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Investigation in the Use of Infrared Absorption Spectrophotometry

Richard Henry Murcott
Union College - Schenectady, NY

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INVESTIGATION IN THE USE OF INFRARED
ABSORPTION SPECTROPHOTOMETRY

by

Richard Henry Murcott   UC 1958

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of their requirements
for the degree of Bachelor of Science with a Major in
Chemistry.

By _Richard Murcott_

Approved by _William B Martin, Jr._

Acknowledgement

I would like to express my sincere appreciation to Dr. William Martin of the Union College Chemistry Department for his advice and guidance in the research procedure concerning this thesis.

I would also like to thank Mr. Joseph Rudmann for his help in constructing some of the infrared cells used in my research.

It would have been difficult, if not impossible, to accomplish all the work necessary for this thesis without the generous aid of these two gentlemen.

Introduction:

Three rather unrelated projects in infrared spectrophotometry were carried out by the writer. First, A, some effort was expended in trying to find cell windows which were suitably transparent to infrared radiation and yet water insoluble. Secondly, B, the effects of dilution on certain ω-lactams was investigated to check for hydrogen bonding effects on their spectra. Thirdly, C, some trial investigations were made using a silver chloride polarizer unit recently acquired for use with the Perkin-Elmer Model 21 spectrophotometer.

Historical:

Section A

One of the material problems in obtaining infrared absorption data for various solutions is that the cells used to hold the solution are made of sodium chloride crystals. Aqueous solutions of compounds can not be used with sodium chloride cells, and water insoluble cell walls must be transparent to infrared frequencies.

Many substances exist that have been used for cells. Silicon[5, 8, 9, 20] has been used with much success. Another substance that can be used is magnesium oxide in thin sheets. Barns[3] explains how fused magnesium oxide can be crystalized to form large, infrared-transparent, disks that are especially useful since acids will not attack them. The magnesium

oxide has absorption bands which have been reported[3] at 8.3μ, 10.8μ and 11.82μ.

Harris[16] has produced alumina films that have been found to transmit infrared light with almost no absorption. An improvement on the construction of extremely thin (25 molecules thick) alumina disks has been announced[29]; this is accomplished by dissolving the aluminum of a thin sheet of aluminum in acid and leaving the protective aluminum oxide coating behind as a thin, transparent sheet.

Germanium[10], lead difluoride[19], lithium fluoride[25], cesium bromide[13], barium tartrate[18] and cesium iodide[22] have all been used as cell material. Adams[1] has used silver chloride plates for cells. These plates are produced by rolling silver chloride under pressure. The resulting solid is clear and flexible and quite transparent to infrared radiation.

For work between 3μ and 12μ, As_2S_3 can be used as cell material[13]. The solid is melted to form a glass at low temperatures. This is then annealed and ground. Blout[7] has found that certain organic high polymers with the absorbing medium held in situ in it works well for the lower end of the spectrum, 1.0μ to 6.0μ.

It has also been reported that red and yellow feldspar can be used as cell material[21].

Section B

Heckeler[17] has prepared ω-lactams and has reproduced infrared curves of these. The lactams used in this work were ω-butyrolactam, ω-pentanolactam, ω-hexanolactam and ω-heptanolactam. The last three

were prepared by Heckeler.   The ω-butyrolactam was a commercial product.

Bellamy[6] discusses the hydrogen bonding in lactams.   Southerland[26] discusses the problems concerned with trying to differentiate O-H absorption and NH absorption bonds because the regions for these two types of absorptions overlap.   This might possibly make it difficult to try to discover any change in absorptions due to H bonding in the lactam molecule, if there should be appreciable enolic O-H bonds present.   Freymann & Heilmann[14] have been able to differentiate three different types of O-H bonding: intramolecular, intermolecular and chelate.   They each absorb at a different wavelength.

It has been reported[11] that $-\overset{H}{N}-\overset{O}{C}-$ exhibit absorptions between 3000 cm^{-1} and 3400 cm^{-1}.   Amides and polyamides, nylon and certain proteins all have strong absorption bonds near 3280 cm^{-1} and less intense bond near 3060 cm^{-1}.   It has been shown[11] that these are both NH stretching absorptions.

It is improbable that the absorption at 3060 cm^{-1} is the overtone of the 1550 cm^{-1} absorption because the intensity variation of the supposed overtone does not shift on dilution, but the 1550 cm^{-1} absorption line does.   If it were truly the overtone, as the 1550 cm^{-1} shifted on dilution, the overtone at 3060 cm^{-1} would also shift.

Darmon & Sutherland[11] have also done work on the effects of dilution on ω-butyrolactam using chloroform as the diluting solvent.   They found that a new bond at 3420 cm^{-1} appeared on dilution.   Straight chain

amides show an absorption at 3280 cm^{-1}, but have not found a similar bond

for any cyclic lactam.

These authors have proposed three different types of intermolecular

hydrogen bonding for cyclic lactams.
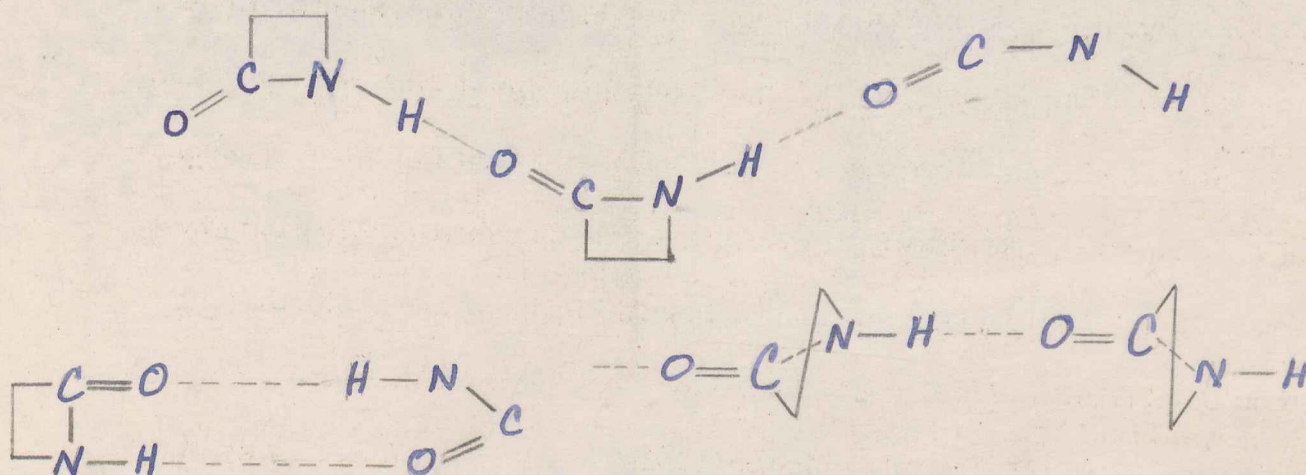
I and II are **cis** configurations; the two hydrogen bonded N-H frequencies

in cyclic amides arise from this. The 3280 cm^{-1} bond not observed in any

of the cyclic amides rises from the N-H group which forms hydrogen bonds

between -$\overset{O}{\overset{\|}{C}}$-NH groups in the trans (III) configuration. The 3060 cm^{-1}

bond arises from N-H bonds involved in hydrogen bonding of the dimeric

cis configuration II rather than that of type I. Darmon & Sutherland[22] also

point out that because of chemical reasons, type II would be expected to

have the strongest hydrogen bonds and, therefore, show the greatest lowering

of the N-H frequency from its unbound value.

Section C

The use of polarized infrared radiation for infrared absorption

spectrophotometry is a fairly modern development. Thompson[27] has

pointed out that single crystals containing either $\overset{O}{\overset{\|}{C}}$, -N-H or -O-H functional

groups will cause changes in the absorption spectra if the plane of incident

polarized light is rotated. Weissberger[28] explains the reason for this.

