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TECHNICAL NOTE 2557

INFRARED SPECTRA OF 59 DICYCLIC HYDROCARBONS

By K. T. Serijan, I. A. Goodman, and W. J. Yankauskas

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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SUMMARY

The infrared spectra are presented for 59 dicyclic hydrocarbons consisting of some diphenylalkanes, dicyclohexylalkanes, alkylbiphenyls and alkylbicyclohexyls ranging from C_{12} through C_{18}. The physical properties of these compounds, which were available in a high state of purity, are tabulated for reference purposes.

INTRODUCTION

As part of an investigation of various classes of dicyclic hydrocarbons as possible components of aviation fuels, a group of 59 hydrocarbons was synthesized and purified at the NACA Lewis laboratory. The preparation and purification of 36 of the compounds included in this group and comprising the diphenylalkane and dicyclohexylalkane series are reported by Serijan and Wise in three papers recently accepted for publication in the Journal of the American Chemical Society. The remaining compounds consisting of nine alkylbiphenyls and twelve alkylbicyclohexyls are described in references 1 and 2. Biphenyl and bicyclohexyl, which may be considered as the parent compounds of the dicylic series, are also included in the group.

The effect of molecular structure on the physical properties for some of these hydrocarbons is discussed in references 2 and 3.

The infrared spectra of the 59 hydrocarbons representing the four designated classes of dicyclic compounds are presented herein. The availability of these hydrocarbons in a high state of purity made this investigation desirable in view of the increasing importance of infrared spectroscopy, particularly in the field of petroleum technology. Very few of the spectra for the hydrocarbons included herein have been reported previously.

MATERIALS

The properties of all the possible diphenyl-n-alkanes from diphenylmethane through the diphenylbutanes and also the α,α- and α,ω-diphenylpentanes and diphenylhexanes are listed in table I. The corresponding dicyclohexylalkanes are given in table II. In addition to biphenyl, a group of alkylbiphenyls consisting of seven hydrocarbons substituted in the 2-position and two compounds substituted in the 3-position were prepared and their properties are presented in table III. The properties of the corresponding saturated derivatives are described in table IV with the exception of the derivatives of 2-sec-butylbiphenyl, 3-methylbiphenyl, and 3-ethylbiphenyl, which compounds could not be purified to the required standards. The hydrogenation products of each of the remaining alkylbiphenyls were readily separable by careful fractionation into two geometric isomers, designated in table IV as the low-boiling and high-boiling isomers.

The procedures used in evaluating these properties, together with the accuracy and precision of each method, are reported in reference 2. Synthesis details are described in reference 1 and also in the previously mentioned unpublished reports; methods of purification are generally outlined in reference 1.

Each sample was freshly distilled and passed through silica gel just prior to the determination of the infrared spectra.

APPARATUS AND PROCEDURE

The infrared spectra shown in figures 1 to 5 were obtained with a double-beam recording spectrophotometer. The precision of the instrument is specified by the manufacturer to be ± 1 percent of the transmission value and ± 0.02 microns for the wavelength (reference 4). Samples were run in a 0.1-millimeter-thick cell both undiluted and, over some wavelength intervals, at approximately 1:10 dilution on a volume basis in either carbon tetrachloride or carbon disulfide; where necessary in order to obtain a still sharper resolution, a dilution of approximately 1:20 in carbon disulfide was also used. When the samples were run in dilution, the pure solvent was used in the reference beam to nullify the effect of any absorption due to the solvent.

In the case of the five hydrocarbons which are solids at room temperature, solutions were prepared for infrared-spectra determinations by dilution with carbon tetrachloride and carbon disulfide. The

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concentration of these hydrocarbons in each solvent is indicated in the appropriate figures in terms of weight-volume percent, which denotes the number of grams of solute (hydrocarbon) per 100 milliliters of solvent.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, August 30, 1951

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REFERENCES

1. Goodman, Irving A., and Wise, Paul H.: Synthesis and Purification of Some Alkylbiphenyls and Alkylbicyclohexyls. NACA TN 2260, 1951.

2. Goodman, Irving A., and Wise, Paul H.: Correlation of Physical Properties with Molecular Structure for Dicyclic Hydrocarbons. II - 2-Alkylbiphenyl and the Two Isomeric 2-Alkylbicyclohexyl Series. NACA TN 2419, 1951.

3. Wise, P. H., Serijan, K. T., and Goodman, I. A.: Correlation of Physical Properties with Molecular Structure for Some Dicyclic Hydrocarbons Having High Thermal-Energy Release Per Unit Volume. NACA Rep. 1003, 1951. (Formerly NACA TN 2081.)

4. Anon.: Infrared Recording Spectrophotometer. Bulletin XXX, Baird Associates, Inc. (Cambridge, Mass.).

5. Doss, M. P.: Physical Constants of the Principal Hydrocarbons. The Texas Co. (New York), 4th ed., 1943.

TABLE I - PROPERTIES OF DIPHENYLALKANE HYDROCARBONS

[S designates solid at indicated temperature]

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (g/ml)	Kinematic viscosity[a] (centistokes)				Net heat of combustion[b] (kcal/mole)
					98.9° C (210° F)	60° C (140° F)	37.8° C (100° F)	0° C (32° F)	
Diphenylmethane	25.20[c]	264.27	1.5776	1.00592	0.97	1.55	2.22	S	1595
1,1-Diphenylethane	-18.01	272.63	1.5725	.99954	1.11	1.89	2.90	8.93	1735
1,2-Diphenylethane	51.16	280.5[d]	S	S	1.14	1.96	S	S	1740
1,1-Diphenylpropane	13.29	283.22	1.5643	.98663	1.23	2.25	3.72	S	1885
1,2-Diphenylpropane	.14	283.66	1.5585	.97739	1.30	2.42	4.02	16.87	1880
1,3-Diphenylpropane	-20.78	298.7[d]	1.5594	.97996	1.31	2.31	3.64	12.38	1885
2,2-Diphenylpropane	29.12	281.19	1.5703	.99806	1.43	2.71	4.56	S	1895
1,1-Diphenylbutane[e]	-28.38 -25.20	295.29	1.5568	.97512	1.38	2.71	4.71	24.78	2035
1,2-Diphenylbutane	Glass	292.52	1.5518	.96734	1.43	2.83	5.04	28.83	2030
1,3-Diphenylbutane	Glass	302.5[d]	1.5523	.96982	1.45	2.71	4.62	20.98	2035
1,4-Diphenylbutane	52.27	315.91	S	S	1.49	2.80	S	S	2035
2,2-Diphenylbutane	21.70	296.16	1.5673	.99446	1.79	3.83	7.52	S	2035
meso-2,3-Diphenylbutane	126.4-127.0[f]	290.91	S	S	S	S	S	S	2035
dl-2,3-Diphenylbutane	Glass	304.0[d]	1.5547	.97229	1.43	2.64	4.36	18.11	2040
1,1-Diphenylpentane	-12.06	307.89	1.5511	.96594	1.62	3.38	6.36	41.50	2190
1,5-Diphenylpentane	- 7.95	330.62	1.5463	.96083	1.64	3.05	5.02	19.48	2180
1,1-Diphenylhexane	-11.76	321.38	1.5449	.95636	1.78	3.78	7.19	46.51	2330
1,6-Diphenylhexane	-11.99	345.67	1.5409	.95237	1.81	3.33	5.72	22.28	2330

[a]A.S.T.M. procedure: D445-46T.
[b]A.S.T.M. procedure: D240-39.
[c]Value obtained from freezing curve.
[d]Some decomposition observed during the determination.
[e]Two crystalline modifications.
[f]This value given by a calibrated immersion thermometer with the substance in an attached capillary tube.

TABLE II - PROPERTIES OF DICYCLOHEXYLALKANE HYDROCARBONS

[S designates solid at indicated temperature]

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (g/ml)	Kinematic viscosity[a] (centistokes)				Net heat of combustion[b] (kcal/mole)
					98.9° C (210° F)	60° C (140° F)	37.8° C (100° F)	0° C (32° F)	
Dicyclohexylmethane	-18.70	252.8[c]	1.4763	0.87646	1.43	2.60	4.10	12.96	1845
1,1-Dicyclohexylethane	-20.87	271.17	1.4845	.89309	1.76	3.37	5.59	21.33	1995
1,2-Dicyclohexylethane	11.45	274.38	1.4759	.87395	1.72	3.24	5.39	S	1995
1,1-Dicyclohexylpropane[d]	-28.21 -23.46	283.56	1.4848	.89299	1.83	3.66	6.42	32.93	2140
1,2-Dicyclohexylpropane	-21.46	284.5[c]	1.4798	.88173	1.88	3.74	6.44	28.33	2165
1,3-Dicyclohexylpropane	-14.82	291.69	1.4752	.87128	1.96	3.82	6.40	24.87	2155
2,2-Dicyclohexylpropane	15.61	286.2[c]	1.4918	.90677	2.41	5.14	9.79	S	2150
1,1-Dicyclohexylbutane	-10.46	292.97	1.4843	.89021	2.10	4.75	9.64	88.30	2285
1,2-Dicyclohexylbutane	Glass	295.90	1.4806	.88316	2.00	4.20	7.83	48.31	2295
1,3-Dicyclohexylbutane	Glass	303.19	1.4797	.88012	2.28	4.82	8.80	45.00	2285
1,4-Dicyclohexylbutane	11.62	309.0[c]	1.4751	.87027	2.19	4.39	7.58	S	2285
2,2-Dicyclohexylbutane	15.38	302.1[c]	1.4957	.91332	2.74	6.47	13.72	S	2290
meso-2,3-Dicyclohexylbutane	57.60	298.51	S	S	2.61	5.85	S	S	2295
dl-2,3-Dicyclohexylbutane	Glass	300.85	1.4842	.89044	2.34	4.90	9.01	48.91	2285
1,1-Dicyclohexylpentane	15.29	308.[c]	1.4838	.88788	2.47	6.16	13.90	S	2445
1,5-Dicyclohexylpentane	-13.61	325.15	1.4751	.86872	2.46	5.01	8.86	38.79	2445
1,1-Dicyclohexylhexane[d]	8.7 3.39	316.[c]	1.4827	.88478	2.77	7.16	16.44	S	2585
1,6-Dicyclohexylhexane	10.21	340.5[c]	1.4750	.86775	2.75	5.75	10.46	S	2585

[a]A.S.T.M. procedure: D445-46T.
[b]A.S.T.M. procedure: D240-39.
[c]Some decomposition observed during the determination.
[d]Two crystalline modifications.

TABLE III - PROPERTIES OF 2-ALKYLBIPHENYL HYDROCARBONS

[S designates solid at indicated temperature]

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (g/ml)	Kinematic viscosity[a] (centistokes)				Net heat of combustion[b] (kcal/mole)
					98.9° C (210° F)	60° C (140° F)	37.8° C (100° F)	0° C (32° F)	
Biphenyl	68.93	254.91	S	1.041[c]	0.99	S	S	S	1445
2-Methylbiphenyl	- .20	255.30	1.5914	1.01134	1.06	----	3.19	13.27	1600
2-Ethylbiphenyl	- 6.13	265.97	1.5805	.99671	1.17	----	3.44	13.84	1740
2-Propylbiphenyl	-11.26	277.22	1.5696	.98018	1.33	----	4.44	22.41	1885
2-Butylbiphenyl[d]	-13.71 - 9.65	291.20	1.5604	.96763	1.43	----	4.87	24.68	2030
2-Isopropylbiphenyl	24.46	269.77	1.5703	.98227	1.46	----	5.76	S	1885
2-sec-Butylbiphenyl	8.12	281.75	1.5622	.97145	1.60	3.52	7.09	S	2055
2-Isobutylbiphenyl	Glass	282.13	1.5583	.96318	1.48	3.17	6.02	48.72	2035
3-Methylbiphenyl	4.53	272.70	1.6039	1.01394	1.09	1.98	3.23	13.21	1590
3-Ethylbiphenyl	-27.57	285.96	1.5930	.99932	1.19	2.13	3.40	12.17	1750

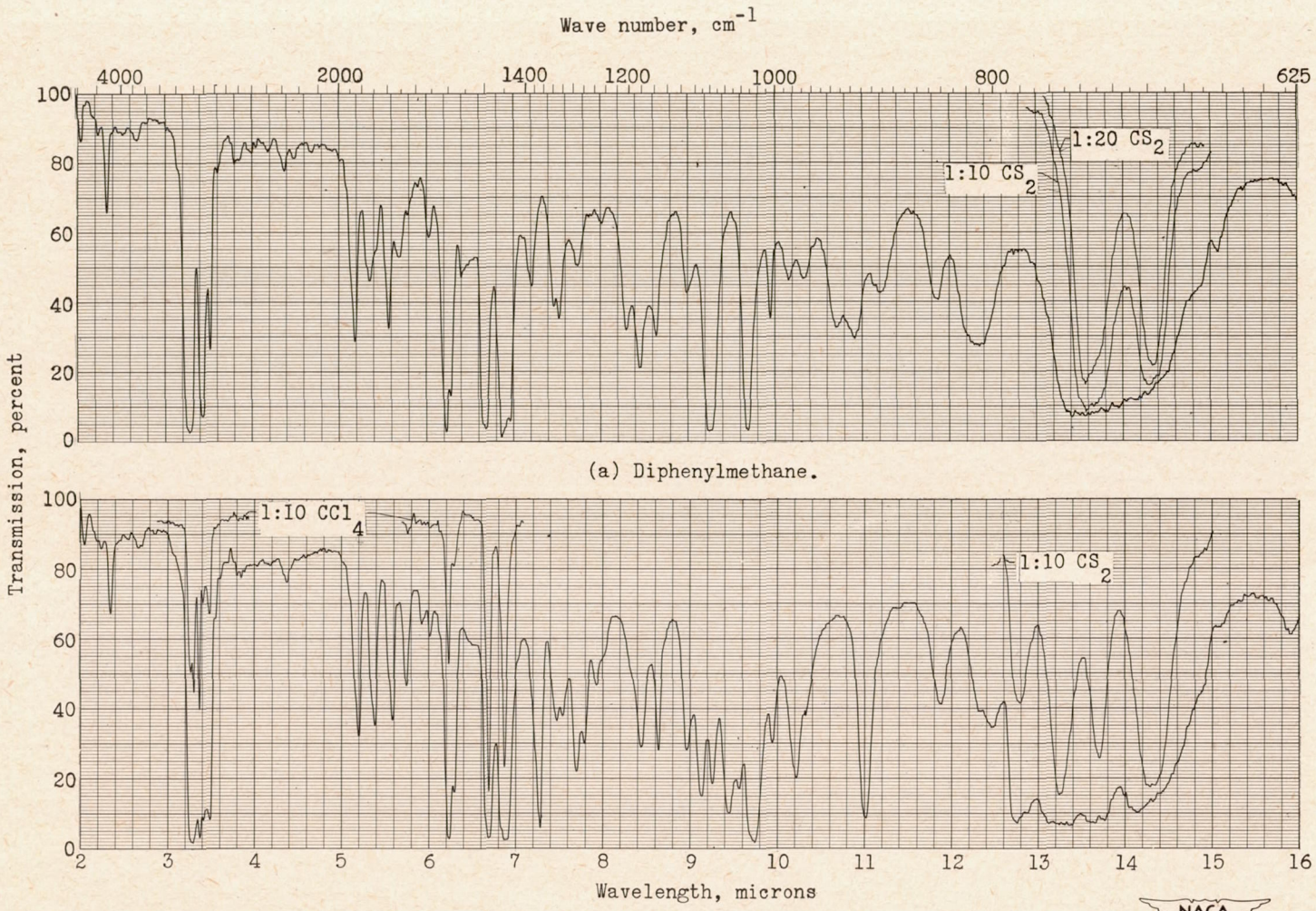
[a]A.S.T.M. procedure: D445-46T.
[b]A.S.T.M. procedure: D240-39.
[c]Reference 5.
[d]Two crystalline modifications.

