSION OF SYNTHESES

Purification of 1-bromonaphthalene by crystallization and fractional distillation indicated that the impurities were naphthalene and dibromonaphthalenes, which would not give troublesome impurities in the final hydrocarbons. After the syntheses had been completed, it was discovered by infrared analysis that a small percentage of the 2-isomer was present in the 1-ethylnaphthalene. The possible presence of the 2-isomer in the hydrocarbons will be discussed under each hydrocarbon.

1-Ethylnaphthalene. - The preparation of 1-ethylnaphthalene involved the reaction of the Grignard reagent, 1-naphthylmagnesium bromide, with diethyl sulfate. For each mole of Grignard reagent, 2 moles of diethyl sulfate are required for the reaction to go to completion (reference 15).

The final product was contaminated with an impurity that had a boiling point approximately 1° C below, and a refractive index considerably below the values for 1-ethylnaphthalene (fig. 1(b)). Samples from various parts of the distillation were checked by infrared spectra in an attempt to identify the contaminant. It was found to be 2-ethylnaphthalene by a comparison with the spectrum of an authentic sample of the 2-isomer, but no quantitative analysis was made.

1-Methylnaphthalene. - The synthesis of 1-methylnaphthalene was similar to that of 1-ethylnaphthalene; 2 moles of dimethyl sulfate were used for each mole of naphthyl Grignard reagent.

If 1-methylnaphthalene is contaminated with 2-methylnaphthalene, it can be purified by fractional distillation (reference 1); however, any contamination of the final product with the 2-isomer will not be indicated by the calculation of purity by the freezing-point method since the two isomers form solid solutions (reference 2). However, the difference between the boiling points of 1- and 2-methylnaphthalene at atmospheric pressure is 3.5° C and of 1- and 2-ethylnaphthalene is only 0.85° C. The purity of the 1-methylnaphthalene should therefore be at least as high as that of the 1-ethylnaphthalene reported herein.

1-Isobutylnaphthalene. - 1-Isobutylnaphthalene was prepared by the reaction of methallyl chloride with the naphthyl Grignard reagent, and the resulting olefin was hydrogenated in the presence of copper chromite catalyst. The naphthalene ring was found to be partly reduced if the temperature of hydrogenation was allowed to rise much above 130° C. Since the heat of reaction was great enough to cause a temperature rise as large as 50° C in a period of 2 minutes, some ring hydrogenation did occur as evidenced by the lower refractive index of the first fractions (fig. 1(c)).

The higher boiling impurity, assumed to be the 2-isomer, was harder to remove because it is concentrated in the residue. As can be seen from figure 1(c), the purest material was obtained in the early part of the distillation, contrary to the behavior of 1-methyl- and 1-ethylnaphthalenes.

1-Butylnaphthalene. - 1-Butylnaphthalene was prepared by three different methods from 1-naphthylmagnesium bromide. Most of the material was prepared by the condensation of butyraldehyde with the naphthyl Grignard reagent, dehydration of the resulting secondary alcohol to the intermediate olefin, and hydrogenation of the olefin over copper chromite catalyst. In this case, the hydrogenation temperature was not allowed to rise above 125° C and very little ring hydrogenation was encountered, as indicated by the absence of material

with a low refractive index (fig. 1(d)). The compound was also made by a Wolff-Kishner reduction of propyl-1-naphthyl ketone, which was synthesized by the condensation of butyronitrile and 1-naphthylmagnesium bromide followed by hydrolysis of the intermediate ketimine. The third method involved the condensation of butyl-p-toluenesulfonate and naphthyl Grignard reagent.

2206

Of the three methods, the Wolff-Kishner reduction of the ketone was the most practical and gave the highest yield of pure material with the least amount of working time involved.

The separation of the higher boiling impurity, assumed to be the 2-isomer, was more difficult with the n-butyl compound than with the isobutyl compound and a smaller percentage of the hydrocarbon was isolated with a purity better than 99 mole percent (fig. 1(d)).

PURIFICATION AND DETERMINATION OF PHYSICAL PROPERTIES

The hydrocarbons were purified by fractional distillation of 2 to 3 liters of material through 6-foot Podbielniak columns at reduced pressure. Melting points were determined for samples from various parts of the distillation, and the purer fractions were combined to obtain the desired 500-milliliter quantity of each hydrocarbon. The physical constants given in table I are for the purest material obtained and not for the 500-milliliter quantity.

The melting curves (fig. 2) and the boiling points were determined with a platinum resistance thermometer and a G-2 Mueller bridge. The accessory equipment and the method for determining the melting points are those of references 16 and 17, respectively. The boiling point apparatus was modified from that of reference 18, and the system was pressurized with dry air from a surge tank, which was held at constant pressure by adjusting a continuous bleed. A gravimetric balance the same as that described in reference 19 was used for determining the densities. The refractive indices were measured with a Bausch & Lomb precision oil-model instrument. The heats of combustion were measured in an oxygen-bomb calorimeter according to the method described in reference 20. The kinematic viscosities were determined in viscosimeters that had been calibrated with the National Bureau of Standards standard viscosity samples H-5, H-7, D-7, or L-17. The A.S.T.M. procedure of reference 21 was followed. The heats of fusion were obtained by use of a method and apparatus similar to that described in reference 22. The estimated mole percent purities, determined according to methods described in reference 23, are also included. Infrared spectra were obtained on a Baird recording spectrophotometer and are presented in figure 3.