If you have a solid single crystal of a ketone and the plane of the incident

plane polarized light is parallel to the alligned C=O bonds, there will be

great absorption due to C=O vibration. This situation is pictured in
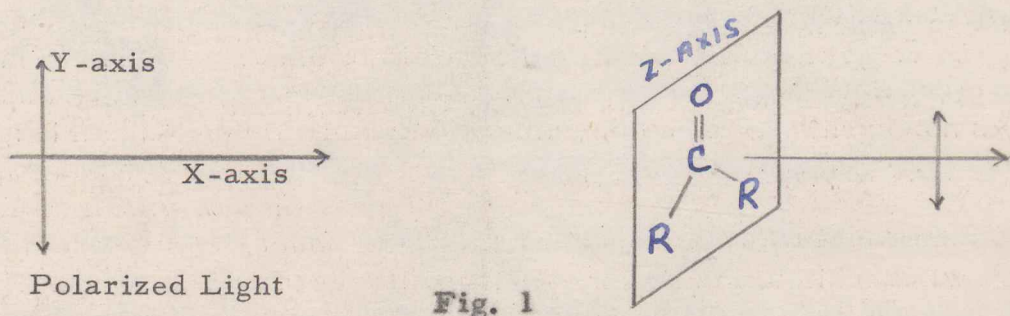
Figure 1.

Fig. 1

If, on the other hand, the plane of incident plane polarized light is

perpendicular to the plane of the alligned C=O groups, there will be little

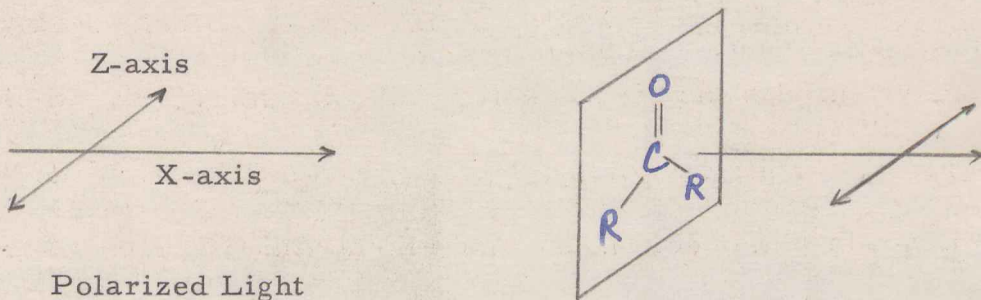absorption because of C=O vibration. Figure 2 shows this situation.

Fig. 2

It seems from this that if the plane of polarized light incident on a

single crystal were rotated until the absorption due to C=O were at a

maximum, the plane of polarized light would be parallel to the oriented

C=O groups and, therefore, the orientation of functional groups in the

crystal might be discovered.

The practical problem arises in obtaining large enough single crystals or orienting many crystals in exactly the same pattern, so that each carbonyl group lines up the same way. Anderson[2] explains a successful way of orienting methylene blue molecules on glass by rubbing the glass in one direction on rouge. Newman[23] explains how sodium nitrite can be crystalized in order to get all of the molecules oriented in the same way by slow crystalization from a water solution at room temperature. Newman & Halford[24] grew ammonium nitrate and thallous nitrate crystals from water solutions and then used a Petrographic microscope to determine how to clean the crystals. By grinding the crystals using water or ethyl alcohol and an abrasive, they were able to obtain crystals only 35-100 microns thick.

Barrow[4] cut crystals of rhombic sulfur with a carborundum glass cutting wheel and then polished them with rouge and water until he obtained disks 1 to 2 mm. thick.

Francei[12] was able to determine the conformation of the nitro group in ortho-nitrophenol using polarized infrared absorption curves and Gutowsky[15] was able to measure the rotation of infrared by quartz crystals for different wavelengths of incident light.

Experimental Results:

Apparatus:

The infrared spectrophotometer used for this research was the Perkin-Elmer Model 21 at Union College in the Chemistry Department.

The polarizing unit used for part C of this research was obtained from Perkin-Elmer in 1958. The polarizing unit consists of six silver chloride plates through which the infrared radiation passed.

Section A

The search for cell material insoluble in water, but transparent in infrared light started with solid, single crystal, silicon, a gift from Sylvania Electric Products Inc.

There were three disks approximately 1.5 cm in diameter and about 2 mm thick, all of slightly different dimensions. These disks were polished using a glass polishing rouge obtained from the American Optical Co. A piece of heavy cloth was placed on a large piece of plate glass, and the rouge mixed with water was placed on the cloth. The pieces of silicon were polished with the rouge until both surfaces were bright enough to reflect light.

The infrared curves obtained using the pieces of silicon alone showed few absorption peaks and generally showed only 17% transmittance. It seemed that the pieces of silicon were too thick to be used, when two pieces of silicon were used with a thin film of liquid between them, there was practically complete absorption of radiation. It would seem probable that splitting the pieces in order to obtain very thin pieces might make more effective cell walls if the thinner wafers should prove strong enough.

Other substances were experimented with to determine their transparency for infrared light. The following table lists the substances used and the areas of transparency:

Table 1

Substance	Estimated Thickness	Area of Transparency and % Transmitance
Iceland spar crystal	1/8"	2-5μ has many peaks-ave. 10%
eisenglass	1/16"	2-2.7μ -60%; 3.4-5.5μ -35%
"scotch tape"	- - -	2.0-2.7μ 75%; 3.4-5.7μ 60%
polyethylene	010"	2.0-3.3μ 75%; 3.4-5.5μ 85%
quartz	1/16"	2.0-5.0μ 70%
$Na_2SO_410H_2O$	1/8"	no transmission
Fluorite (Pink)	3/16"	2.0-10.0μ 40%
Fluorite (Blue)	1/4"	2.0-10.0μ 20%
Cryolite	1/4"	no transmission
soft glass	1/8"	2.0-2.7μ 87%; 2.7-4.5μ 40%
pyrex glass	1/8"	2.0-2.7μ 67%; 2.7-3.6μ 35%
cobalt blue glass	1/8"	2.0-2.7μ 67%; 2.7-4.5μ 30%
AgCl sheet	1/16"	2-15μ 67%
charcoal block	1/2"	no transmission
gold leaf	very thin	no transmission
Platinum	1/32"	no transmission
lead	1/16"	no transmission
tin	1/16"	no transmission
aluminum	.001"	no transmission
tantalum	1/16"	no transmission
Si unbalanced, unpolished	1/8"	2-15μ 17%
Si polished	1/8"	2-15μ 28% except peak at 9.05μ to 12%
FeS	1/2"	no transmission

None of these, obviously, were very transparent to infrared

radiation.

The AgCl sheet that was used was a commercial product and was

as clear to visible light as glass. The production of one of these AgCl

clear plates was attempted. Pure AgCl was precipitated from an aqueous solution of silver nitrate by NaCl. Equal molar solutions were used. The AgCl was precipitated in the dark to prevent any oxidation due to sunlight. The white solid after washing and drying was placed between flat iron plates and subjected to a pressure of 11000 lbs/sq. inch in a press for a time of 5 minutes. An amazing physical change took place. The white granular solid turned into a semi-transparent solid resembling the commercial variety except that the pressed product was extremely brittle, whereas the rolled commercial type was pliable and could be bent without fear of breaking. Another difference was that the rolled commercial type was transparent to infrared radiation (67% transparent) whereas the type formed by pressure alone was completely opaque to infrared radiation.

It was desired to construct a small cell using either AgCl plates or polethylene as windows so that thick samples of liquids might be analysed. One was constructed using aluminum and having a 1/8" aluminum spacer between the two plates. See Fig. 3

screws

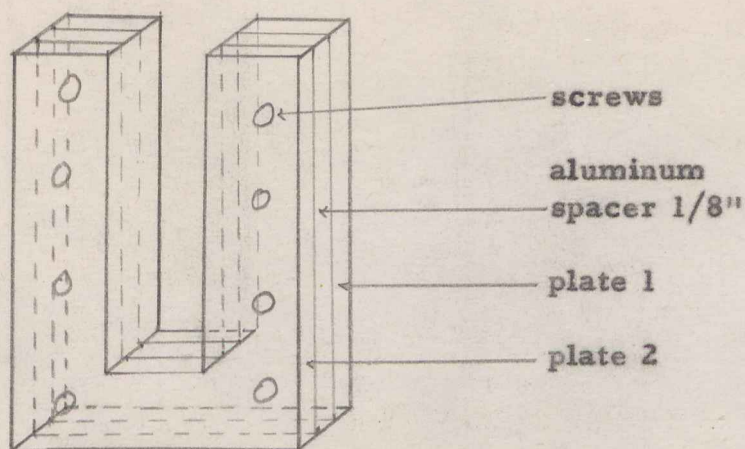aluminum spacer 1/8"

plate 1

plate 2

Fig. 3

The two windows were placed between the spacer and plates one and two.