TABLE IV - PROPERTIES OF 2-ALKYLBICYCLOHEXYL HYDROCARBONS

[S designates solid at indicated temperatures]

Hydrocarbon	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (g/ml)	Kinematic viscosity[a] (centistokes)				Net heat of combustion[b] (kcal/mole)
					98.9° C (210° F)	60° C (140° F)	37.8° C (100° F)	0° C (32° F)	
Bicyclohexyl	3.64	238.70	1.4796	0.88609	1.23	----	3.07	S	1700
2-Methylbicyclohexyl[c]	-26.43	249.87	1.4791	.88447	1.22	2.08	3.11	8.84	1855
2-Methylbicyclohexyl[d]	-10.27	255.00	1.4836	.89450	1.51	2.69	4.20	12.85	1870
2-Ethylbicyclohexyl[c,e]	Glass	266.23	1.4827	.89065	1.40	2.58	4.20	16.33	1995
2-Ethylbicyclohexyl[d]	- .35	269.54	1.4851	.89624	1.54	2.89	4.75	18.53	2015
2-Propylbicyclohexyl[c,e]	Glass	279.40	1.4807	.88527	1.56	3.05	5.38	28.32	2145
2-Propylbicyclohexyl[d]	.25	282.22	1.4838	.89205	1.71	3.46	6.20	34.08	2160
2-Butylbicyclohexyl[c,e]	Glass	294.15	1.4799	.88227	1.76	3.64	6.74	42.37	2300
2-Butylbicyclohexyl[d]	- 6.51	296.56	1.4827	.88819	1.91	4.05	7.65	51.18	2300
2-Isopropylbicyclohexyl[c,e]	Glass	277.18	1.4843	.89305	1.80	3.75	6.94	46.82	2140
2-Isopropylbicyclohexyl[d]	- 9.13	283.06	1.4901	.90365	1.91	3.78	6.54	29.12	2165
2-Isobutylbicyclohexyl[c,e]	Glass	286.87	1.4787	.87964	1.77	3.68	6.95	51.70	2285
2-Isobutylbicyclohexyl[d]	13.48	288.53	1.4819	.88688	1.90	4.00	7.53	55.30	2295

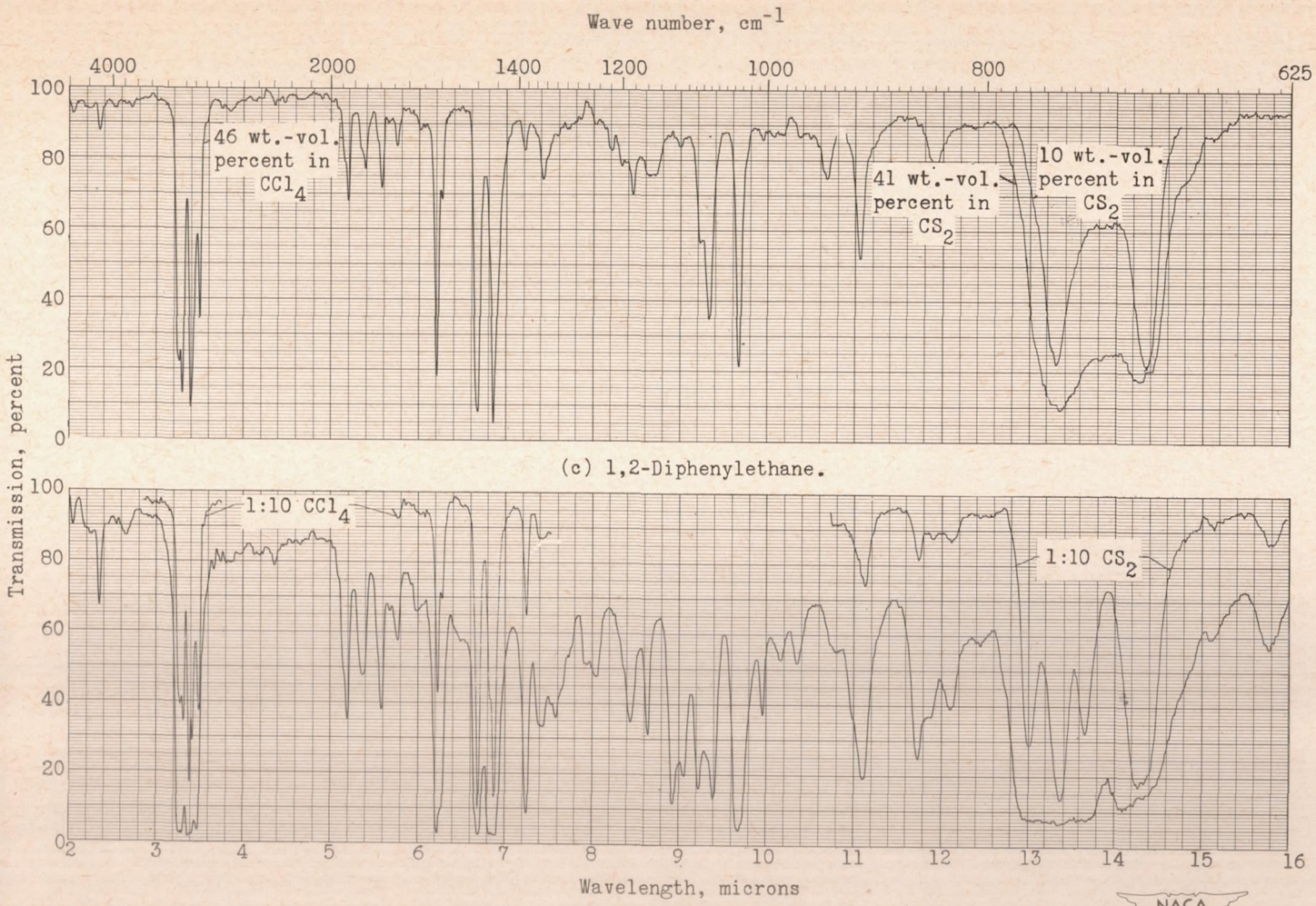
[a]A.S.T.M. procedure: D445-46T.
[b]A.S.T.M. procedure: D240-39.
[c]Low-boiling isomer.
[d]High-boiling isomer.
[e]Physical properties determined on fractions with most nearly constant density values.



(a) Diphenylmethane.

(b) 1,1-Diphenylethane.

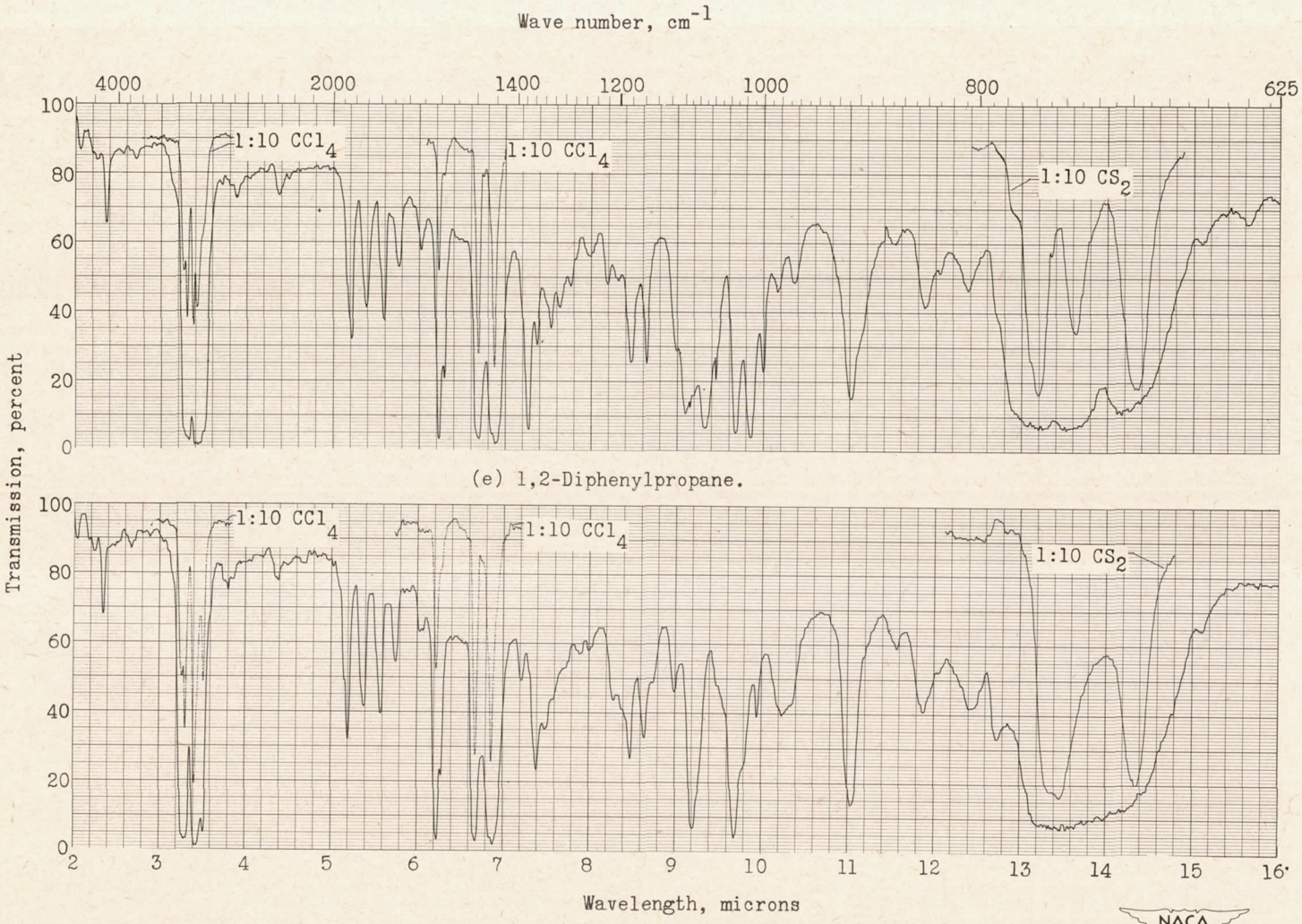
Figure 1. - Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(c) 1,2-Diphenylethane.

(d) 1,1-Diphenylpropane.

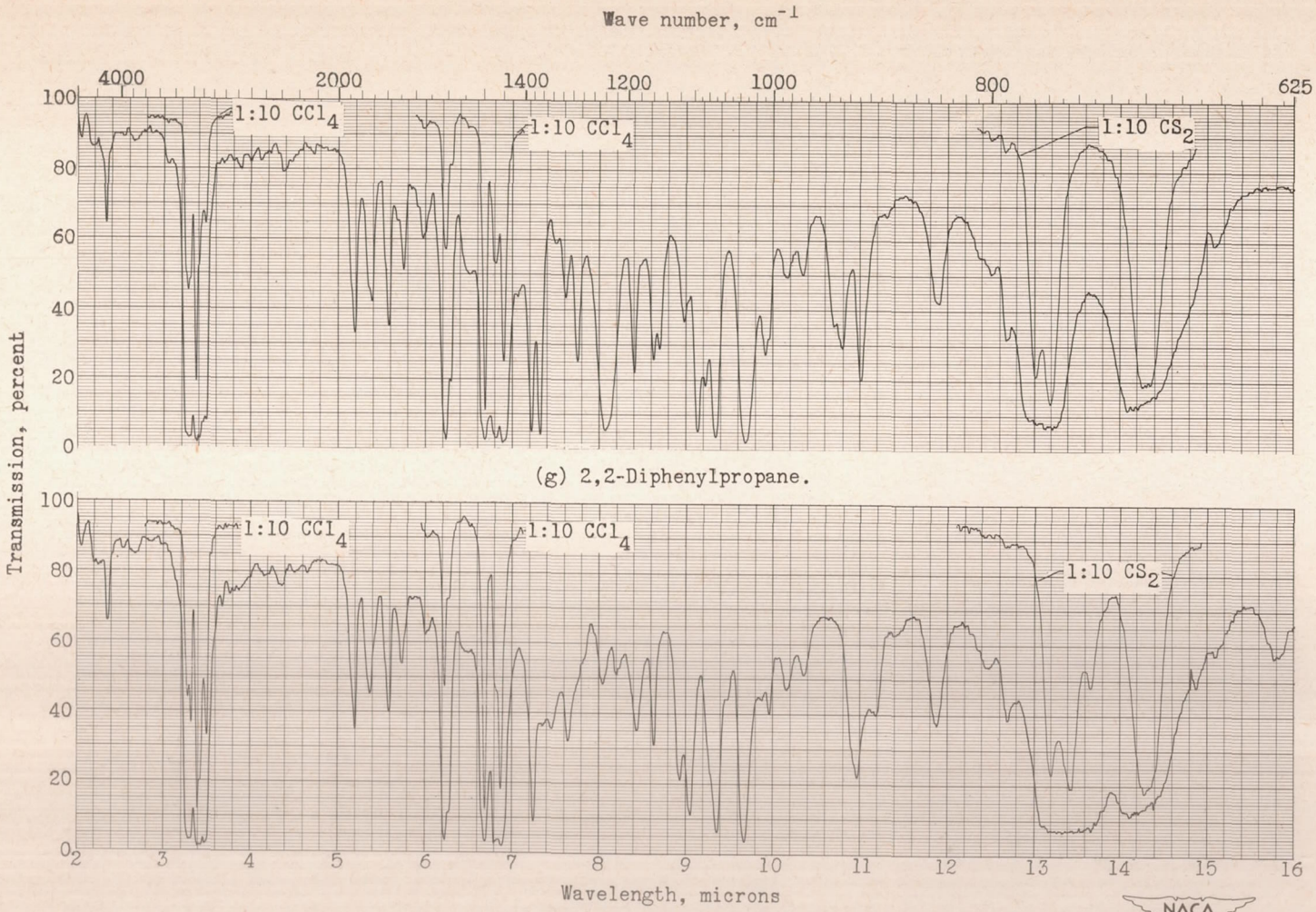
Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(e) 1,2-Diphenylpropane.

(f) 1,3-Diphenylpropane.

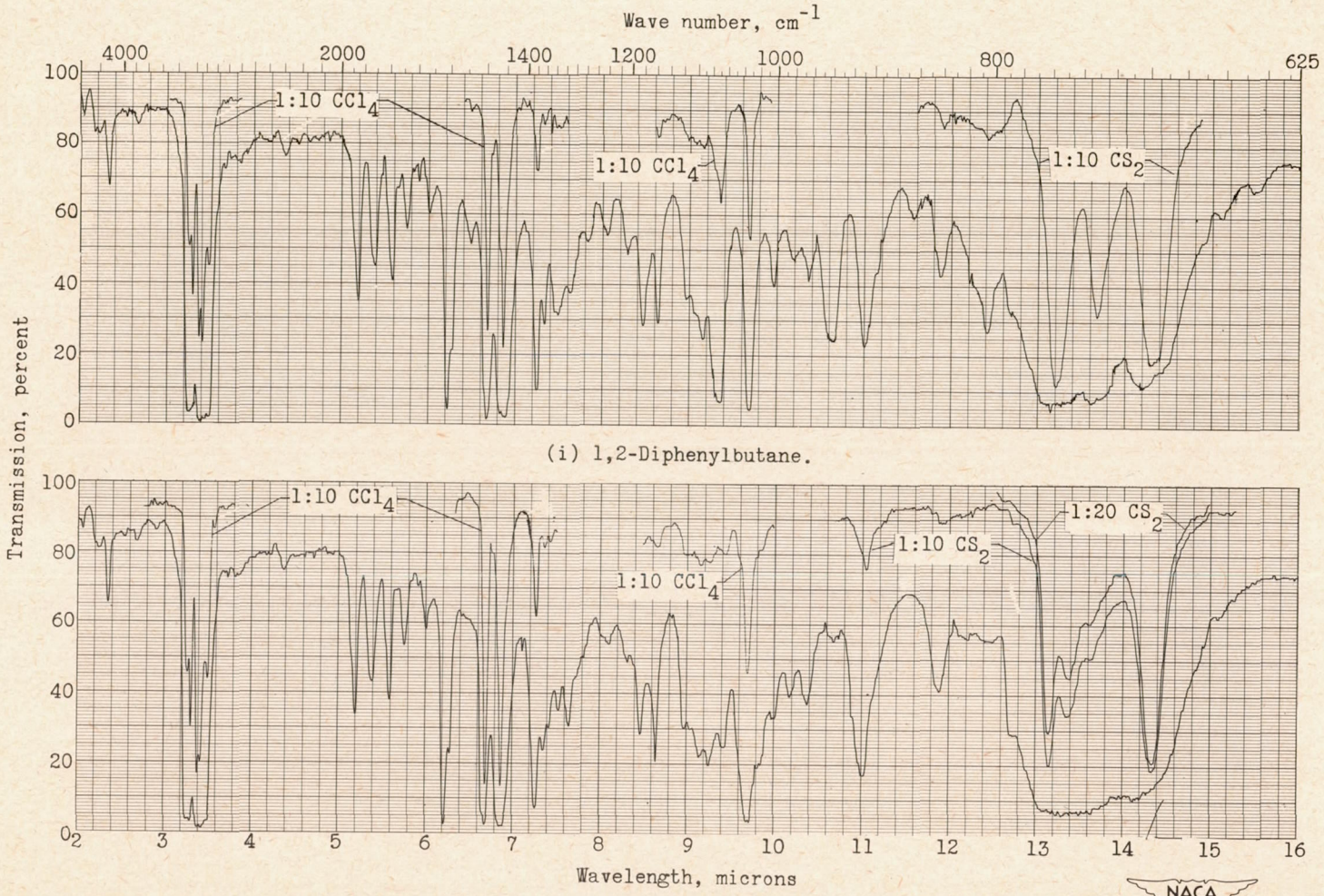
Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(g) 2,2-Diphenylpropane.