The magnitude of the uncertainties and the precision of the measurements, respectively, are estimated as follows: for the melting point, 0.02° and ±0.003° C; boiling point, 0.1° and ±0.04° C; density, 0.00005 and ±0.00003 gram per milliliter; refractive index n_D^{20}, 0.0002 and ±0.0001; heat of combustion, 20 and ±12 kilogram-calories per mole; kinematic viscosity relative to 1.007 centistokes for water at 20° C, 0.5 and ±0.2 percent of the determined value; and heat of fusion, 5 and 2.5 percent of the determined value.

2206

EXPERIMENTAL DETAILS

The yields reported are based on the amount of 1-bromonaphthalene unless otherwise stated.

1-Naphthylmagnesium Bromide

The 1-naphthyl Grignard reagent was used in each preparation, and the following procedure was employed for each mole of Grignard reagent required. In each case, 1 gram atom (24.3 grams) of magnesium turnings in the reaction vessel was covered with 200 to 300 milliliters of dry ethyl ether; approximately 10 grams of the required 207.1 grams of 1-bromonaphthalene was added with a crystal of iodine or approximately 0.5 gram of methyl iodide to initiate the reaction. After the initial reaction had subsided, the remainder of the 1-bromonaphthalene, dissolved in 150 to 200 milliliters of dry benzene, was added with stirring. The benzene is necessary to keep the Grignard reagent in solution.

1-Methylnaphthalene

The Grignard reagent was prepared from 30 moles of 1-bromonaphthalene and 30 gram atoms of magnesium in a 30-gallon glass-lined reactor. A total of 61 moles (7700 grams) of dimethyl sulfate dissolved in 10 liters of dry ether was added over a period of 2.5 hours. The reaction mixture was stirred overnight and allowed to cool to room temperature. It was refluxed 8 hours and again allowed to cool to room temperature overnight. The mixture was hydrolyzed with 2.2 liters of concentrated hydrochloric acid (approximately 27 moles of hydrogen chloride) dissolved in 40 liters of water. The ether-benzene solution was washed successively with 40 liters of water, 40 liters of 5-percent sodium bicarbonate solution, and again with 40 liters of water. Most of the ether and benzene were distilled by heating with steam. The excess dimethyl sulfate was hydrolyzed by refluxing the product with an equal volume (approximately 5 liters) of 50-percent alcohol containing 775 grams of sodium hydroxide. The product was separated from the alcohol-water layer, the alcohol-water

layer was extracted with ether, and the combined ether extract and product were washed with water and distilled. After the preliminary distillation, which removed 630 grams of naphthalene, the product was fractionally distilled under reduced pressure to give 260 grams of napthalene (24 percent total yield) and 2955 grams (68 percent yield) of 1-methylnaphthalene, 78 percent of which was calculated to be at least 99.7 mole percent pure (fig. 1(a)). 2206

The horizontal lines appearing in the top half of each part of figure 1 correspond to the percentage of the distillate in each sample that was used for estimating the purity. The dashed lines indicate the expected purity of the parts of the distillate on which no melting points were determined.

1-Ethylnaphthalene

1-Naphthylmagnesium bromide was prepared from 25 moles of 1-bromonaphthalene and 25 gram atoms of magnesium in a 30-gallon glass-lined reactor. A total of 50 moles (7700 grams) of freshly distilled diethyl sulfate in 10 liters of dry ether was added in 1.5 hours and the reaction mixture was kept at reflux temperature for an additional 5 hours. The mixture was cooled to room temperature overnight, and hydrolyzed with 40 moles of hydrochloric acid in 24 liters of water. The ether-benzene solution was washed with water, with a 5-percent sodium bicarbonate solution, and again with water. The ether and benzene were distilled under reduced pressure, and the excess diethyl sulfate was hydrolyzed by refluxing with 4 liters of 50-percent alcohol and 500 grams of sodium hydroxide. The product was distilled under reduced pressure and yielded 990 grams (31 percent) of naphthalene, and 2359 grams (60 percent) of crude 1-ethylnaphthalene, 52 percent of which was at least 99.4 mole percent pure (fig. 1(b)).

1-Isobutylnaphthalene

The Grignard reagent was prepared from 40 moles of 1-bromonaphthalene and 40 gram atoms of magnesium; an additional 13 liters of dry ether was added so that the reaction products would remain in suspension. A total of 44 moles (3986 grams) of methallyl chloride dissolved in 10 liters of dry ether was added over a 2.5-hour period. The reaction mixture was stirred overnight without heating and then heated to reflux for 8 hours. The mixture was hydrolyzed with 27 moles of hydrochloric acid dissolved in 25 liters of water. The ether-benzene solution was washed with water, with a 10-percent sodium bicarbonate solution, and again with water. The ether and benzene were distilled by heating with steam, and the product was distilled under

reduced pressure. There was obtained 6235 grams (85 percent) of crude 1-methallyl naphthalene, of which 4085 grams was further purified by fractional distillation at 5 millimeters of mercury pressure to yield 3680 grams of olefin. The range of boiling point (118° to 134° C) and of refractive index n_D^{20} (1.6038 to 1.6137) indicated that there was rearrangement to 1(1-naphthyl)2-methyl-1-propene on prolonged heating, and therefore the other physical constants were not determined.