Two pieces of polyethylene plastic material were placed in the cell as windows and several liquids were run. The instrument was set at 4.1μ since at this wavelength, the polyethylene had least absorbance. Acetone, ether and dioxane were placed in the cell and were found to absorb all the 4.1μ radiation. Changing the cell thickness and changing the window material were tried.
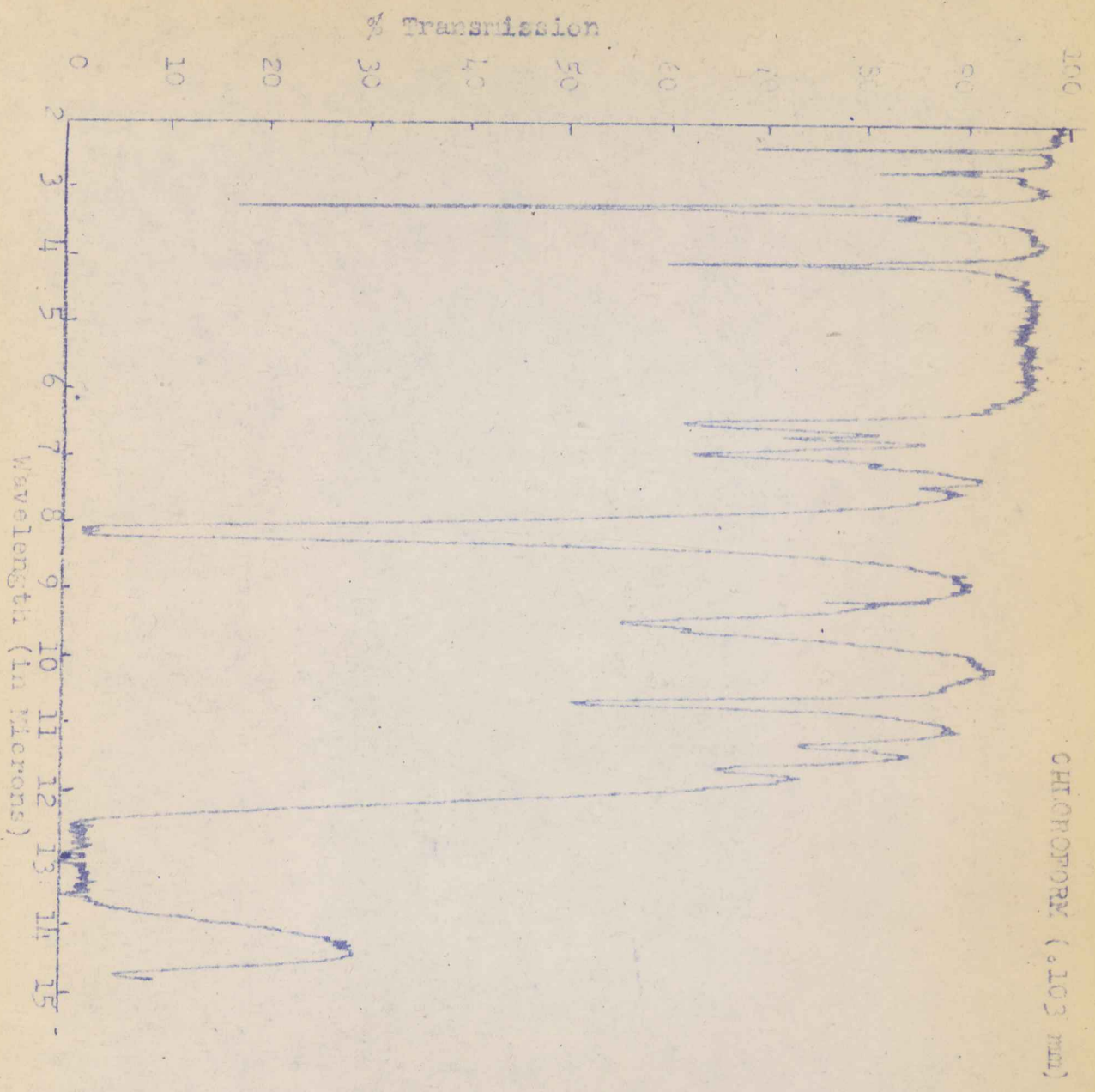
Table 2

Materials for Cell Windows

Material	Transmitance at 4.1μ
polyethylene	66%
mylar	50%
cellophane	50%
polystyryene	50%
colloiden	45%

As may be seen from Table 2, polyethylene had the greatest % transmission. When the spacer of the cell was changed, to one of 1/16", acetone showed 15% transmission and methanol 5%.

Section B

The next area of investigation was that of assessing the degree of hydrogen bonding in ω-lactams. Samples of ω-lactams were diluted with chloroform. Table 3 shows the actual makeup of each solution used. A possible source of error was the evaporation of chloroform from the solutions of lactams.

CHLOROFORM (.103 mm.)

% Transmission

Wavelength (in Microns)

Table 3

Lactam Dilutions with Chloroform

Lactam	Solution No.	Cell thickness in mm	Grams of Lactam	Grams CHCl₃	Approximate Mole Ratio
pyrrolidone	I	.025	.7602	1.0937	1-1
"	II	.05	.8733	5.7320	1-5
"	III	.1	.8143	11.3312	1-10
"	IV	.1	.8324	25.3575	1-20
n-methyl-2-pyrrolidone	V	.025	2.0212	3.9790	1-1
"	VI	.05	1.2660	6.2359	1-5
"	VII	.1	.6694	6.1732	1-10
"	VIII	.1	.9234	23.1243	1-20
ω-Heptanolactam	IX	.025	.0941	.0995	1-1
"	X	.05	.0851	.4410	1-5
"	XI	.1	.0655	.7410	1-10
"	XII	.1	.0486	2.0628	1-20
ω-Hexanolactam	XIII	.025	.0844	.1156	1-1
"	XIV	.1	.0778	.8382	1-10
"	XV	.1	.0184	.2071	1-20
ω-Pentalolactam	XVI	.025	.0745	.1674	1-1
"	XVII	.05	.0972	.5097	1-5
"	XVIII	.1	.1111	1.0190	1-10
"	XIX	.1	.1004	2.9969	1-20

Each lactam was diluted four times making mole ratios of solute to solvent 1-1, 1-5, 1-10 and 1-20. The absorption curve was also obtained for the neat (undiluted) substances.

Pyrrolidone showed many interesting changes in its infrared absorption curve with successive dilution. The structure for pyrrolidone is:

$$
\begin{array}{ccc}
 & H & H \\
 & | & | \\
H-C & - & C-H \\
| & & | \\
H_2C & & C=O \\
 & \diagdown \; N \; \diagup & \\
 & | & \\
 & H &
\end{array}
$$
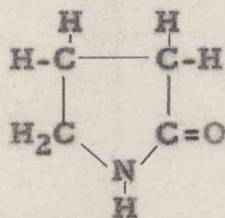
There was shifting of the 9.45μ in the 1-20 molar concentration solution. Neither OH nor NH groups absorb in that region of the spectrum, so no simple explanation presented itself. Upon dilution, the absorption at 3.1μ became more important. This is the N-H stretch absorption. Upon dilution this became relatively stronger, signifying that the percent of NH in the lactam increases with dilution. In concentrated solutions of the pyrrolidone, there must exist much intermolecular bonding between the hydrogen of the NH group and the oxygen of the carbonyl group.