(h) 1,1-Diphenylbutane.

Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(i) 1,2-Diphenylbutane.

(j) 1,3-Diphenylbutane.

Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.

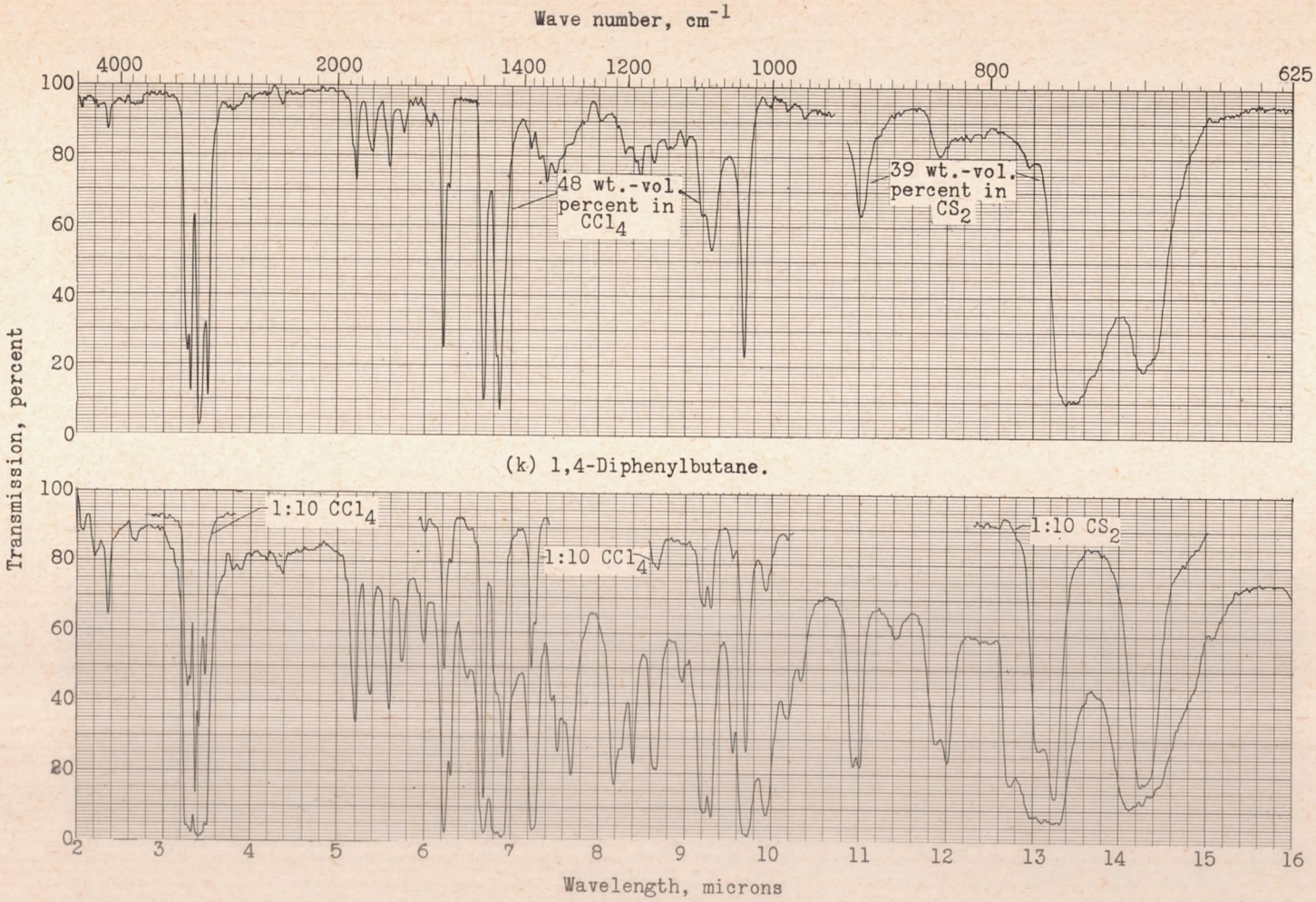
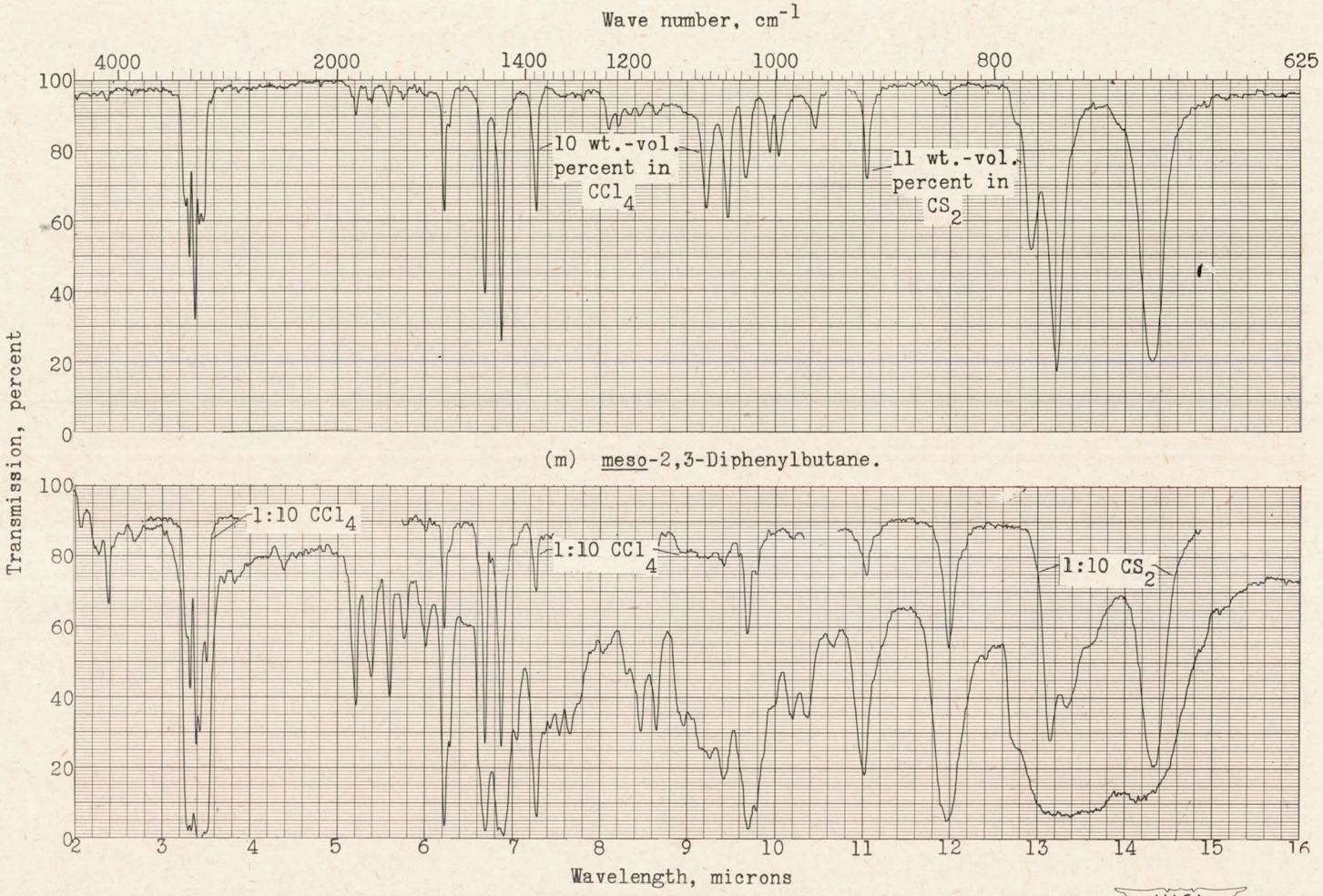


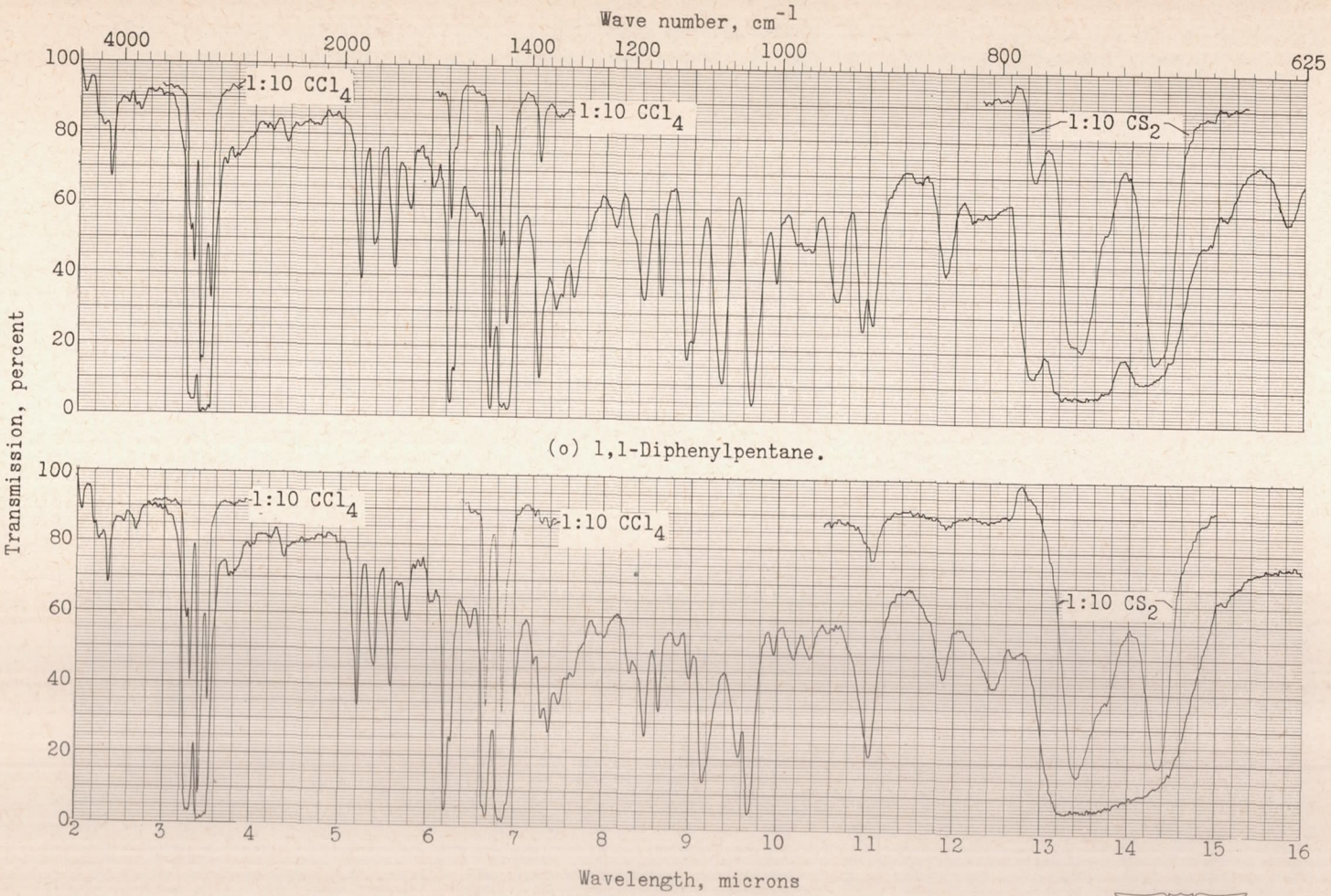
Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(m) meso-2,3-Diphenylbutane.

(n) dl-2,3-Diphenylbutane.

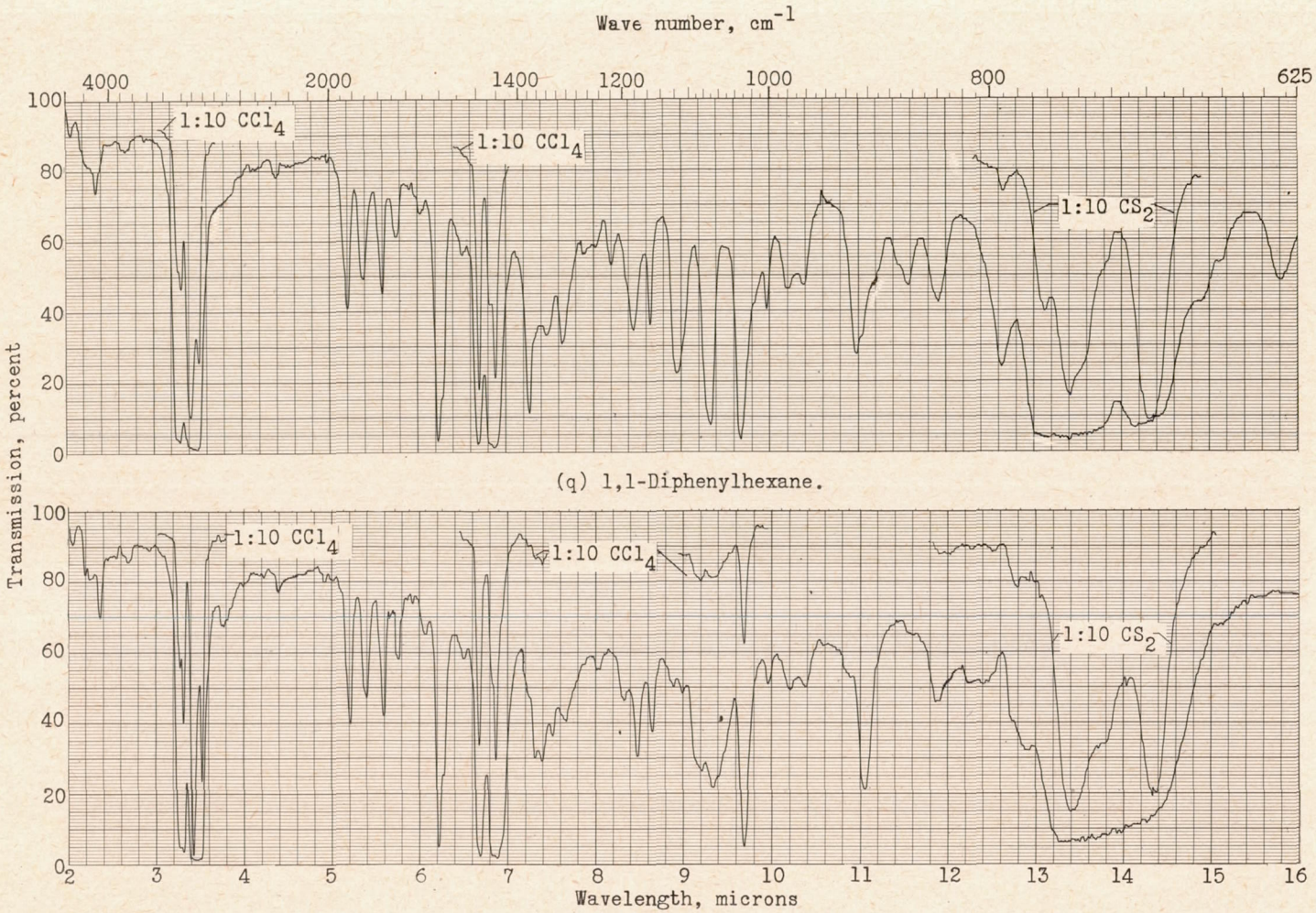
Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(o) 1,1-Diphenylpentane.

(p) 1,5-Diphenylpentane.