2206

The structures of the two olefins were established by ozonolysis (reference 24). 1(1-Naphthyl)2-methyl-2-propene gave fragments of formaldehyde and 1(1-naphthyl)2-propanone. The fragments were identified by means of their 2,4-dinitrophenylhydrazones (melting points 166°-167° C and 178°-179° C, respectively) and the semicarbazone of 1(1-naphthyl)2-propanone (melting point, 190°-191° C; reference 25 gives 205° C).

Analysis of 1(1-naphthyl)2-propanone-2,4-dinitrophenylhydrazone -

Calculated for $C_{19}H_{16}O_4N_4$: N, 15.38 percent

Found: N, 15.55 and 15.43 percent

1(1-Naphthyl)2-methyl-1-propene gave fragments of acetone, which gave a positive iodoform test, and 1-naphthaldehyde, which gave a 2,4-dinitrophenylhydrazone (melting point, 262.5°-264° C). A sample mixed with the 2,4-dinitrophenylhydrazone of known 1-naphthaldehyde (melting point, 259°-261° C) melted at 261°-262.5° C.

The olefin was hydrogenated to 1-isobutylnaphthalene in five runs in a 3.35-liter rocking autoclave; 4 moles (729 grams) of the olefin was diluted to 1350 milliliters with methylcyclohexane and charged to the autoclave with 73 grams of copper chromite catalyst. The initial hydrogen pressure was 1600 pounds per square inch at 30° C and the mixture was heated to 115° C before the rocker was started. In approximately 3 minutes, 3.5 moles of hydrogen had reacted, and the temperature had risen to 163° C from the heat of reaction. When the rocker was started at 95° to 100° C, the reaction proceeded more slowly; 3.7 moles reacted in 10 to 12 minutes and the temperature rose to approximately 135° C. The reaction solution was filtered to remove the catalyst, and the methylcyclohexane was distilled at atmospheric pressure. The recovery of 1-isobutylnaphthalene was 99 percent (3543 grams), 54 percent of which was 99.5 to 99.8 mole percent pure after fractional distillation at reduced pressure (fig. 1(c)). Purity was not determined for the final 35 percent of the distillation product.

1-Butylnaphthalene

First method. - A quantity of 25 moles (1802 grams) of freshly distilled butyraldehyde, dissolved in 7.5 liters of dry ether, was added to the Grignard reagent from 25 moles of 1-bromonaphthalene in a 30-gallon glass-lined reactor. After being refluxed for 3 hours, the reaction mixture was hydrolyzed with 9.5 liters of saturated ammonium chloride solution, and the ether-benzene solution was decanted from the precipitated salt. The salt was then dissolved in water, and the remainder of the product, absorbed on the salt cake, was recovered. The ether and benzene were removed by distillation and the 1(1-naphthyl)1-butanol distilled at reduced pressure (1 to 2 mm Hg). There was obtained 517 grams (16 percent) of naphthalene and 4020 grams (80 percent) of halogen-free carbinol. The carbinol was dehydrated by passing a methylcyclohexane solution (50 percent by volume) through a 2.5- by 135-centimeter column of activated alumina heated to 240° to 300° C at the rate of approximately 400 milliliters of solution per hour. There was obtained 320 milliliters of water (theory requires 317 ml), and 2857 grams (89-percent recovery) of olefin from 3520 grams of carbinol.

The ozonide of 1(1-naphthyl)1-butene gave fragments identified as 1-naphthaldehyde (melting point of 2,4-dinitrophenylhydrazone, 259°-261° C; melting point of p-nitrophenylhydrazone, 235°-238° C; reference 26 gives 254° and 237° C, respectively).

The olefin (2575 grams) was hydrogenated as described for 1-isobutylnaphthalene and yielded 2240 grams (86-percent recovery) of 1-butylnaphthalene. Of this material, 42 percent was 99.0 to 99.8 mole percent pure (fig. 1(d)).

Second method. - In a typical experiment, 3 moles (207.3 grams) of butyronitrile dissolved in 250 milliliters of ether was added over a period of 1.2 hours to the Grignard reagent prepared from 3.6 moles of 1-bromonaphthalene. The reaction was heated at reflux for a total of 22.5 hours, allowed to cool, and hydrolyzed by pouring it into a mixture of 4000 grams of ice and 500 grams of 98-percent sulfuric acid. The hydrolysis mixture was heated on a steam bath for 1.5 hours to hydrolyze the ketimine to the ketone. The ketone, combined with the ether extract of the acid layer, was washed with water and sodium bicarbonate solution. The product was combined with the product of a 4.3-mole reaction and distilled (boiling point, 171° to 172° C at 9 mm Hg) to yield 1175 grams of propyl-1-naphthyl ketone (81-percent yield, based on butyronitrile).

The ketone was reduced to the hydrocarbon by the Wolff-Kishner reaction at atmospheric pressure (reference 27). The evolved nitrogen amounted to 67 liters (theory requires 66.5 liters). The product was

2206

isolated by dilution with approximately 10 volumes of water, the hydrocarbon layer was separated, and the water layer was extracted with benzene. The product obtained from two such preparations was combined and distilled to give a yield of 959 grams (87 percent, based on ketone) of 1-butylnaphthalene with a constant refractive index n_D^{20} of 1.5818.