Dilution with solvent reduces the chances for hydrogen bonding association. Because of the decrease of hydrogen bonding on dilution, the unbonded N-H stretch absorption bonds should increase relatively in intensity. This was found to be the case. Because the cell thickness varied for the absorption data, a quantitative study was undertaken on this absorption peak at 2.89μ, using the base line technique with the 7.05μ bond absorption peak (which was assumed to be $-CH_2-$ deformation absorption), to compare intensities with. Table 4 shows the results.
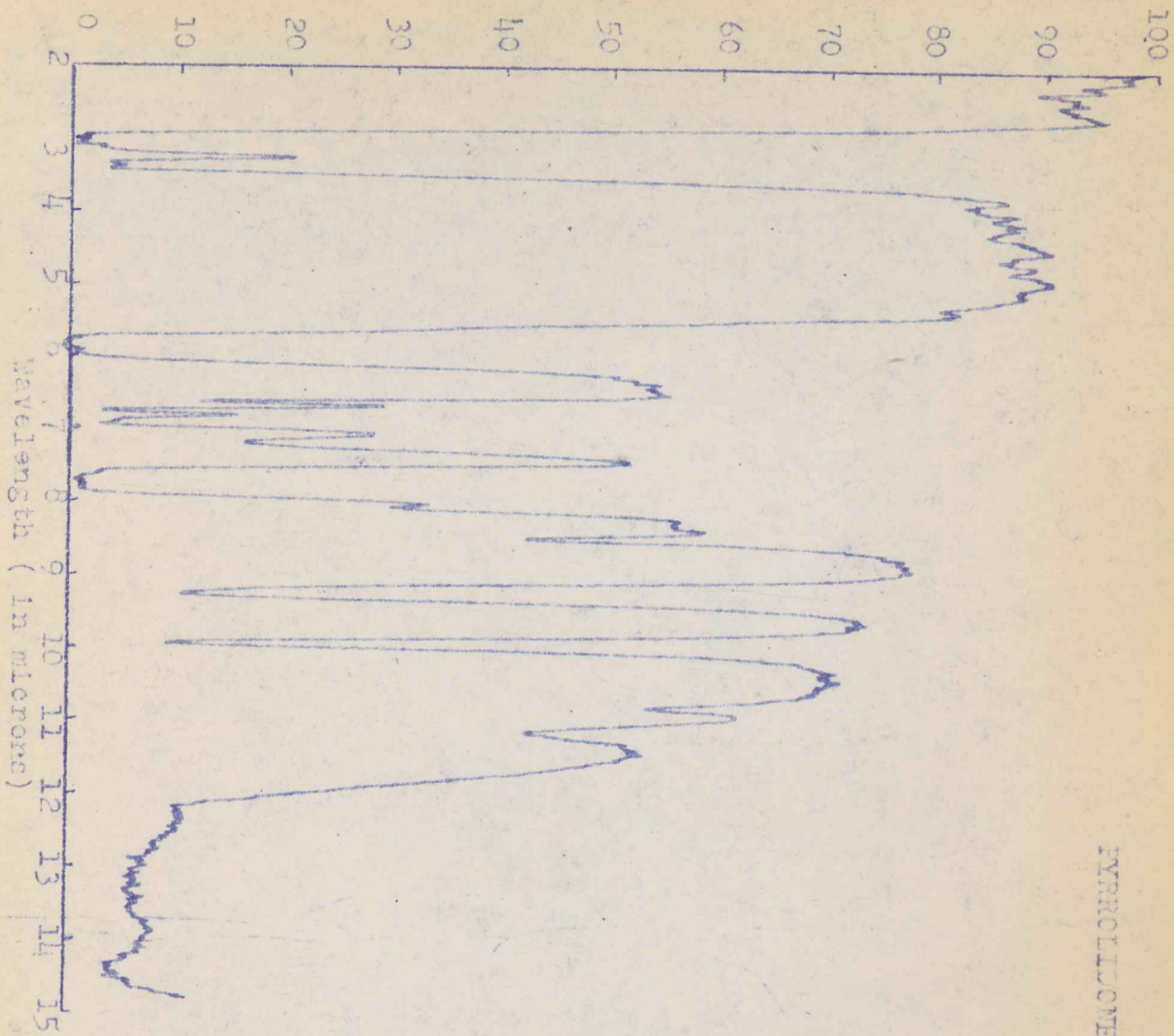
Table 4

*Quantitative Study of The 3.1μ Absorption Peak of Pyrrolidone (Using 7.05μ Absorption Peak as Reference)
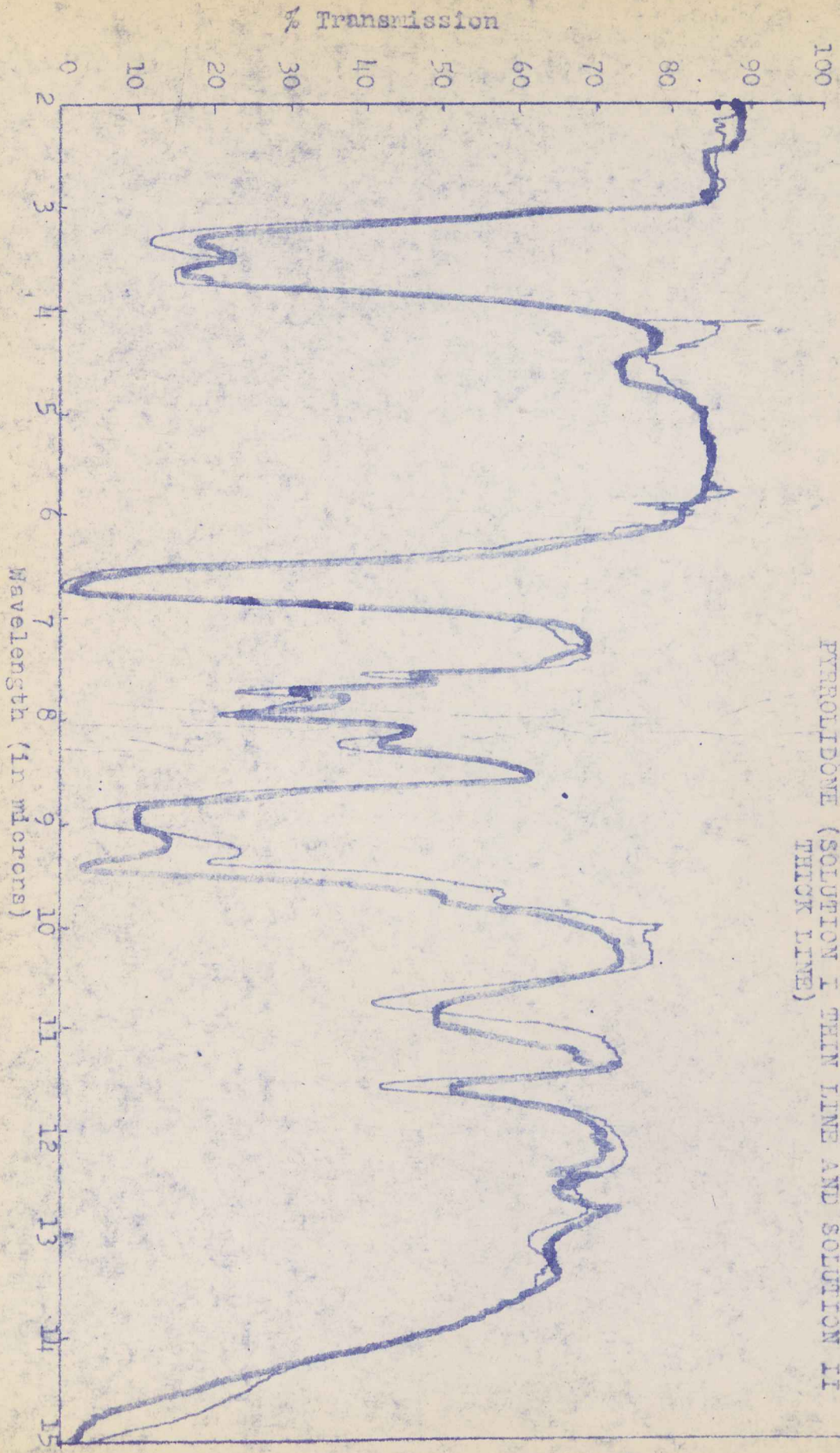
Solution Concentration (mole ratio)	Peak Height in Absorbance Units		Ratio of Peak Heights
	at 3.1μ	at 7.05μ	
neat	.98	.58	.582
1-1	1.45	.46	.312
1-5	.65	.43	.654
1-10	.75	.69	.873
1-20	.31	.26	.84