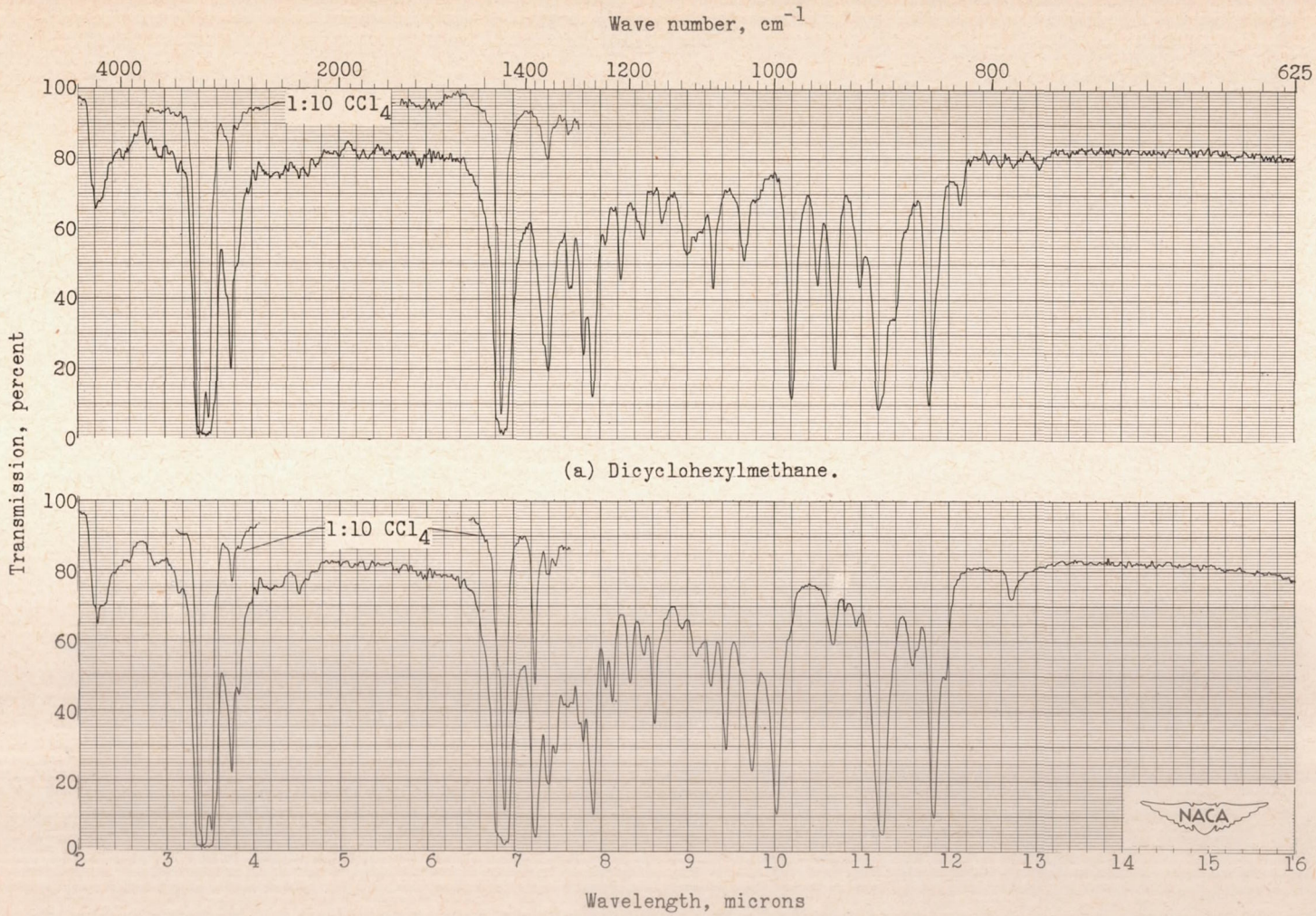
Figure 1. - Continued. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(q) 1,1-Diphenylhexane.

(r) 1,6-Diphenylhexane.

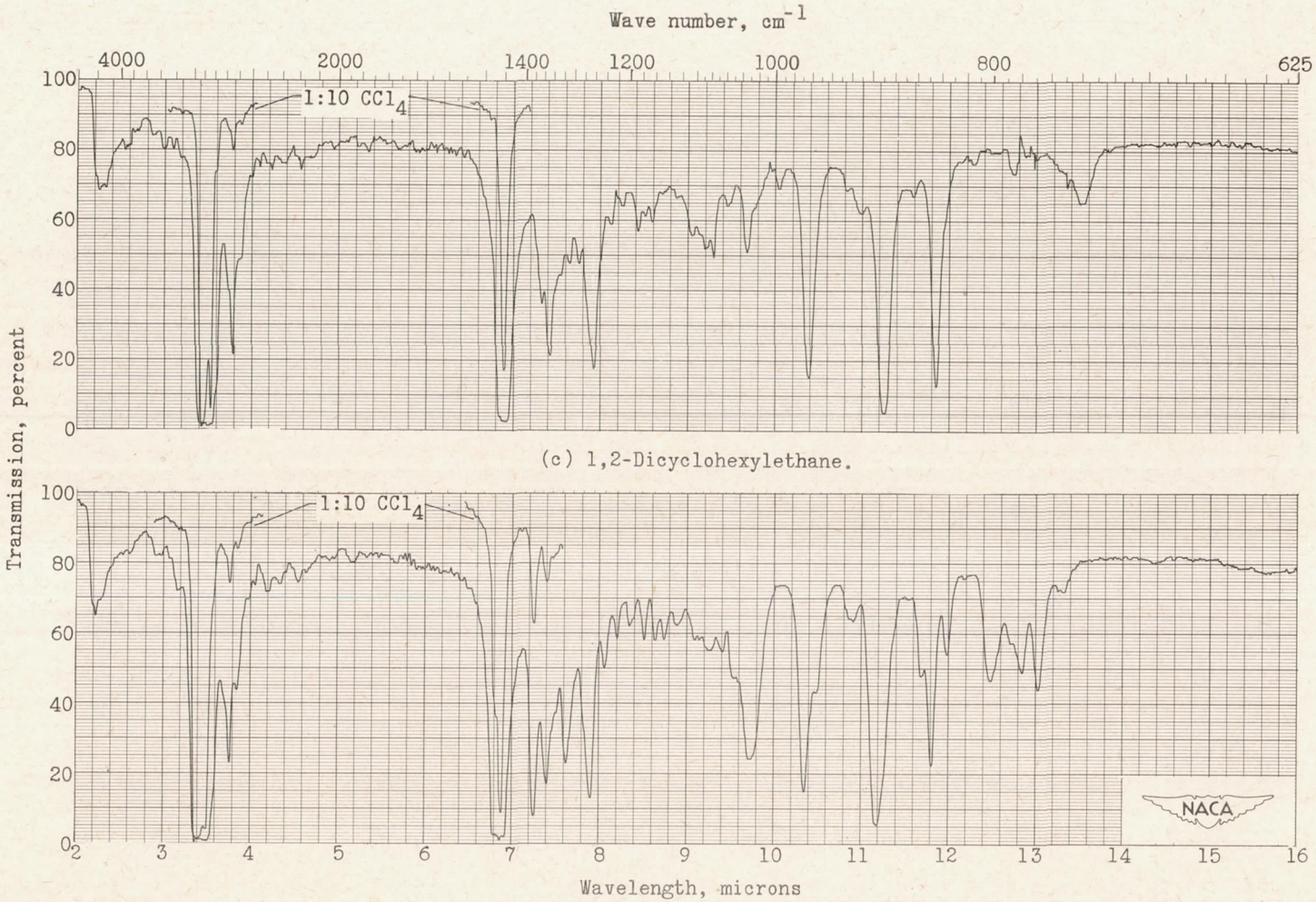
Figure 1. - Concluded. Infrared spectra for diphenylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(a) Dicyclohexylmethane.

(b) 1,1-Dicyclohexylethane.

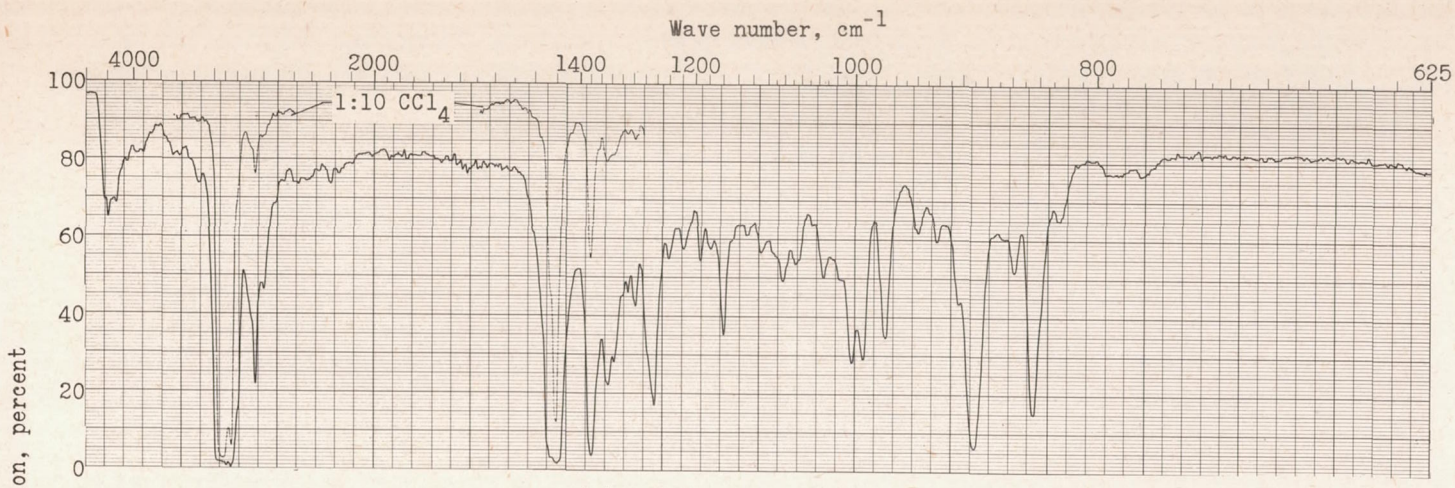
Figure 2. - Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



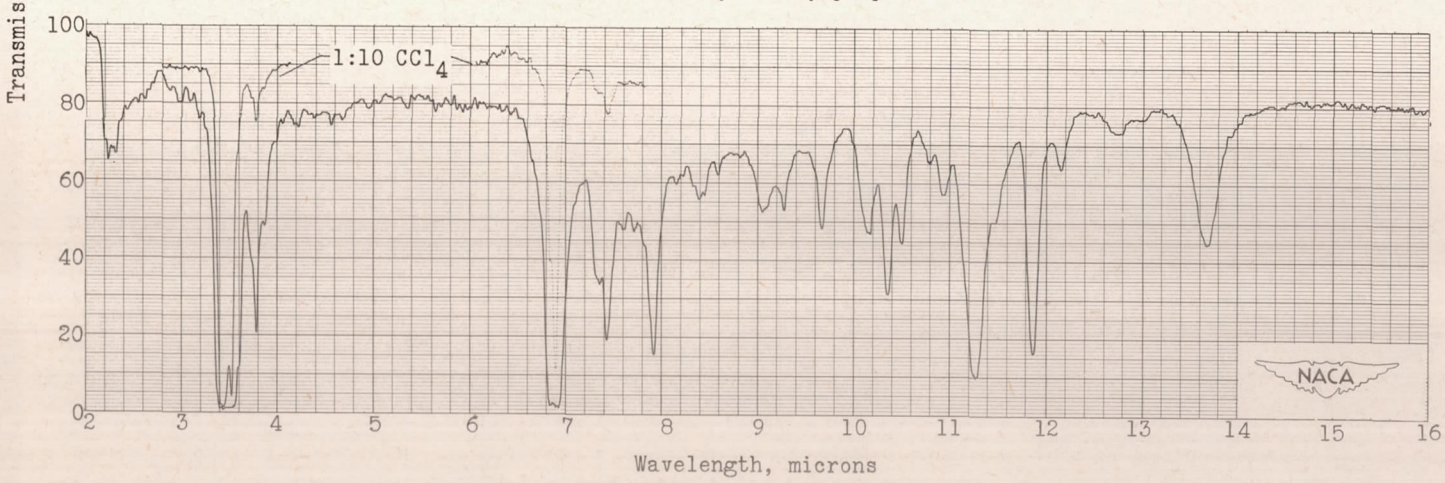
(c) 1,2-Dicyclohexylethane.

(d) 1,1-Dicyclohexylpropane.

Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.

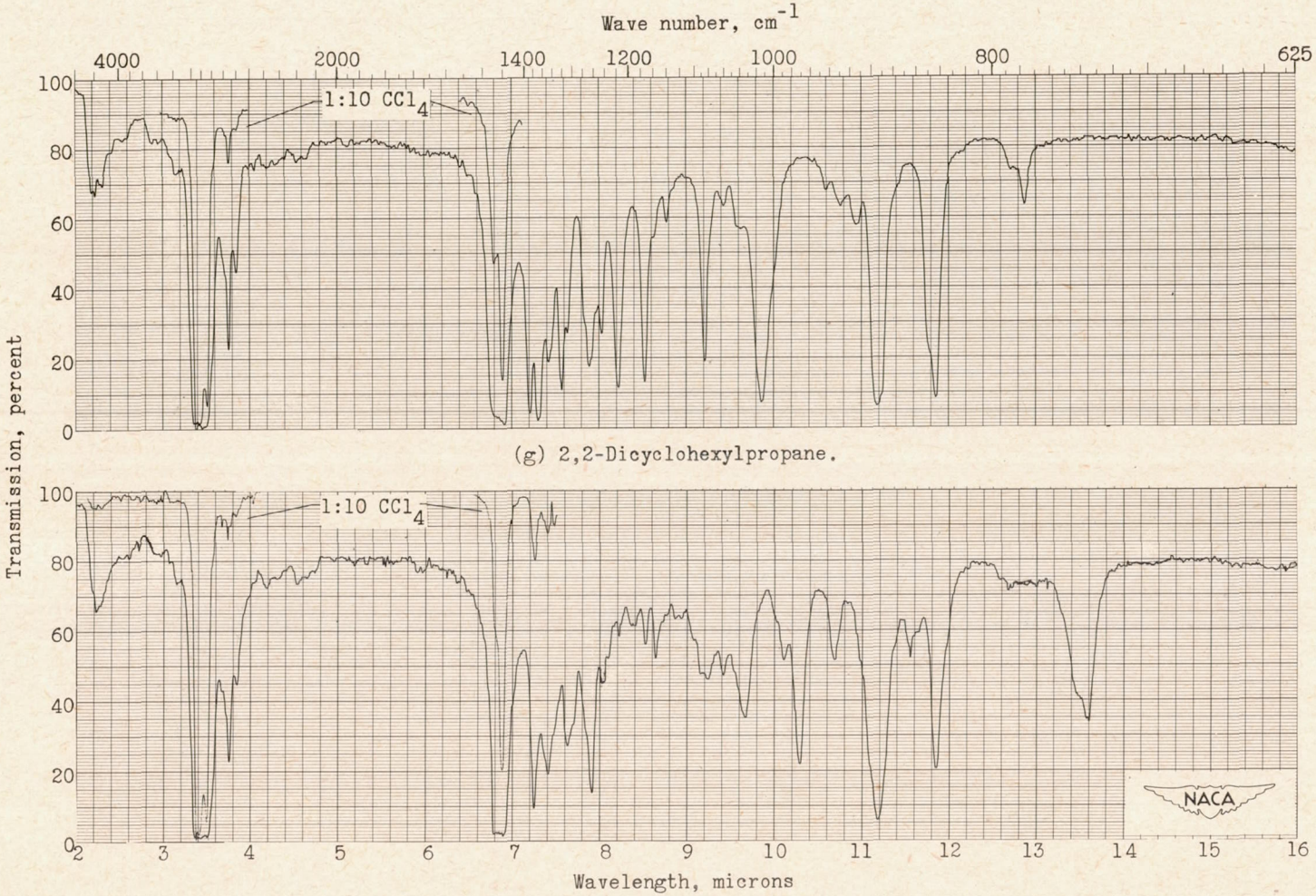


(e) 1,2-Dicyclohexylpropane.



(f) 1,3-Dicyclohexylpropane.