2206

Third method. - A total of 5.1 moles (1164 grams) of butyl-*p*-toluenesulfonate, dissolved in 1 liter of dry benzene, was added during a 3-hour period to the Grignard reagent prepared from 5 moles of 1-bromonaphthalene. The mixture was kept at reflux with stirring for an additional 5 hours. The semisolid reaction mixture was poured into 2000 grams of ice and 200 grams of concentrated hydrochloric acid. The solid was separated by filtering on a Büchner funnel and washed with warm 10-percent aqueous sodium hydroxide solution and water, and the solvents were removed by distillation. The product was distilled at reduced pressure and yielded 714.4 grams (39-percent yield) of 1-butylnaphthalene with a refractive index n_D^{20} of 1.5813 to 1.5819.

CONCLUDING REMARKS

The preparation and the purification of four 1-alkylnaphthalenes, 1-methylnaphthalene, 1-ethylnaphthalene, 1-butylnaphthalene, and 1-isobutylnaphthalene, are described. The hydrocarbons were prepared in a quantity to obtain a minimum of 500 milliliters of each with a purity calculated to be at least 99 mole percent. The physical constants of samples of these hydrocarbons, estimated to be at least 99.8 mole percent pure, were determined by precise measurements.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, April 23, 1951.

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2206

2206

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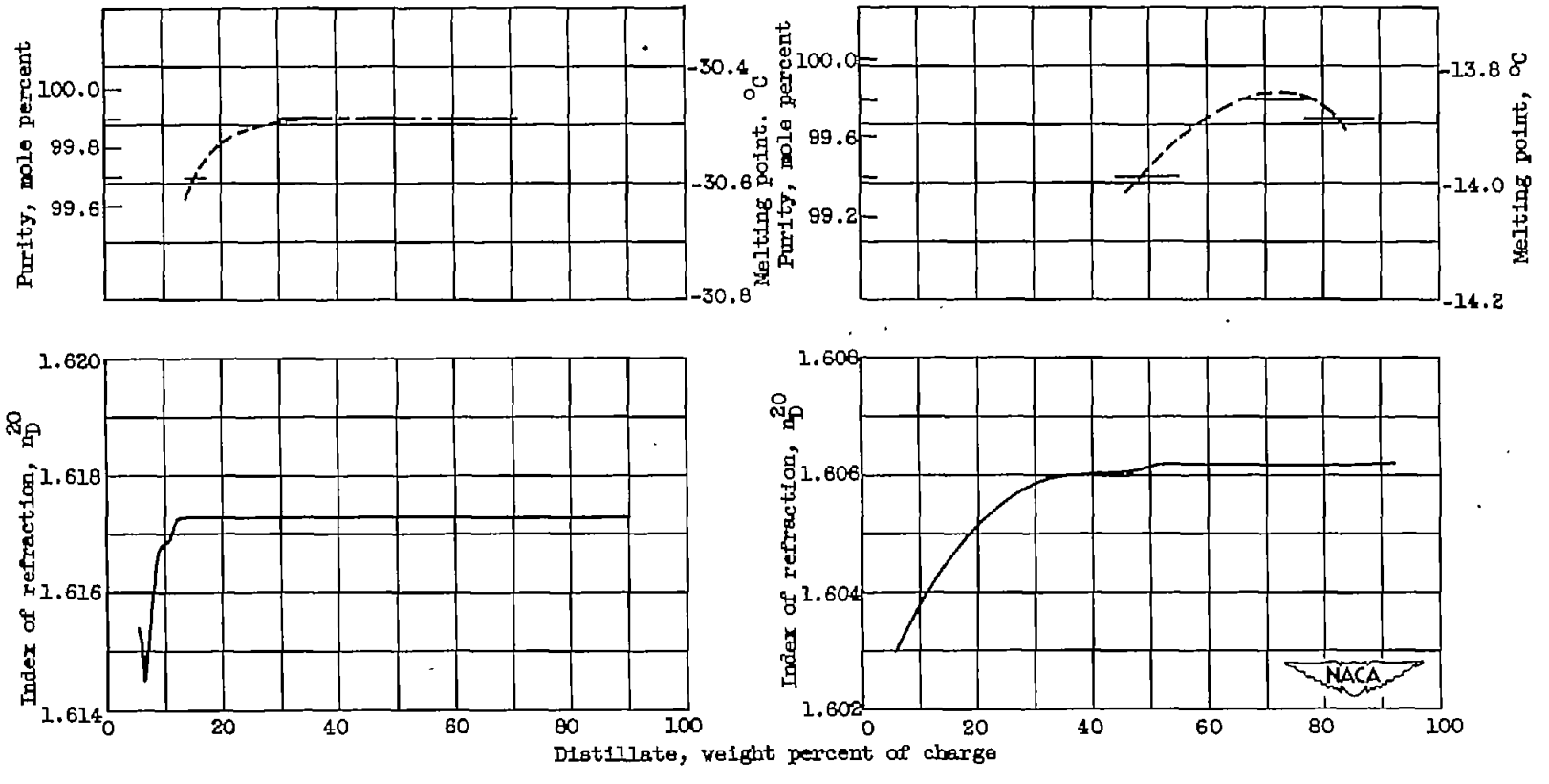
2206