*For method used, see Ewing, G. "Instrumental Methods of Chemical Analysis" page 208.
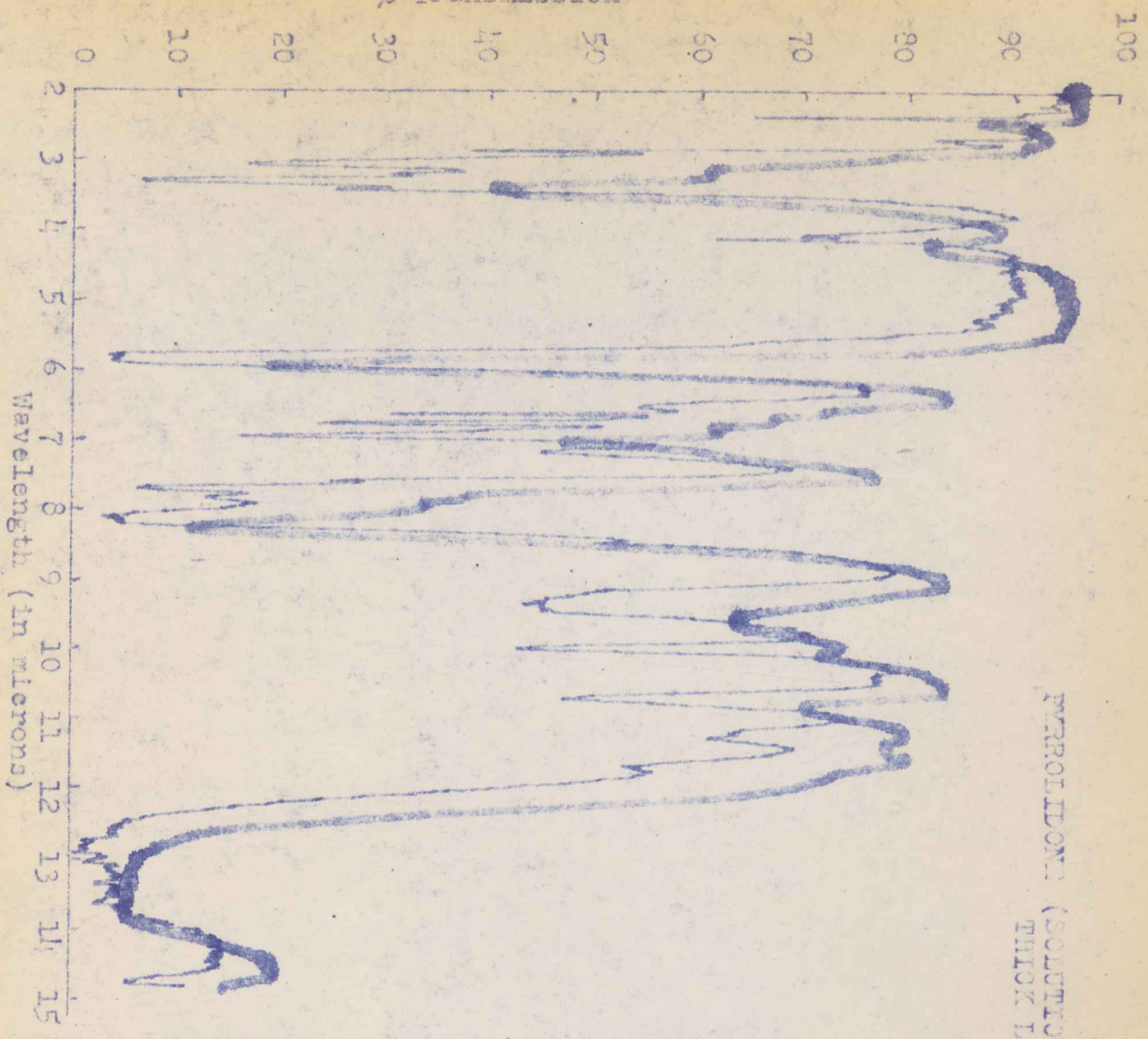
PYRROLIDONE (NEAT 0.025mm)

PYRROLIDONE (SOLUTION I THIN LINE AND SOLUTION II THICK LINE)

% Transmission

Wavelength (in microns)

PYRROLIDONE (SOLUTION III THIN LINE AND SOLUTION IV THICK LINE)

As can be seen from Table 4, the absorption at 3.1μ increased relatively on dilution, even taking into account the increase in cell thickness for the more dilute solutions. An OH absorption peak appeared at 7.35μ. This appeared to be decreasing on dilution. The absorption peak at 8.55μ also decreased on dilution. This was also a hydroxyl absorption area.

N-methyl-2-pyrrolidone has a methyl group replacing the hydrogen on the nitrogen atom. Because of the methyl hydrogens do not hydrogen bond with the adjacent carbonyl oxygen, there should be no change on dilution because of N-H bonding. Table 5 given the quantitative results for the N-H absorption at 3.1μ.
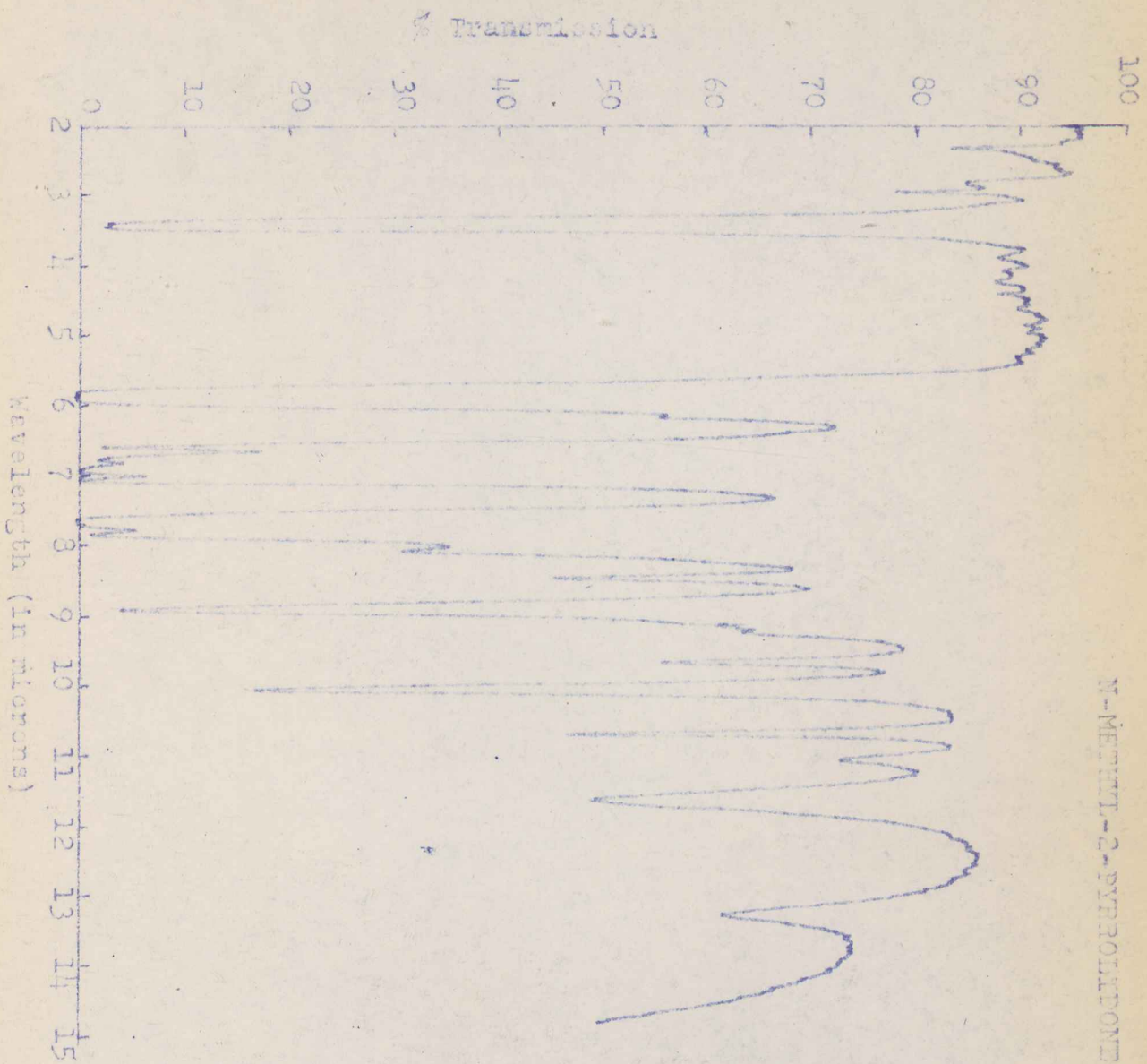
Table 5

N-methyl-2-pyrrolidone Quantitative Study at 3.1μ
(11.8μ Absorption Peak as Reference)