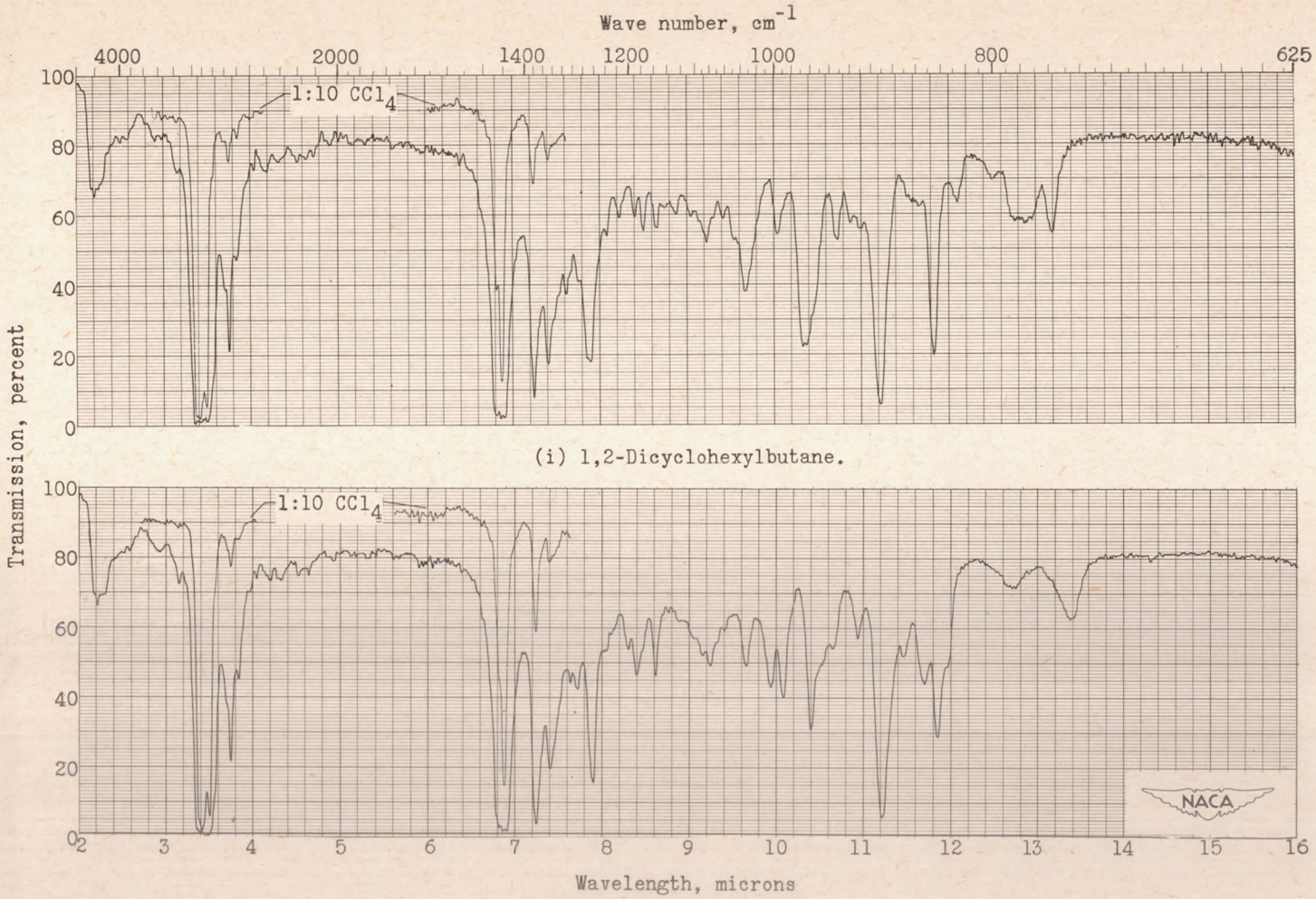
Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(g) 2,2-Dicyclohexylpropane.

(h) 1,1-Dicyclohexylbutane.

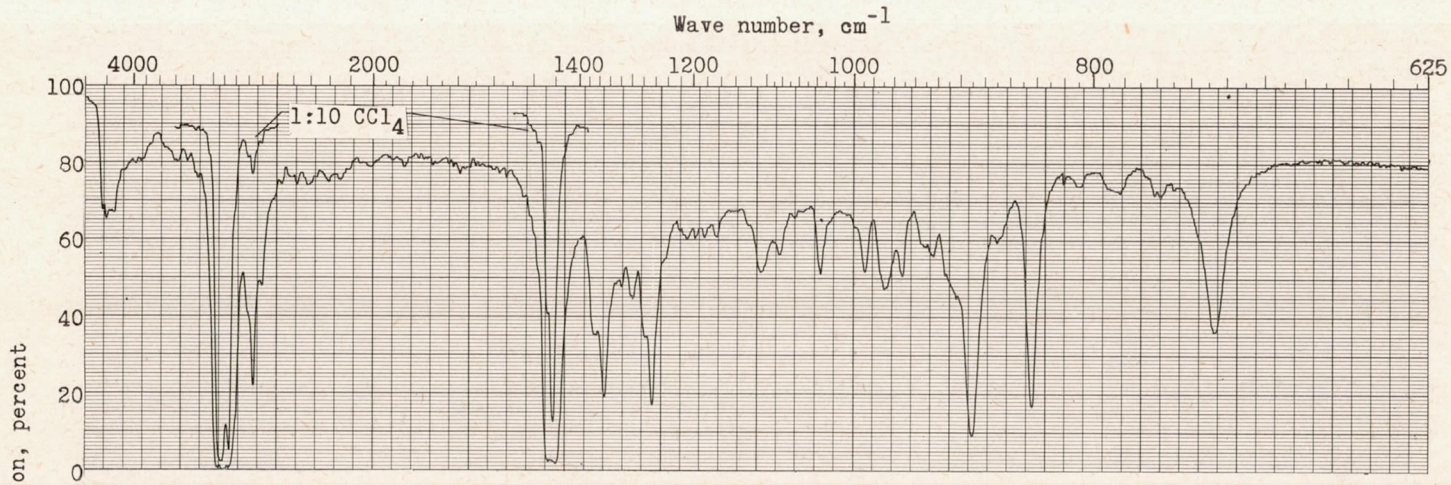
Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



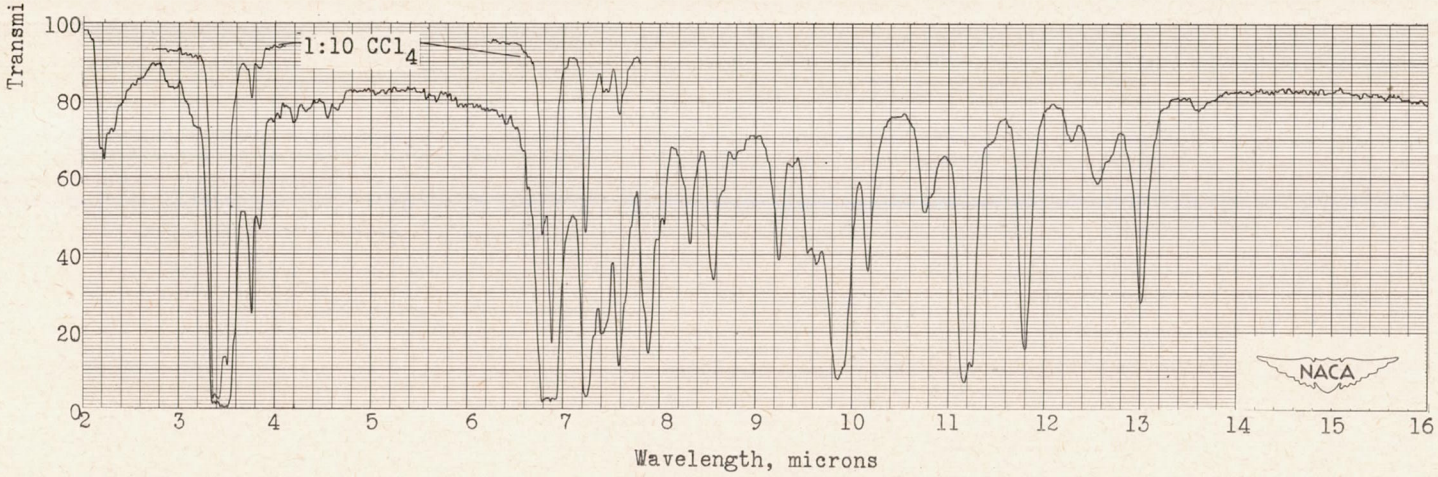
(i) 1,2-Dicyclohexylbutane.

(j) 1,3-Dicyclohexylbutane.

Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.

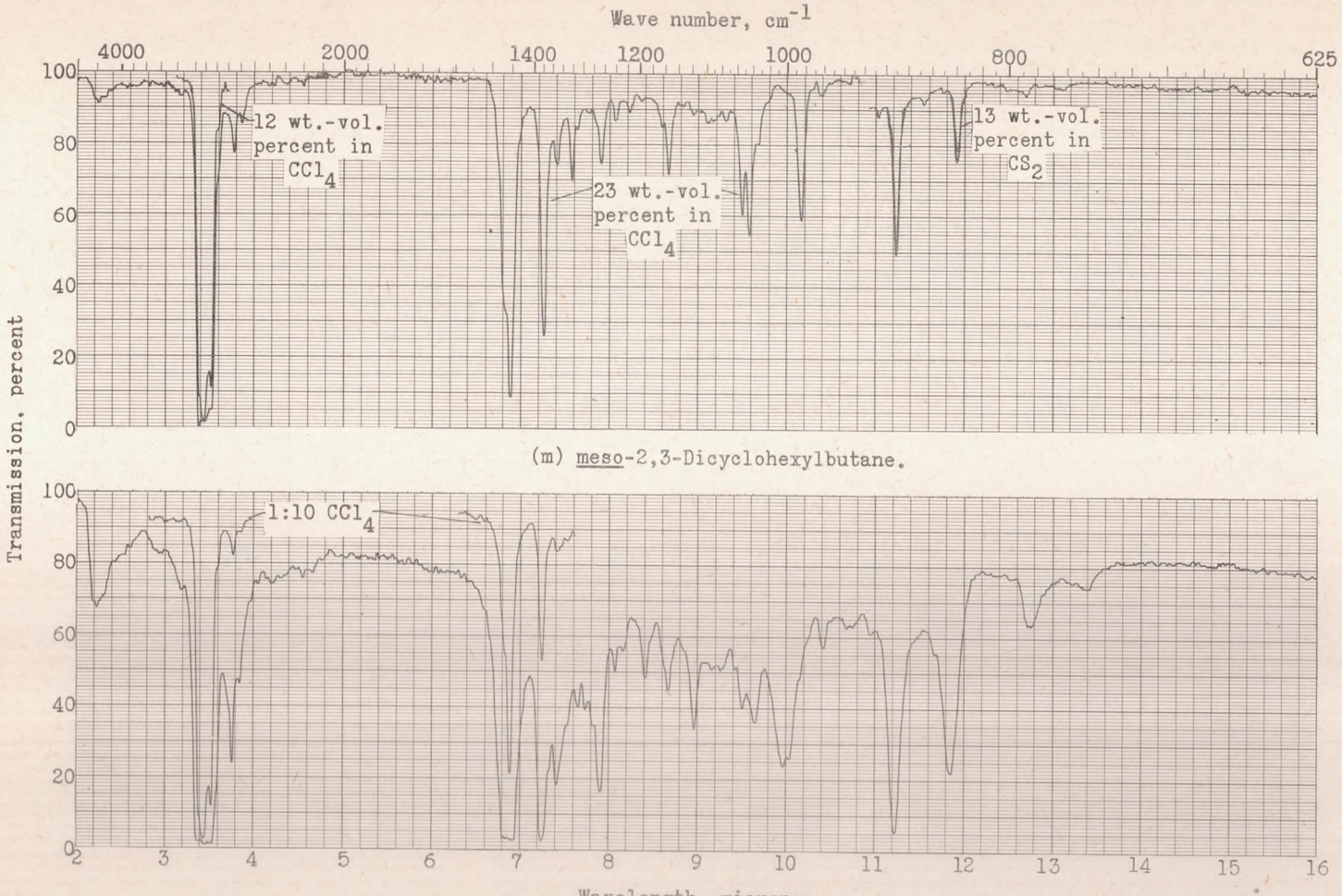


(k) 1,4-Dicyclohexylbutane.



(l) 2,2-Dicyclohexylbutane.

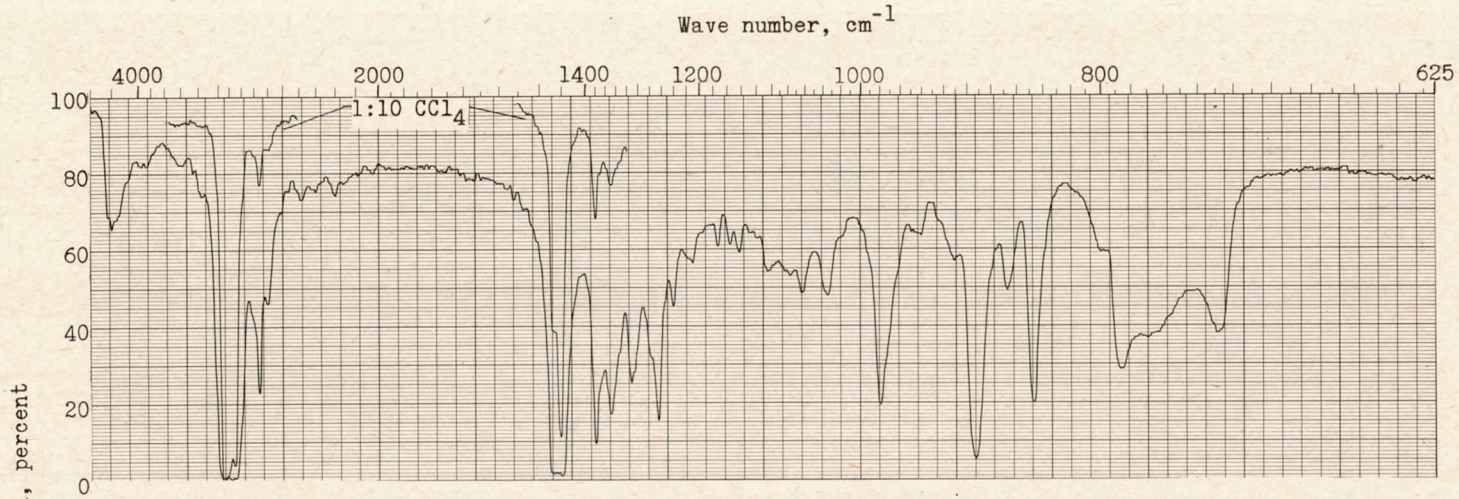
Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



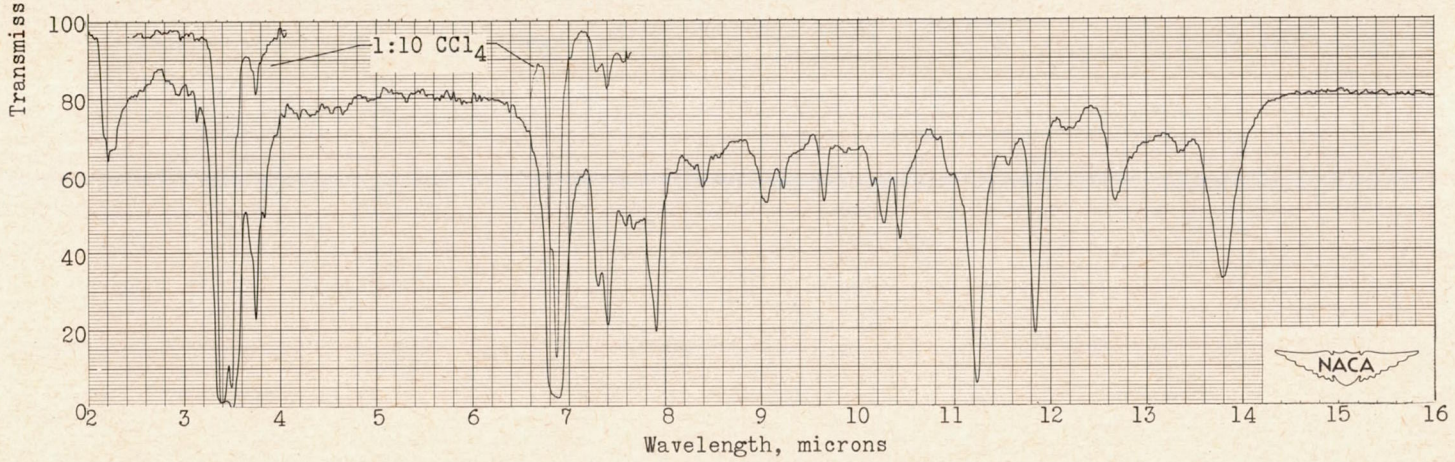
(m) meso-2,3-Dicyclohexylbutane.

(n) dl-2,3-Dicyclohexylbutane.

Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.