TABLE I - PHYSICAL CONSTANTS

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density d^{20} (grams/ml)	Heat of fusion ΔH_f (kcal/mole)	Estimated purity (mole percent)	Net heat of combustion (kcal/mole)
1-Methylnaphthalene	-30.50	244.42	1.6174	1.02015	2.3	99.9	1345
1-Ethylnaphthalene	-13.88	258.67	1.6062	1.00816	3.9	99.8	1475
1-Isobutylnaphthalene	- 9.37 -22.14	279.54	1.5794	.97144	5.4	99.8	1771
1-Butylnaphthalene	-19.76	289.34	1.5819	.97673	6.0	99.8	1773

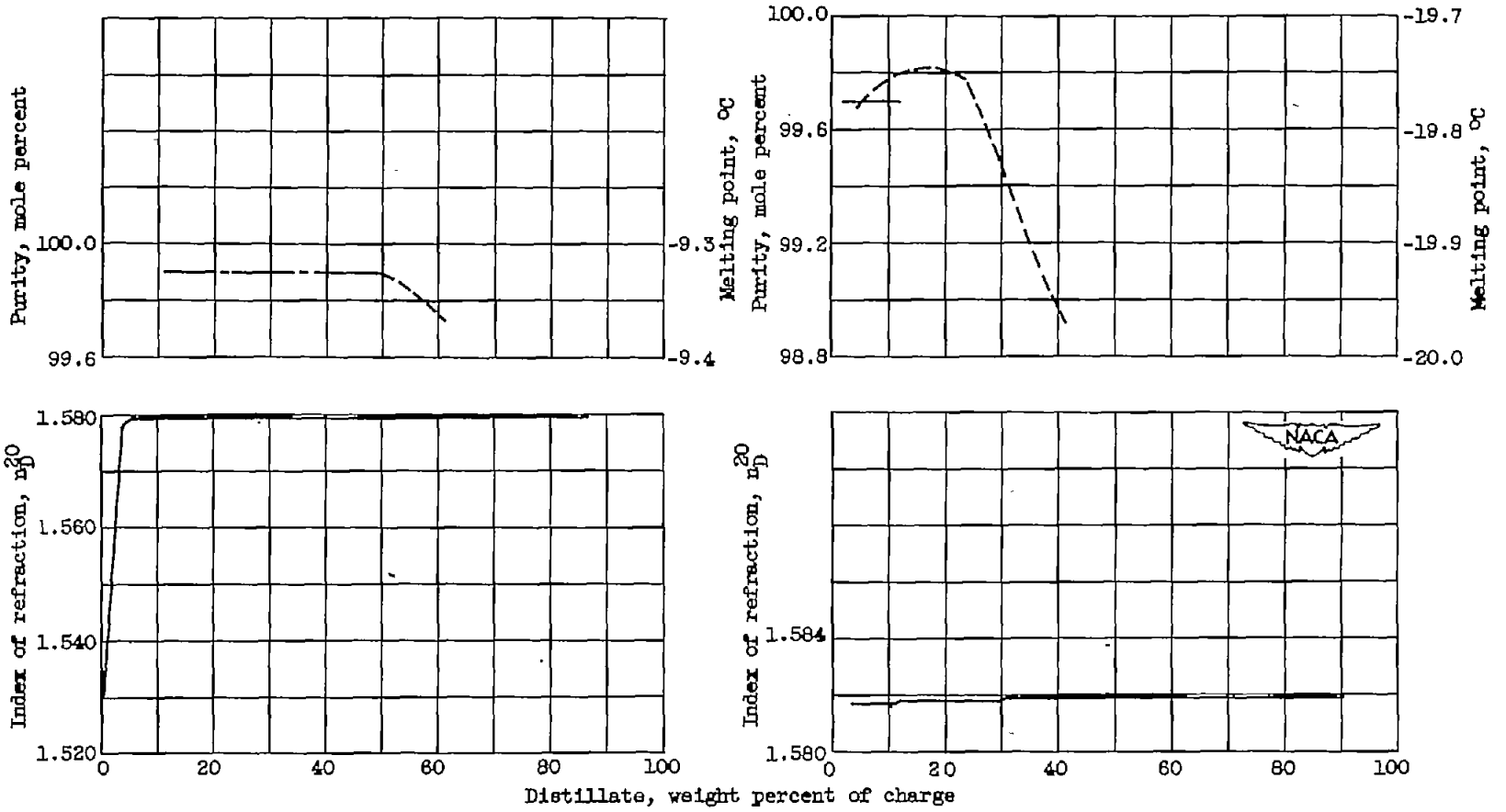
Hydrocarbon	Analysis (percent)				Kinematic viscosity (centistokes)			
	Carbon		Hydrogen		98.9° C (210° F)	60.0° C (140° F)	37.8° C (100° F)	0° C (32° F)
	Calc.	Found	Calc.	Found				
1-Methylnaphthalene	92.91	92.92	7.09	7.13	0.919	1.51	2.21	5.99
1-Ethylnaphthalene	92.26	92.20	7.74	7.80	.987	1.68	2.57	7.83
1-Isobutylnaphthalene	91.25	91.28	8.75	8.80	1.32	2.55	4.42	23.53
1-Butylnaphthalene	91.25	91.29	8.75	8.75	1.28	2.37	3.95	15.86



(a) 1-Methylnaphthalene.

(b) 1-Ethylnaphthalene.

Figure 1. - Distillation of 1-alkylnaphthalenes.