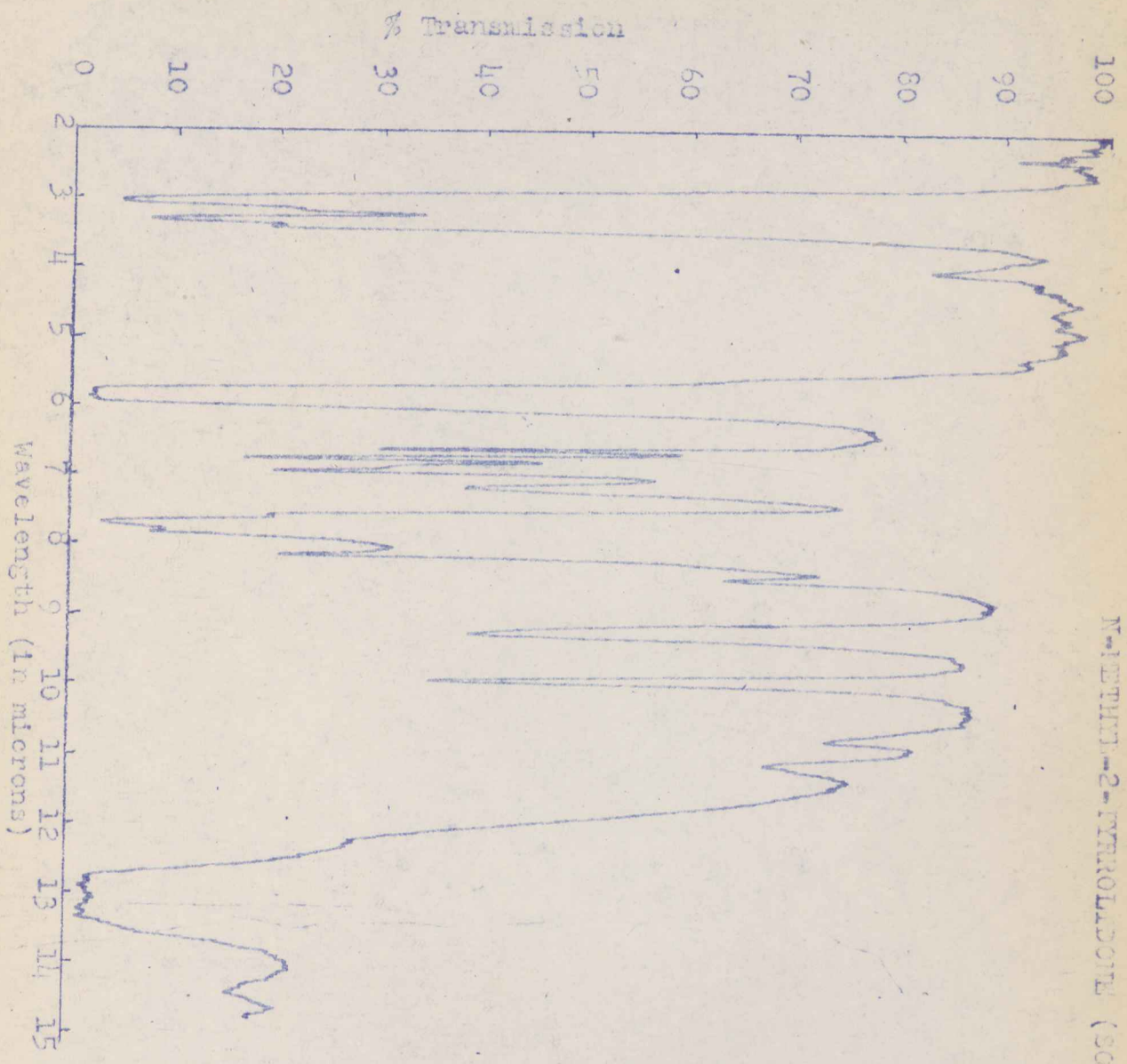| Solution Concentration (mole ratio)	Peak Height in Absorbance Units		Ratio of Peak Heights
	at 3.1μ	at 11.8μ	
neat	.092	.130	1.41
1-1	.045	.068	1.51
1-5	.080	.085	1.06
1-10	.110	.105	.95
1-20	.060	.070	1.17

Discounting the neat and the 1-1 mole ratio solutions, the values probably remain within experimental errors.

ω-pentalolactam had an absorption at 3.1μ. When this was compared with the 9.0μ absorption, the results shown in Table 6 were obtained.
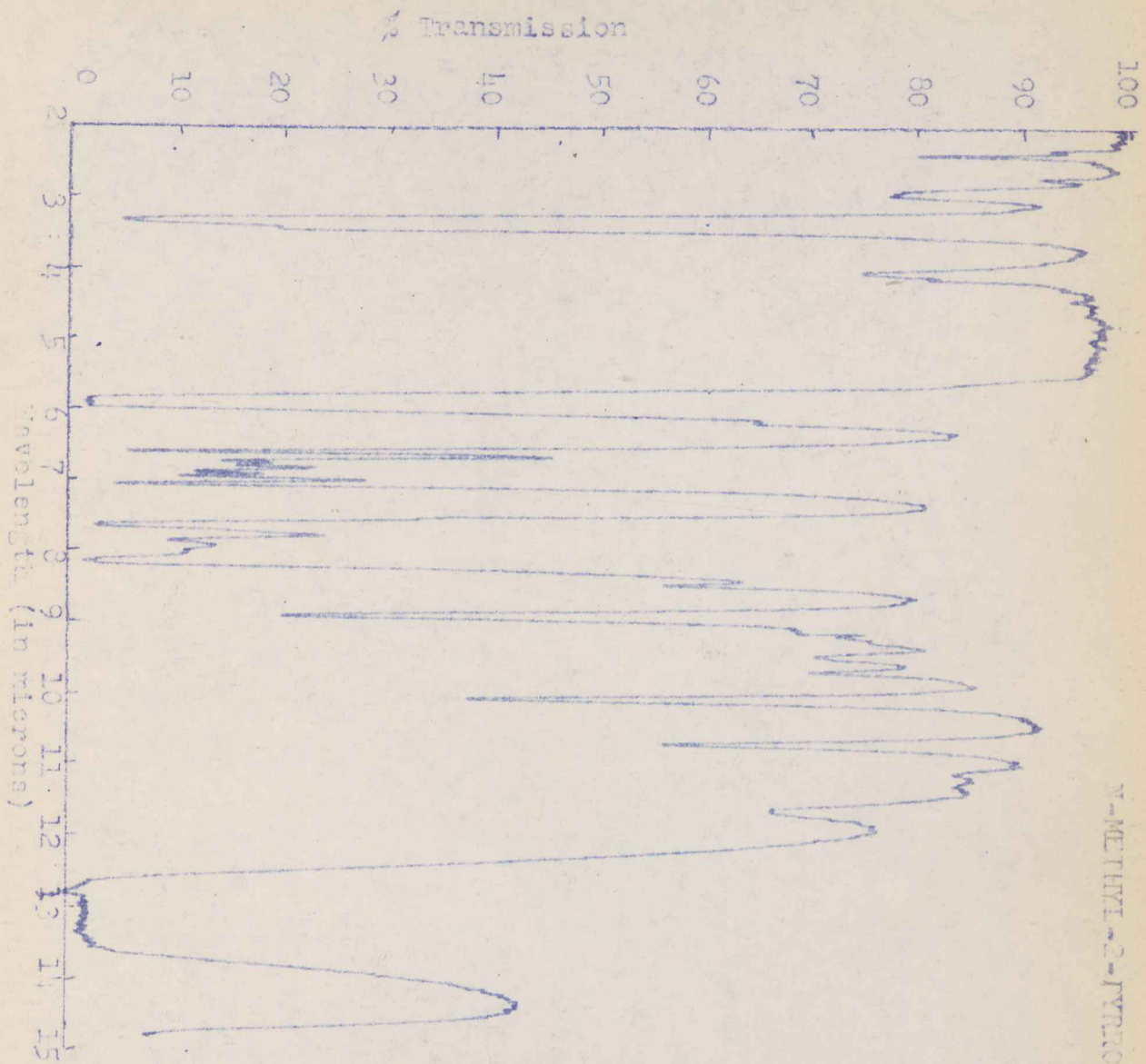
% Transmission

Wavelength (in microns)

N-METHYL-2-PYRROLIDONE (SOLUTION NEAT .025mm)

N-METHYL-2-PYRROLIDONE (SOLUTION V)

% Transmission

0 10 20 30 40 50 60 70 80 90 100

Wavelength (in microns)

2 3 4 5 6 7 8 9 10 11 12 13 14 15

N-METHYL-2-PYRROLIDONE (SOLUTION VI)

N-METHYL-2-PYRROLIDONE (SOLUTION VII)