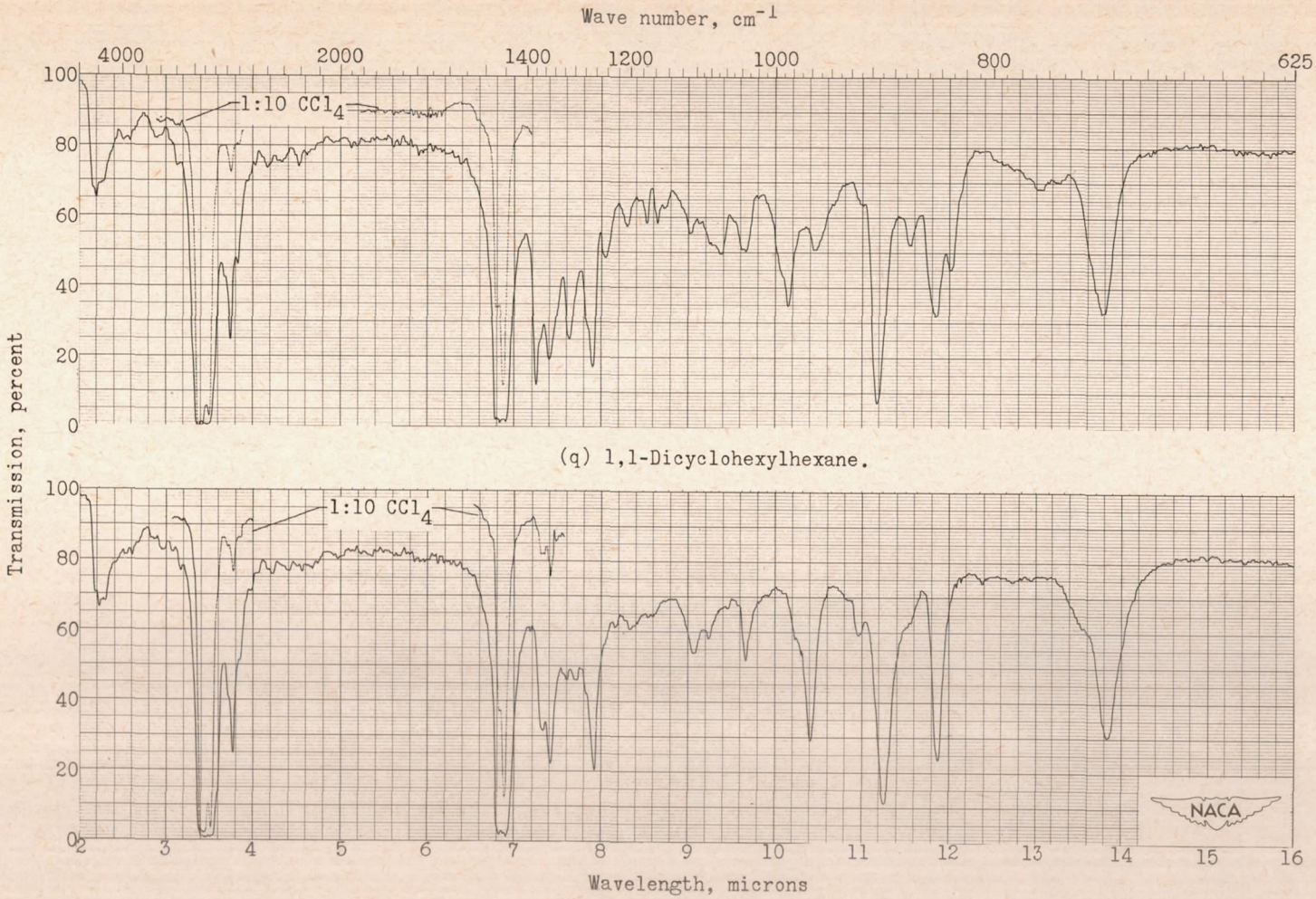


(o) 1,1-Dicyclohexylpentane.



(p) 1,5-Dicyclohexylpentane.

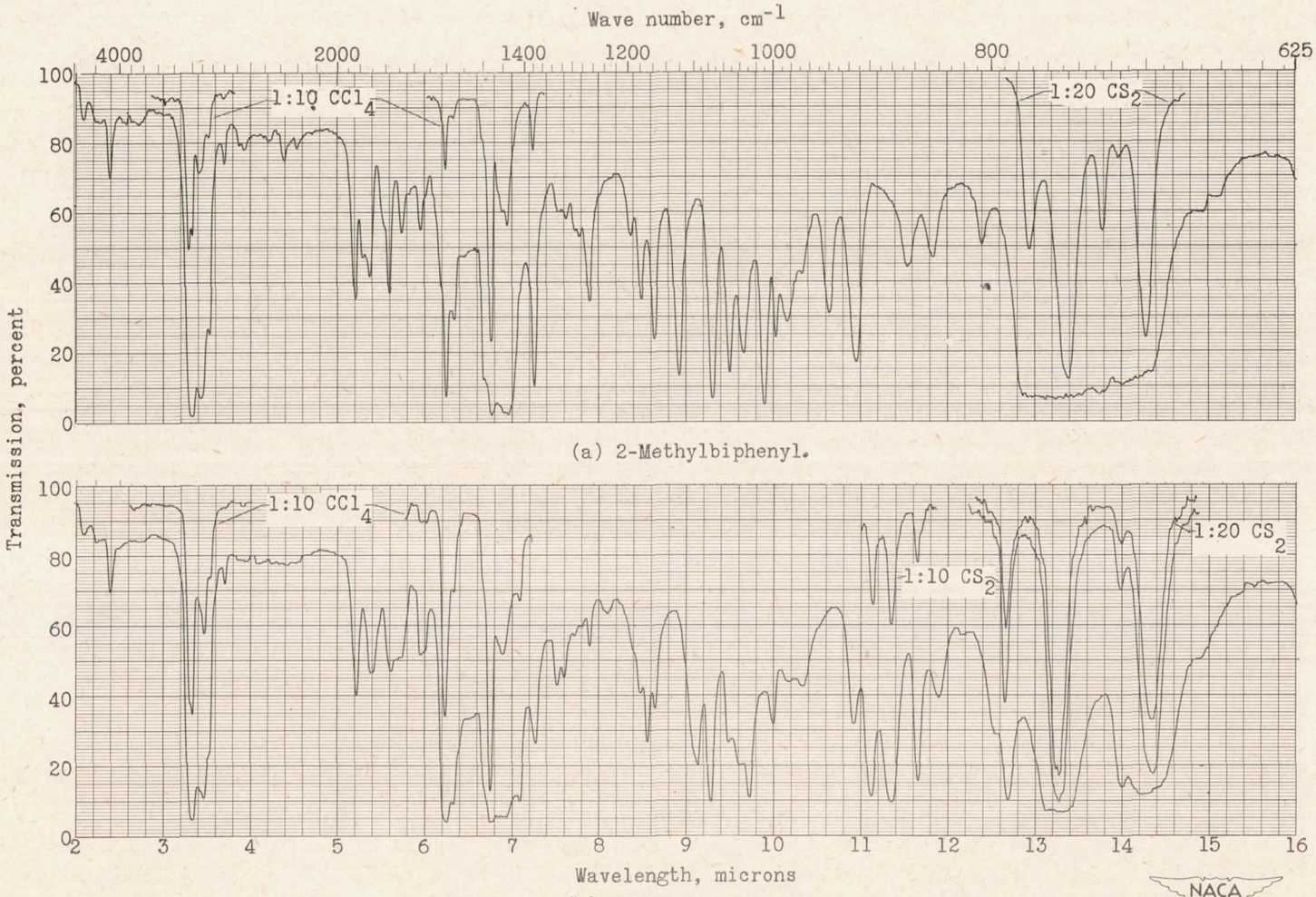
Figure 2. - Continued. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(q) 1,1-Dicyclohexylhexane.

(r) 1,6-Dicyclohexylhexane.

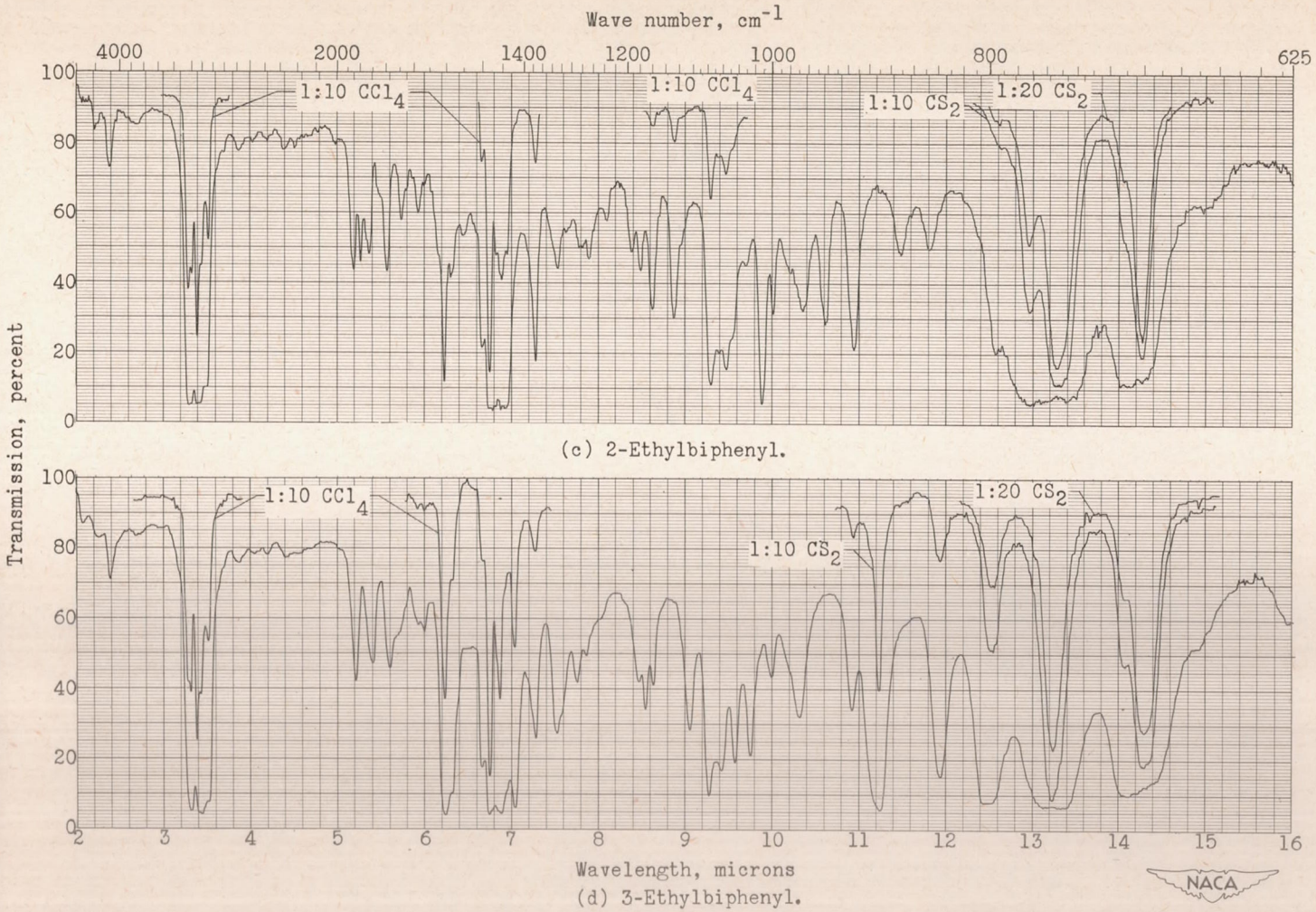
Figure 2. - Concluded. Infrared spectra for dicyclohexylalkanes. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(a) 2-Methylbiphenyl.

(b) 3-Methylbiphenyl.

Figure 3. - Infrared spectra for alkylbiphenyls. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(d) 3-Ethylbiphenyl.

Figure 3. - Continued. Infrared spectra for alkylbiphenyls. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.

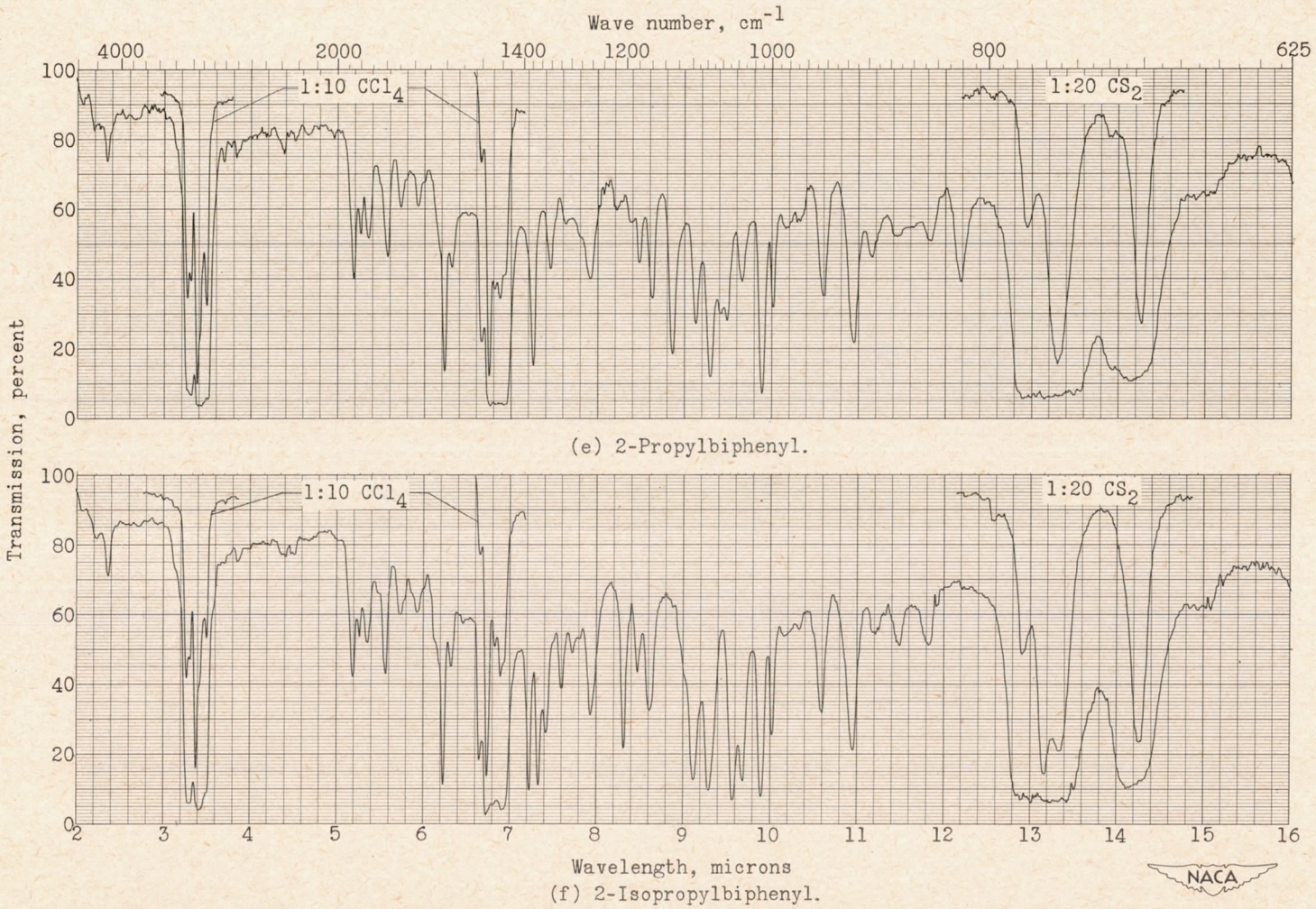
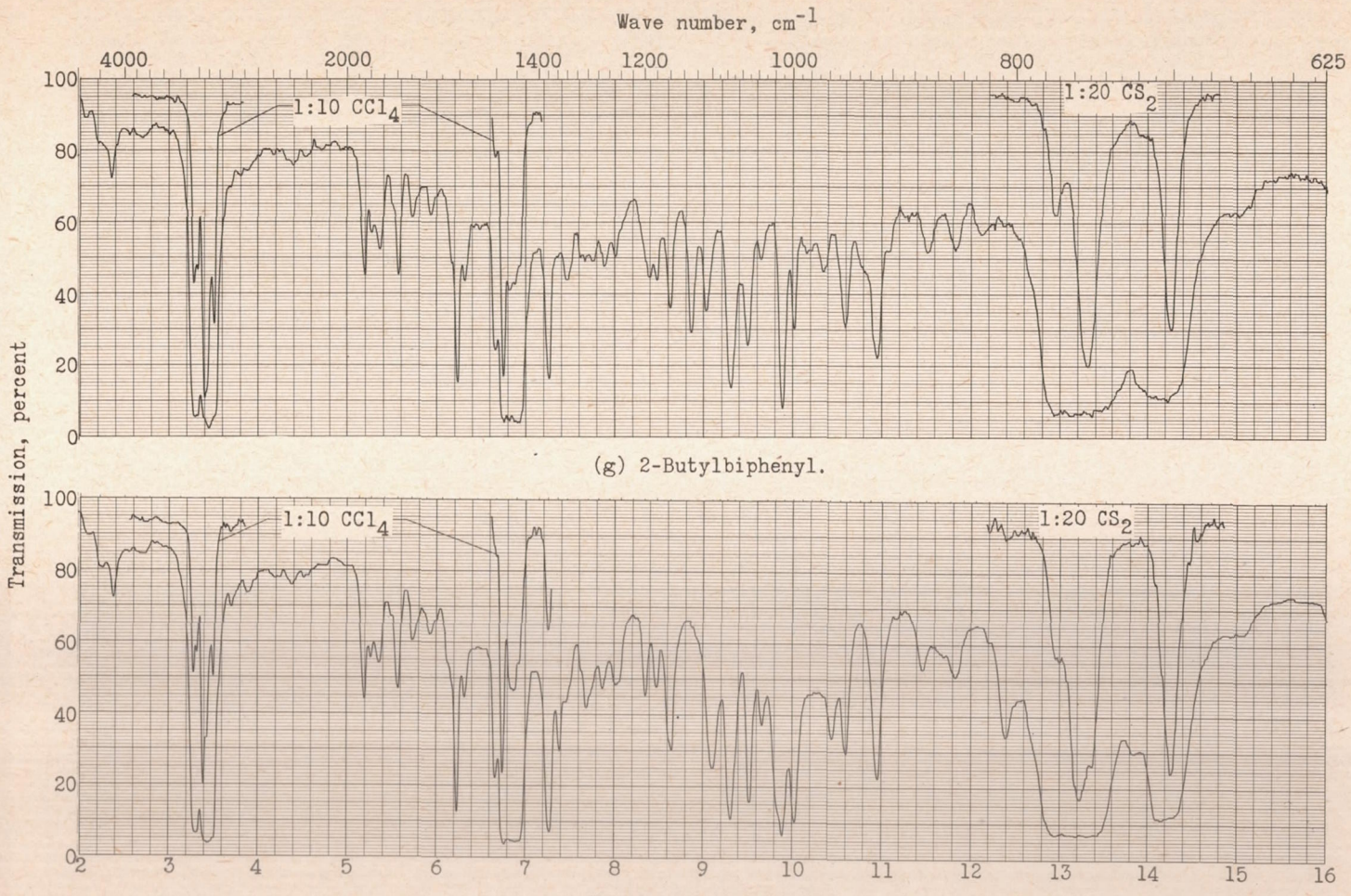