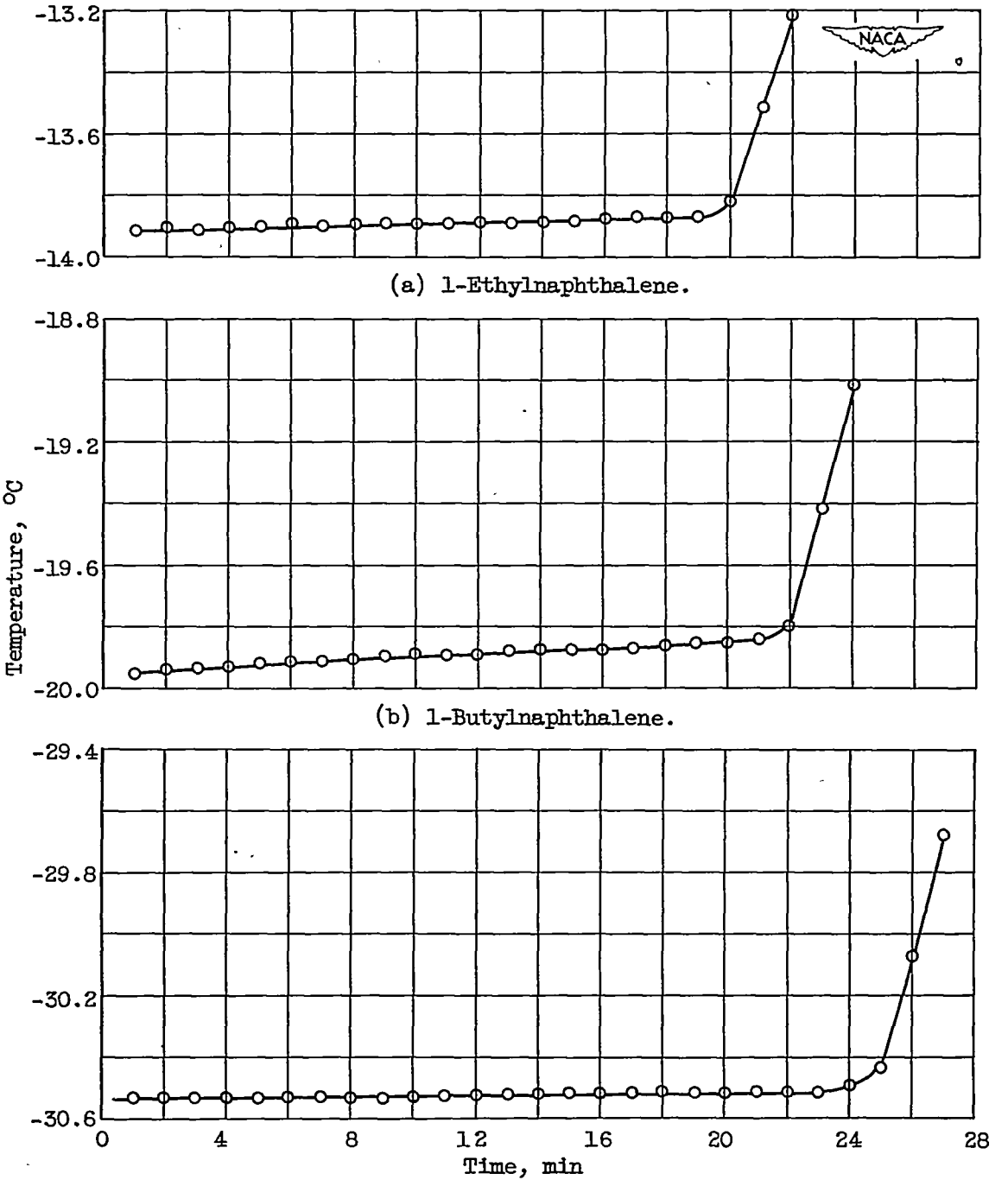


(c) 1-Isobutylnaphthalene.

(d) 1-Butylnaphthalene.

Figure 1. - Concluded. Distillation of 1-alkylnaphthalenes.

2206

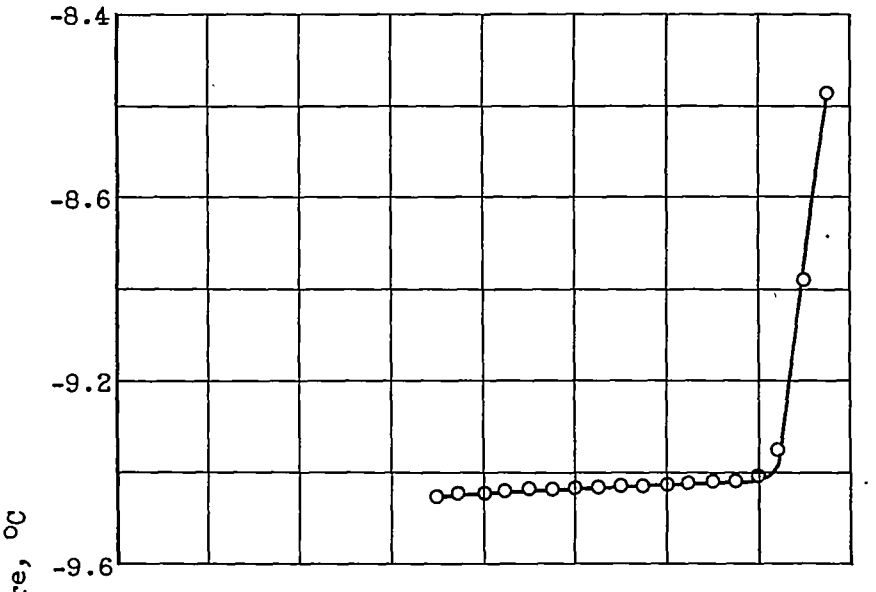


(a) 1-Ethylnaphthalene.