% Transmission

100 90 80 70 60 50 40 30 20 10 0

Wavelength (in microns)
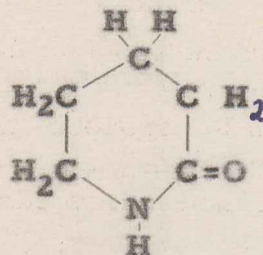
2 3 4 5 6 7 8 9 10 11 12 13 14 15
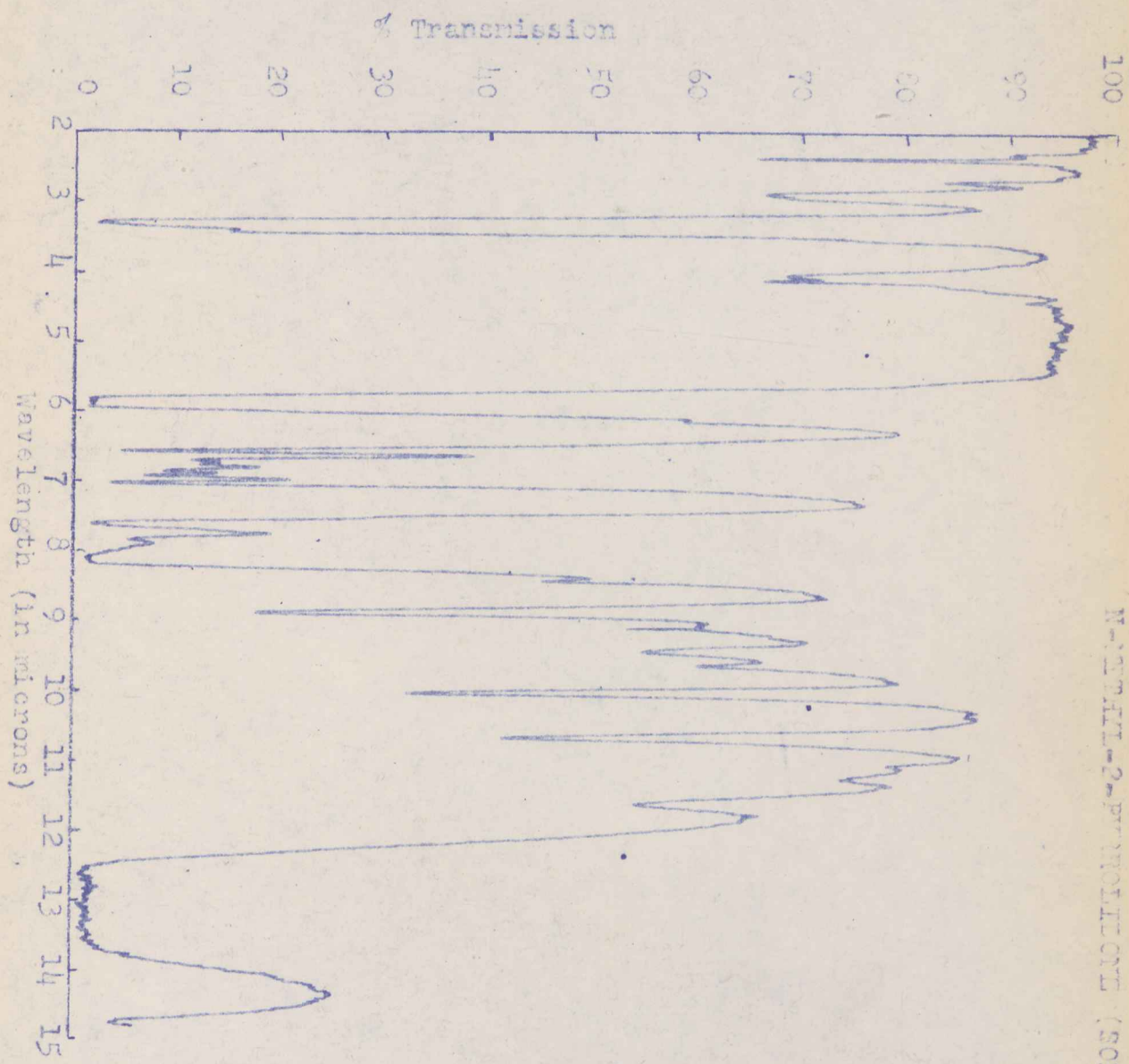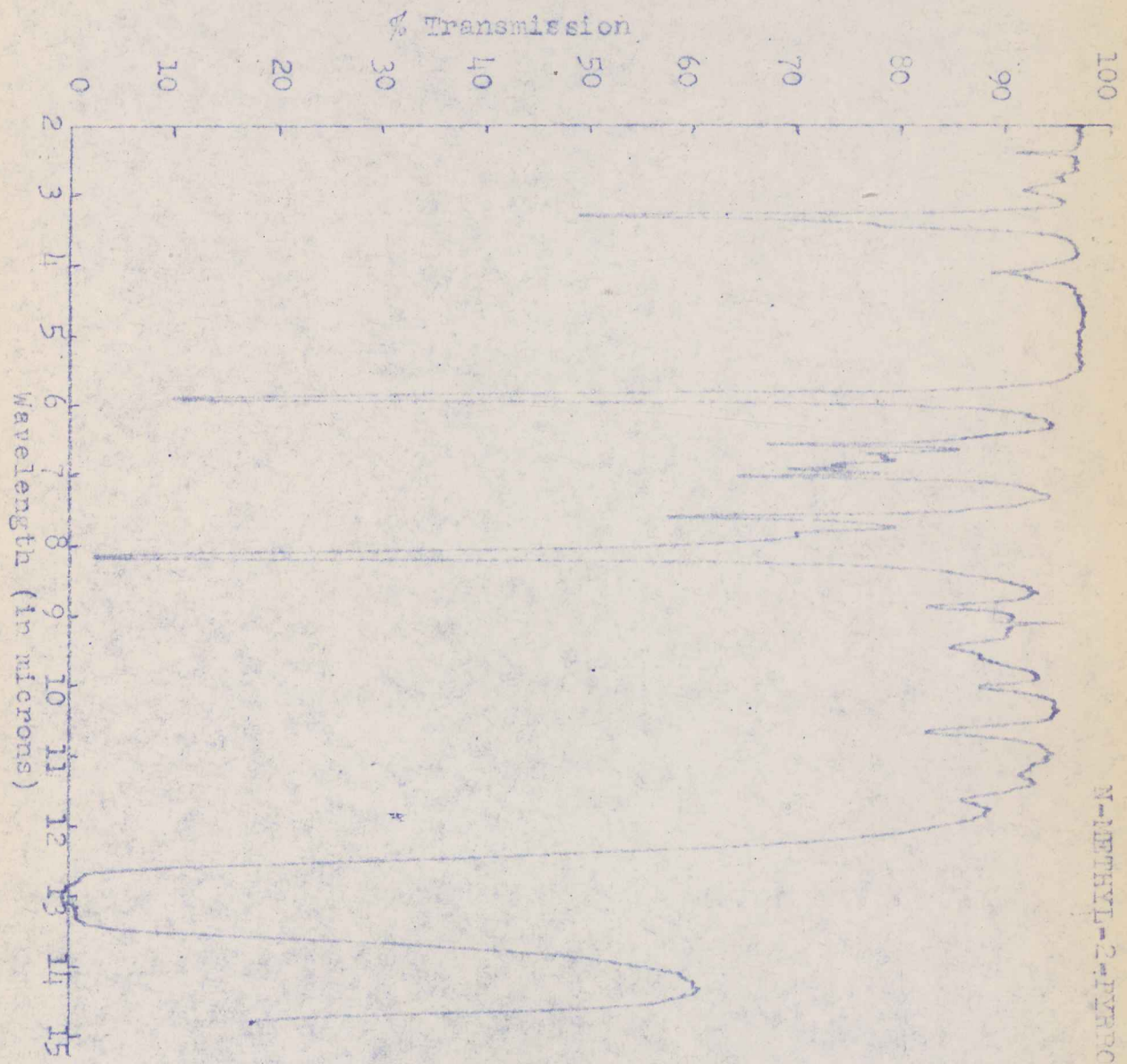
N-METHYL-2-PYRROLIDONE (SOLUTION VIII)

Table 6

Quantitative Study of Absorption at 3.1μ in ω-Pentanolactam
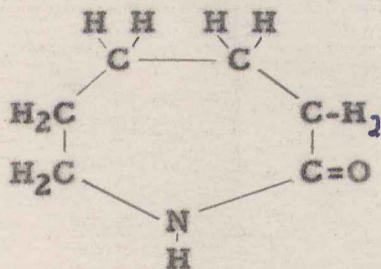Using Peak at 9.0μ as Reference Absorption