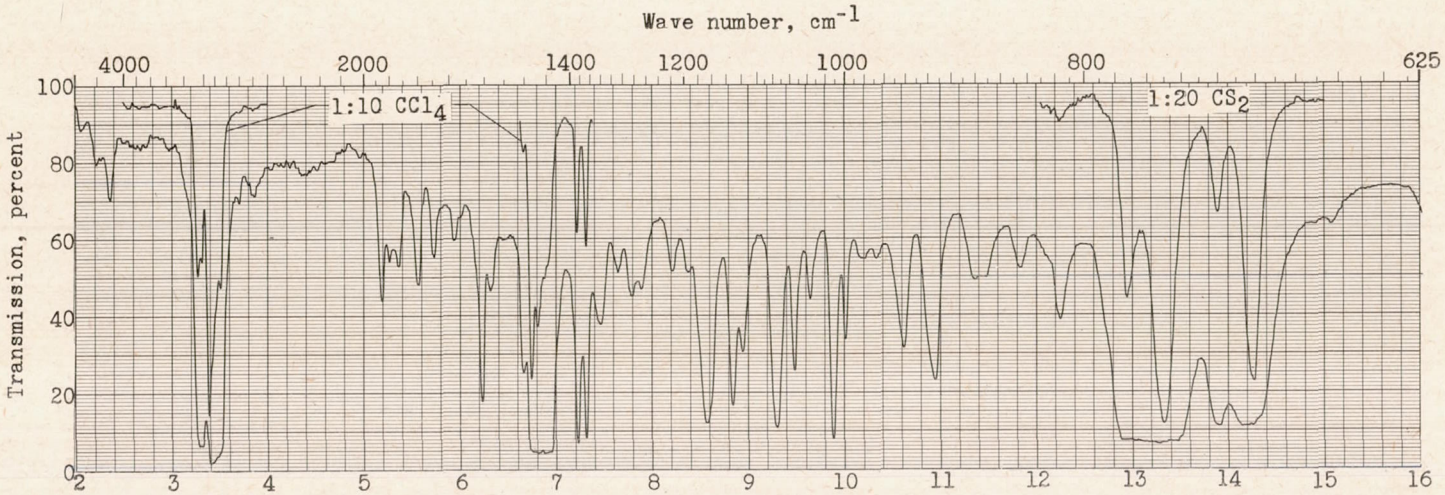
Figure 3 - Continued. Infrared spectra for alkylbiphenyls. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(g) 2-Butylbiphenyl.

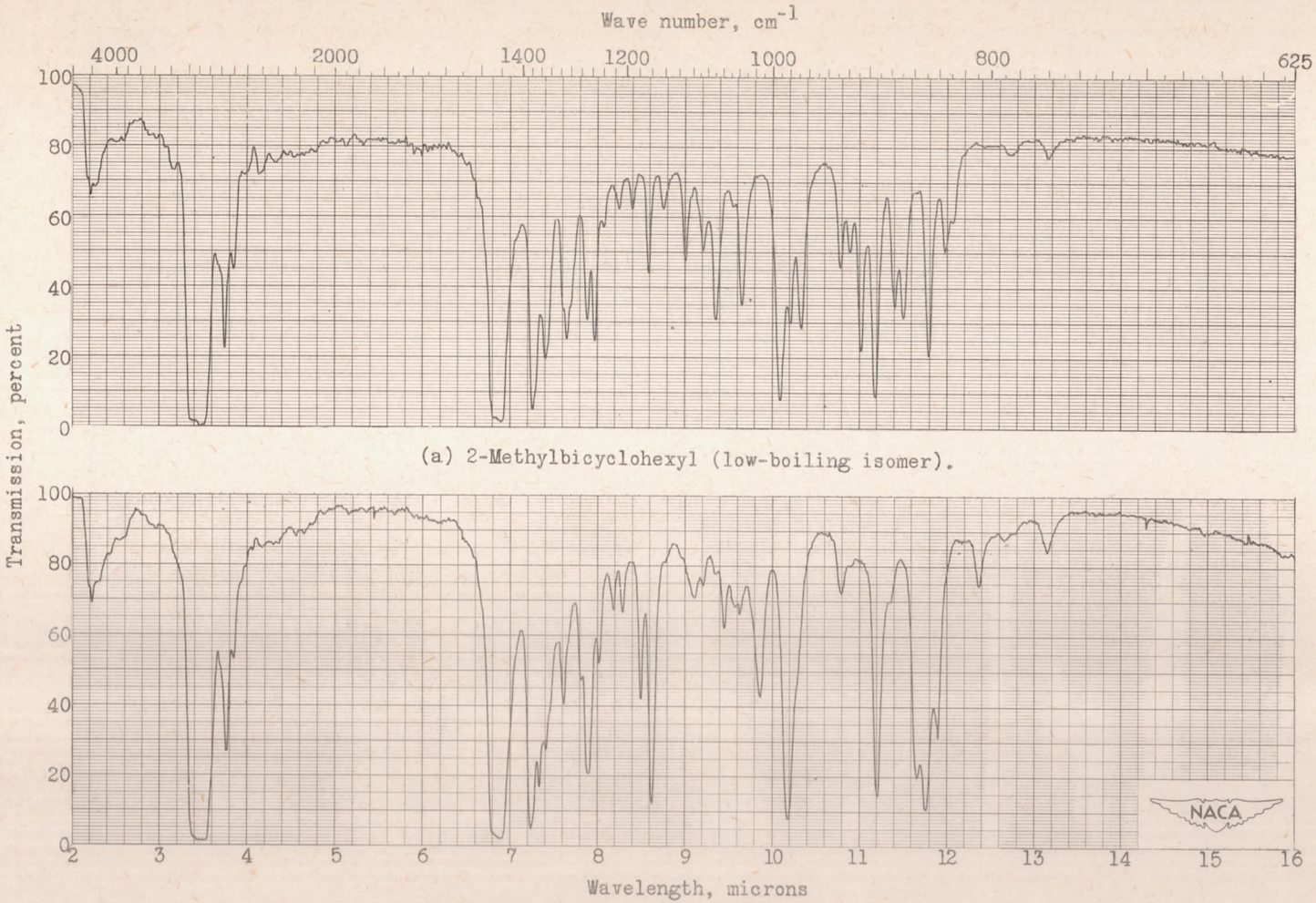
(h) 2-sec-Butylbiphenyl.

Figure 3. - Continued. Infrared spectra for alkylbiphenyls. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(i) 2-Isobutylbiphenyl.

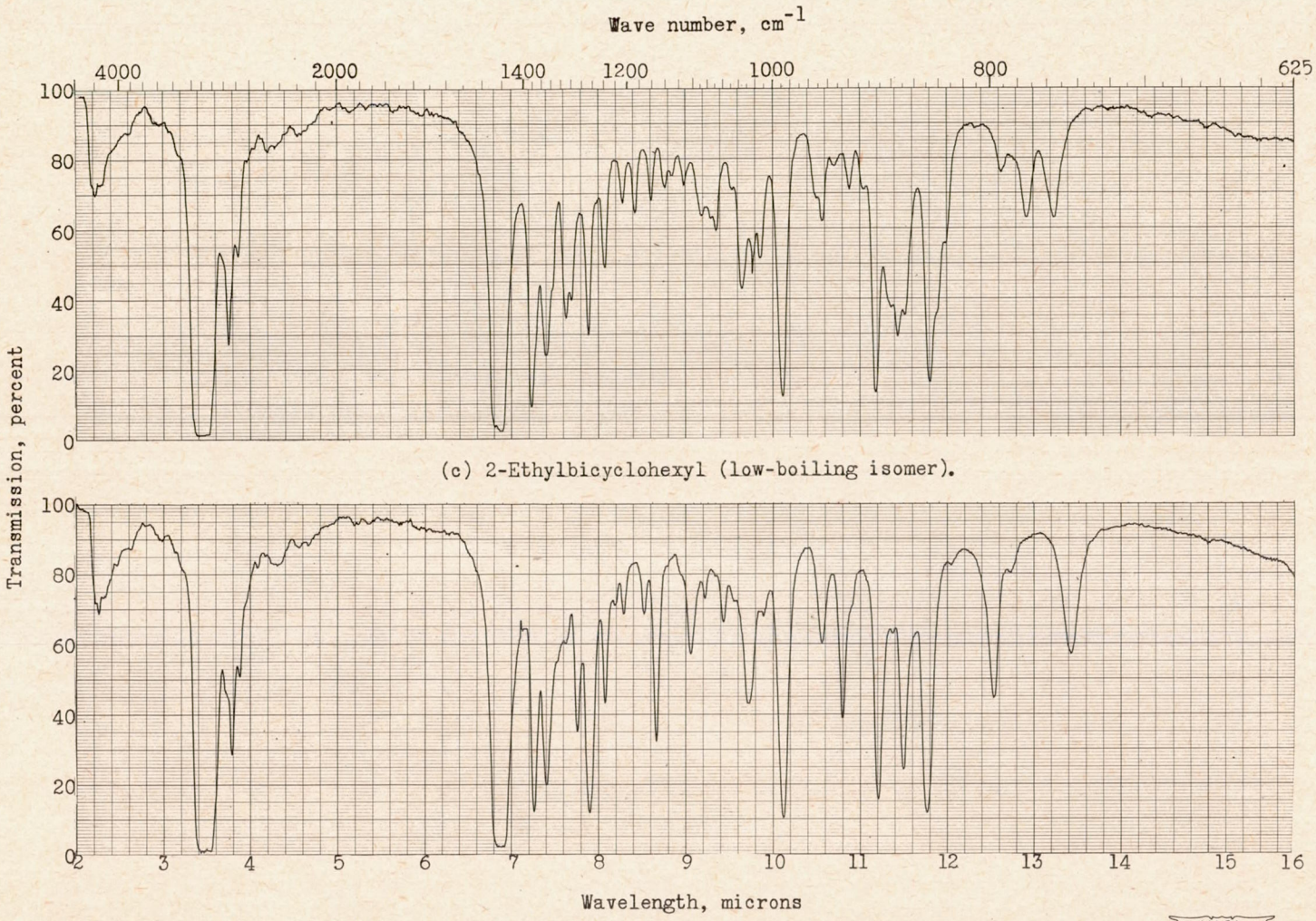
Figure 3. - Concluded. Infrared spectra for alkylbiphenyls. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.



(a) 2-Methylbicyclohexyl (low-boiling isomer).

(b) 2-Methylbicyclohexyl (high-boiling isomer).

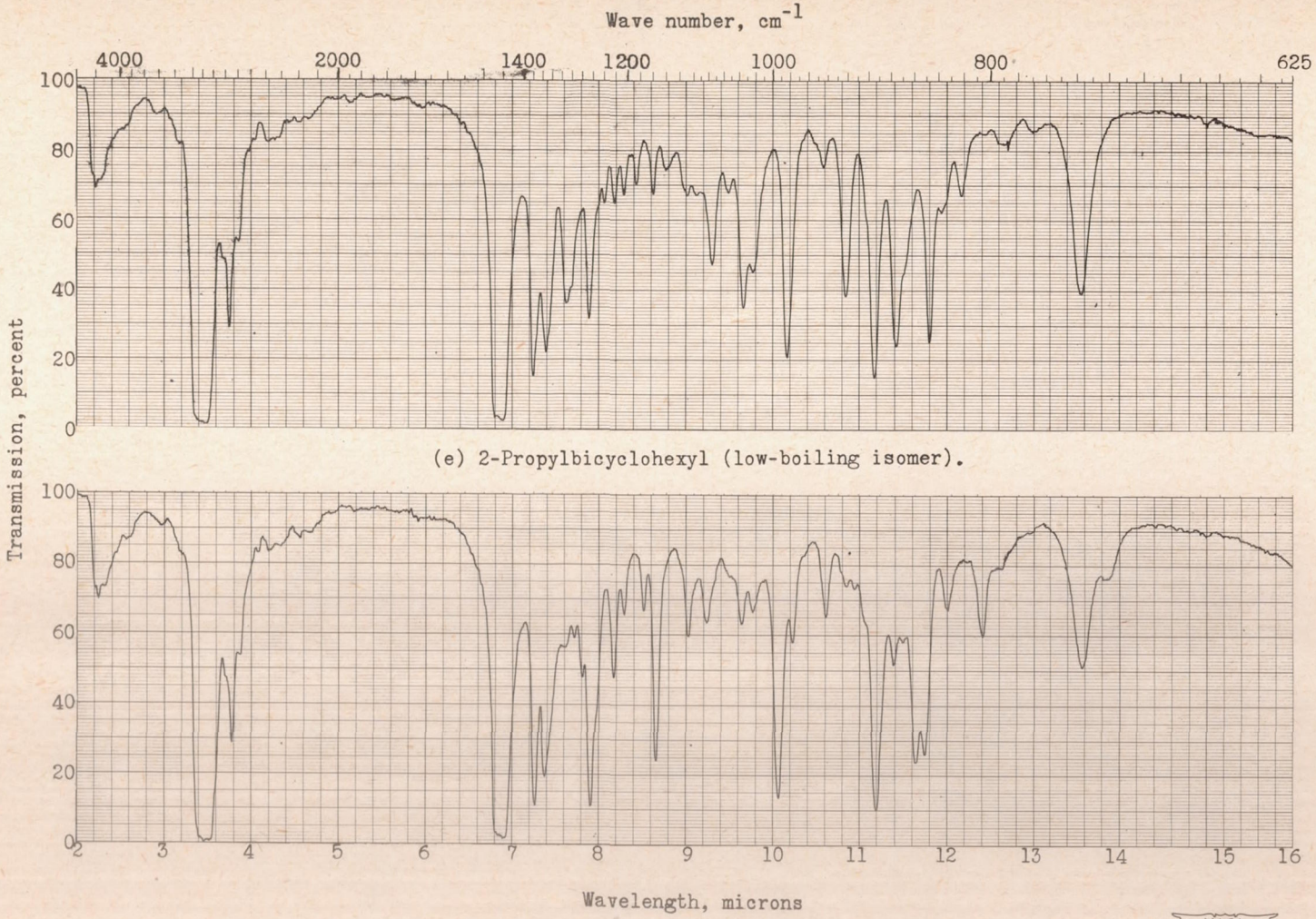
Figure 4. - Infrared spectra for alkylbicyclohexyls. Cell width, 0.1 millimeter; sample undiluted.



(c) 2-Ethylbicyclohexyl (low-boiling isomer).

(d) 2-Ethylbicyclohexyl (high-boiling isomer).

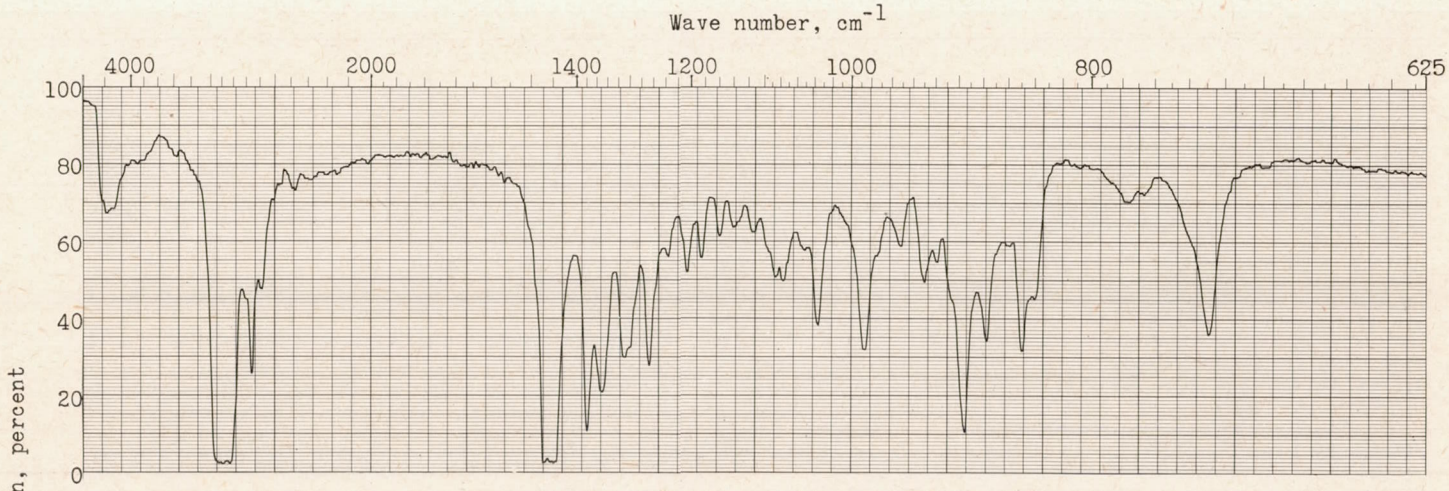
Figure 4. - Continued. Infrared spectra for alkylbicyclohexyls. Cell width, 0.1 millimeter; sample undiluted.