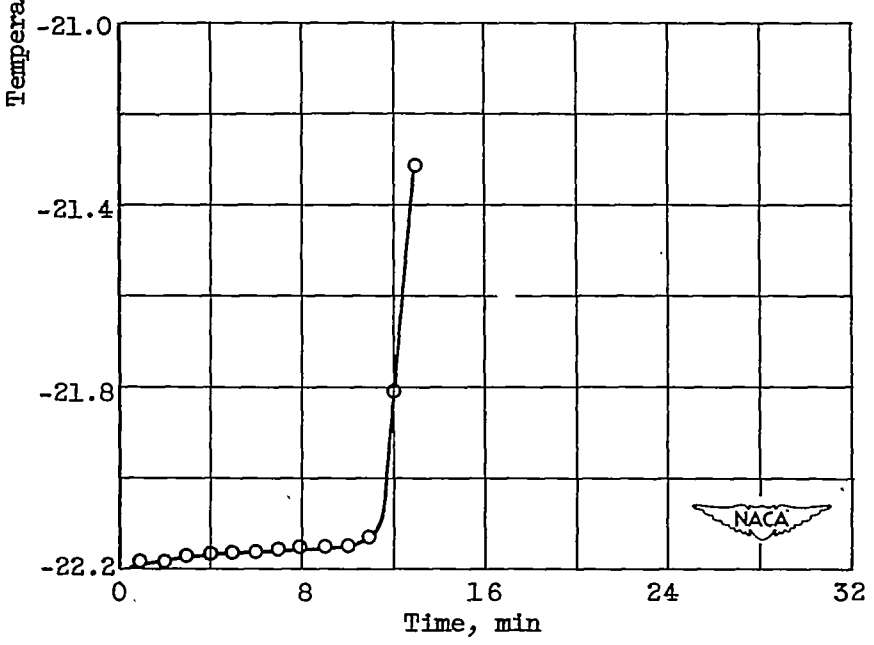
(b) 1-Butylnaphthalene.

(c) 1-Methylnapthalene.

Figure 2. - Time-temperature melting curves for four 1-alkylnaphthalenes.

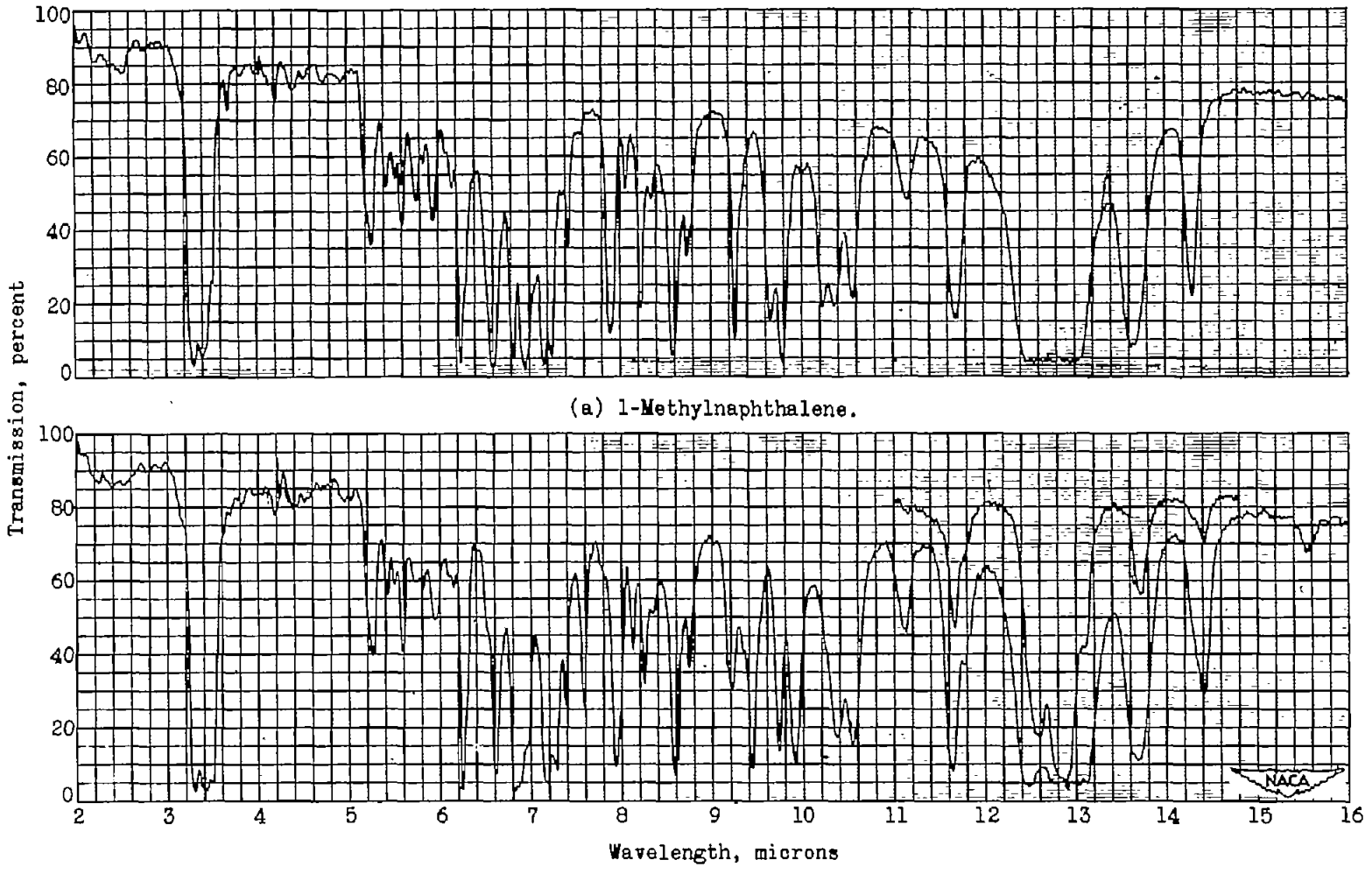


(d) 1-Isobutylnaphthalene; higher melting modification.



(e) 1- Isobutylnaphthalene; lower melting modification.

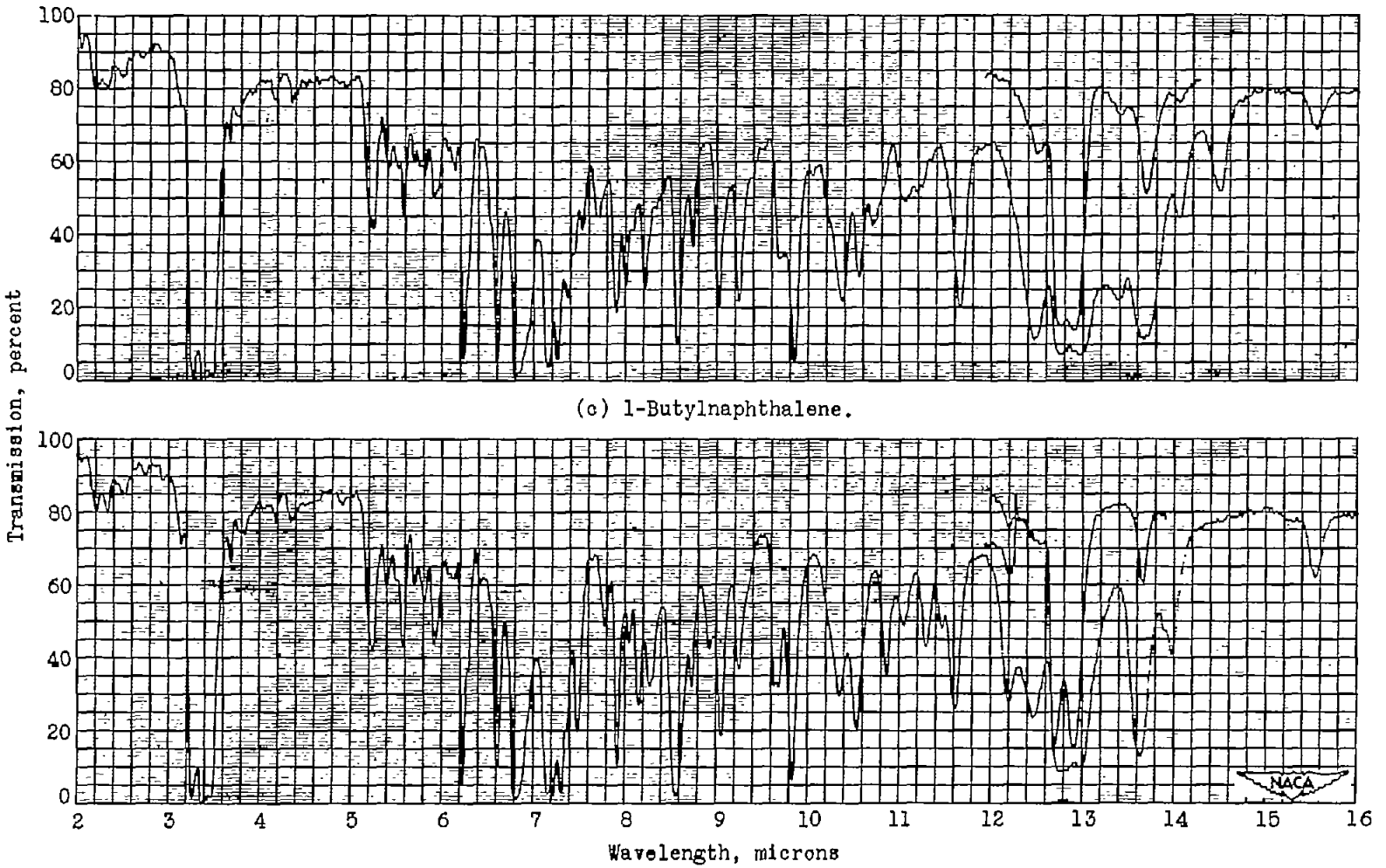
Figure 2. - Concluded. Time-temperature melting curves for four 1-alkylnaphthalenes.



(a) 1-Methylnaphthalene.

(b) 1-Ethylnaphthalene.

Figure 3. - Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon disulfide.



(c) 1-Butylnaphthalene.

(d) 1-Isobutylnaphthalene.

Figure 3. - Concluded. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon disulfide.

NACA-Langley - 8-6-51 - 1000