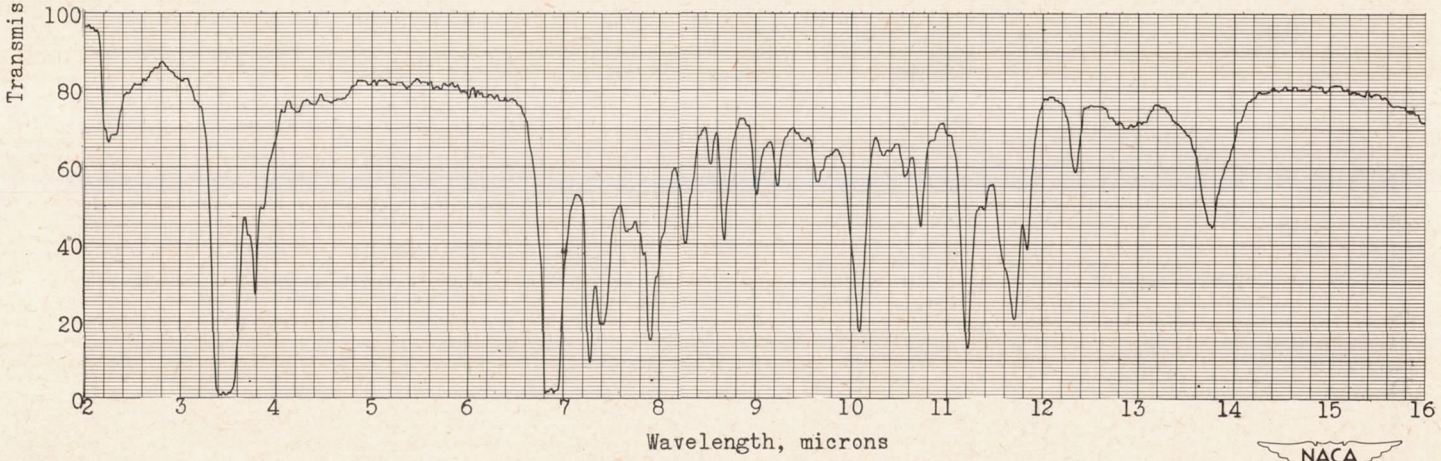
(e) 2-Propylbicyclohexyl (low-boiling isomer).

(f) 2-Propylbicyclohexyl (high-boiling isomer).

Figure 4. - Continued. Infrared spectra for alkylbicyclohexyls. Cell width, 0.1 millimeter; sample undiluted.

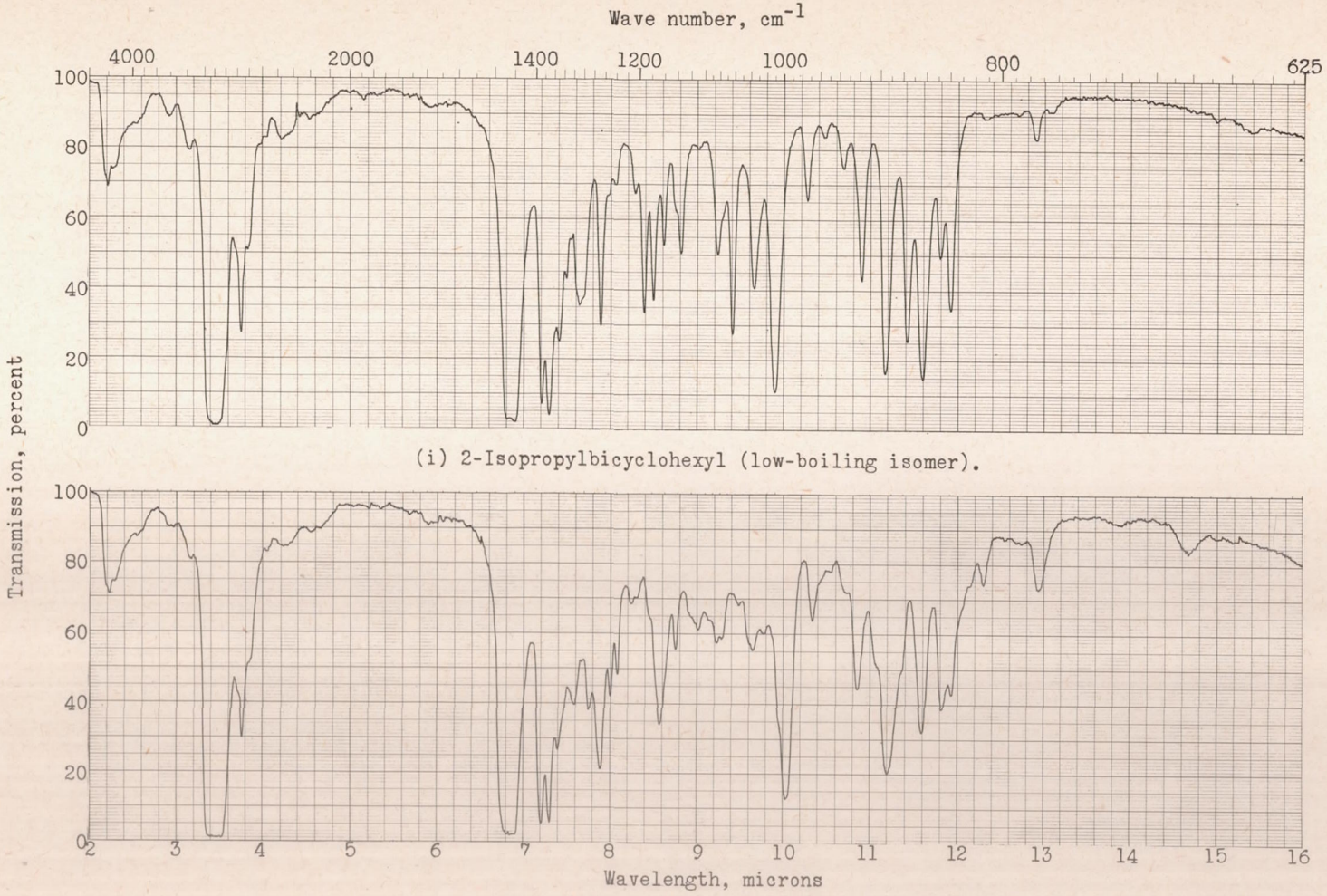


(g) 2-Butylbicyclohexyl (low-boiling isomer).



(h) 2-Butylbicyclohexyl (high-boiling isomer).

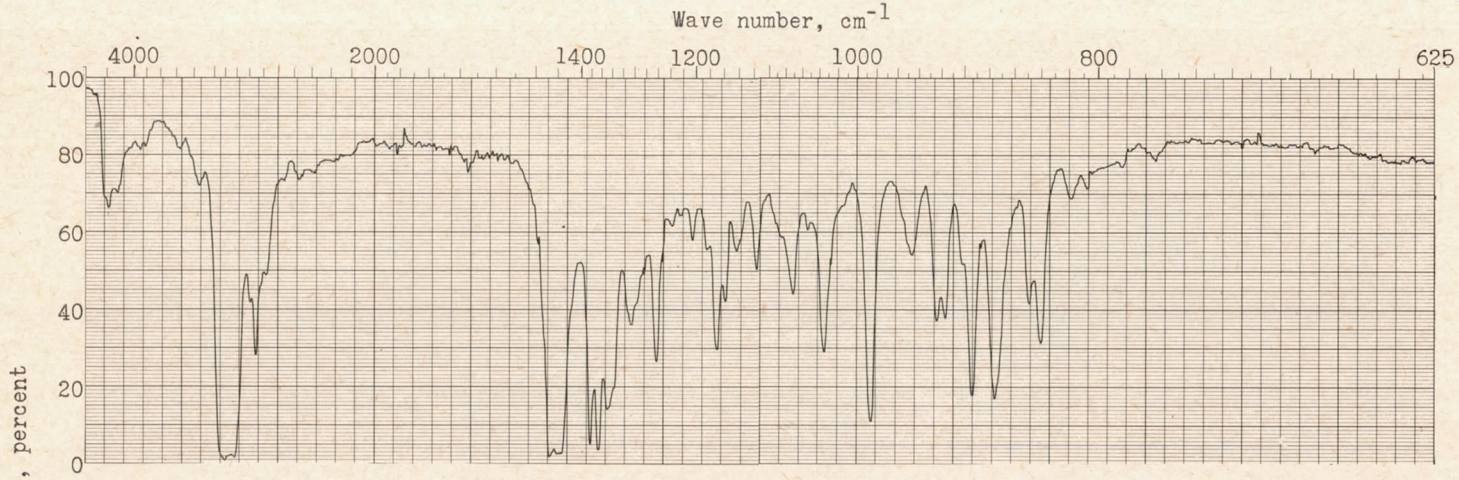
Figure 4. - Continued. Infrared spectra for alkylbicyclohexyls. Cell width, 0.1 millimeter; sample undiluted.



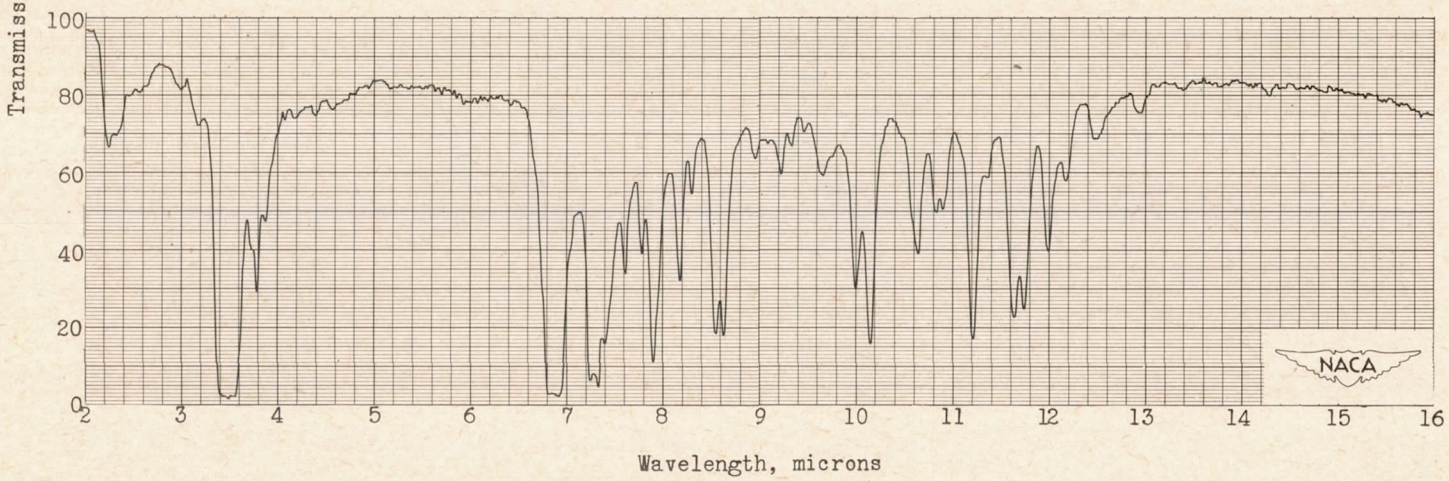
(i) 2-Isopropylbicyclohexyl (low-boiling isomer).

(j) 2-Isopropylbicyclohexyl (high-boiling isomer).

Figure 4. - Continued. Infrared spectra for alkylbicyclohexyls. Cell width, 0.1 millimeter; sample undiluted.

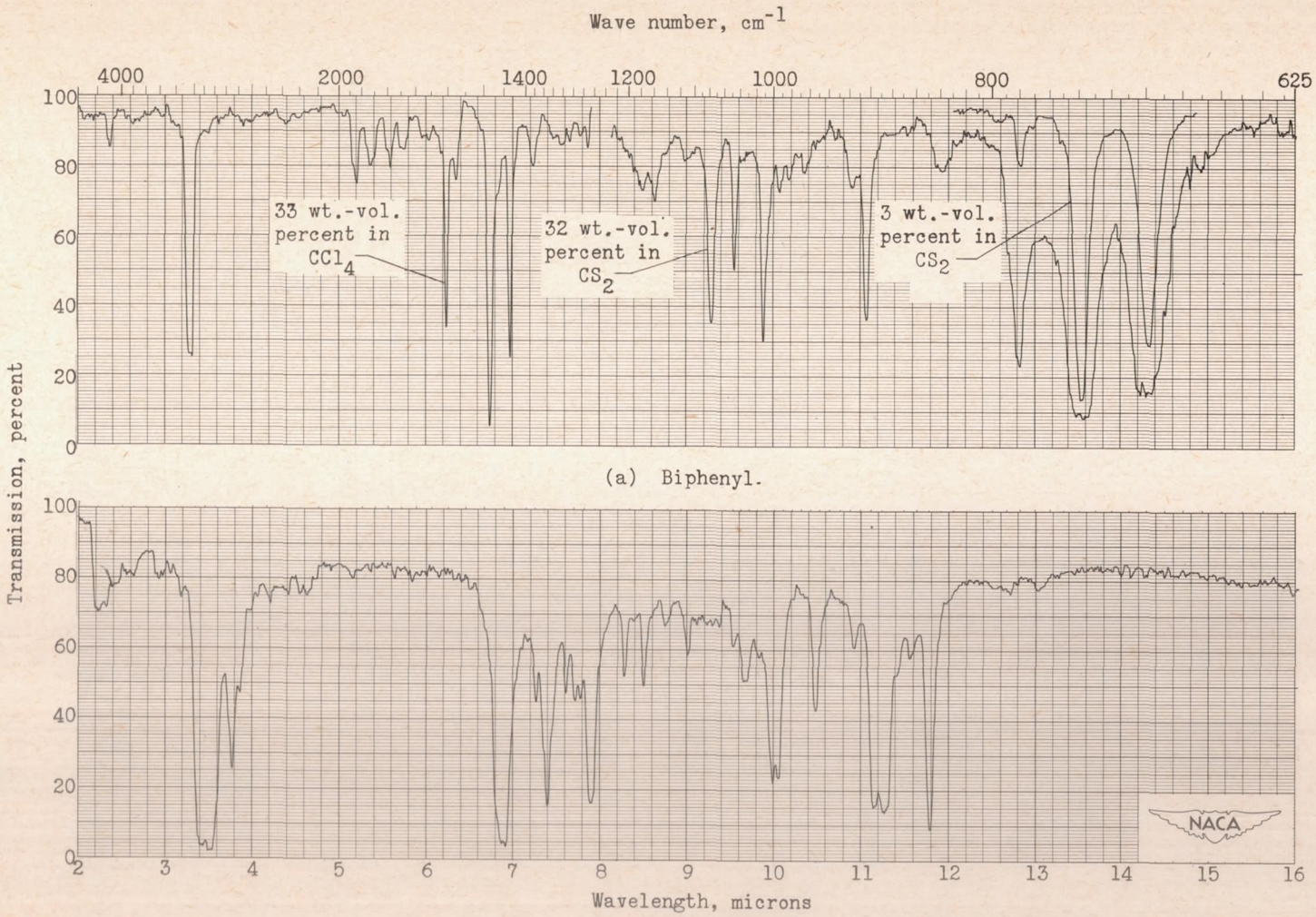


(k) 2-Isobutylbicyclohexyl (low-boiling isomer).



(l) 2-Isobutylbicyclohexyl (high-boiling isomer).

Figure 4. - Concluded. Infrared spectra for alkylbicyclohexyls. Cell width, 0.1 millimeter; sample undiluted.



(b) Bicyclohexyl.

Figure 5. - Infrared spectra for biphenyl and bicyclohexyl. Cell width, 0.1 millimeter; sample undiluted or diluted as indicated.

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