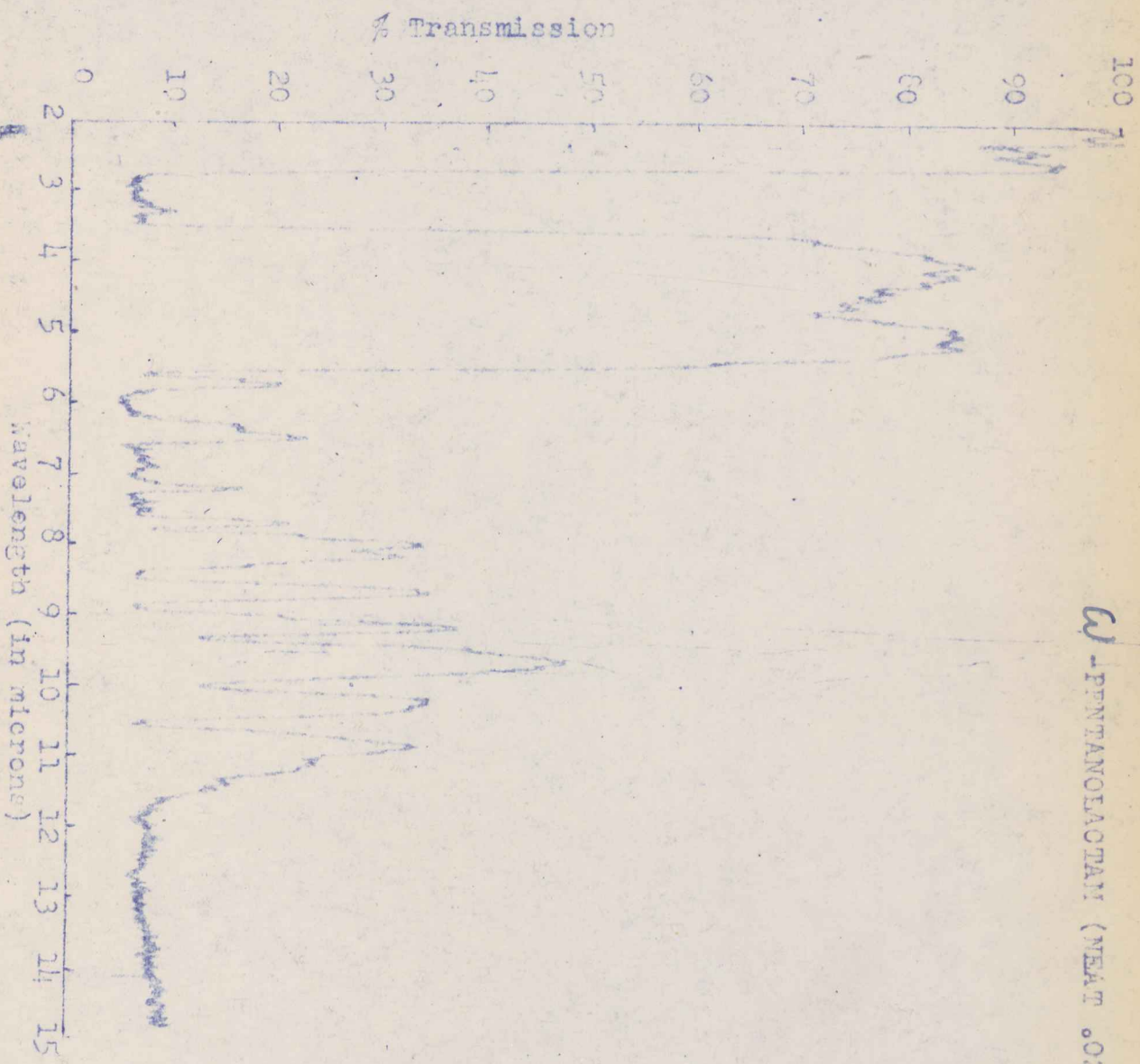| Solution Concentration (mole ratio)	Peak Height in Absorbance Units		Ratio of Peak Heights
	at 3.1μ	at 9.0μ	
neat	.353	.25	.71
1-1	.22	.74	.34
1-5	.15	.52	.35
1-10	.69	.29	.43
1-20	.31	.11	.37

The structure of ω-pentalolactam is:

With increasing dilution, the 3.1μ absorption became more important. The

3.1μ NH unbonded absorption increase showed that the hydrogen bonding

prevalent in concentrated solutions decreased on dilution as theory suggests,

but after 1:1 dilation remained essentially unchanged. There were some

unexplainable changes in the spectra of ω-pentalolactam. These were the

8.9μ shift to 9.04μ and the 10.69μ shift to 10.80μ on dilution; the 11.82μ
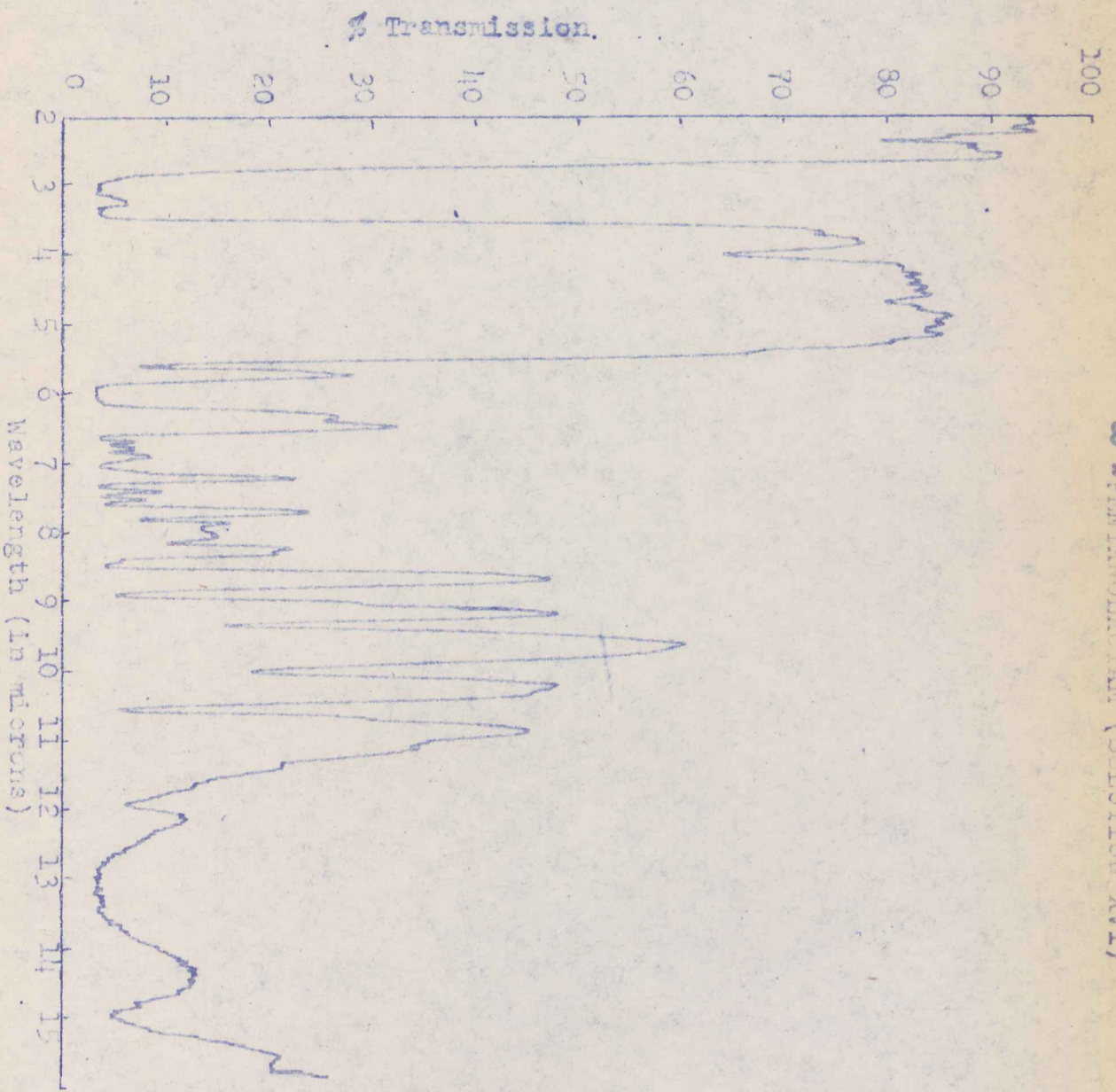
peak became relatively more intense on dilution.
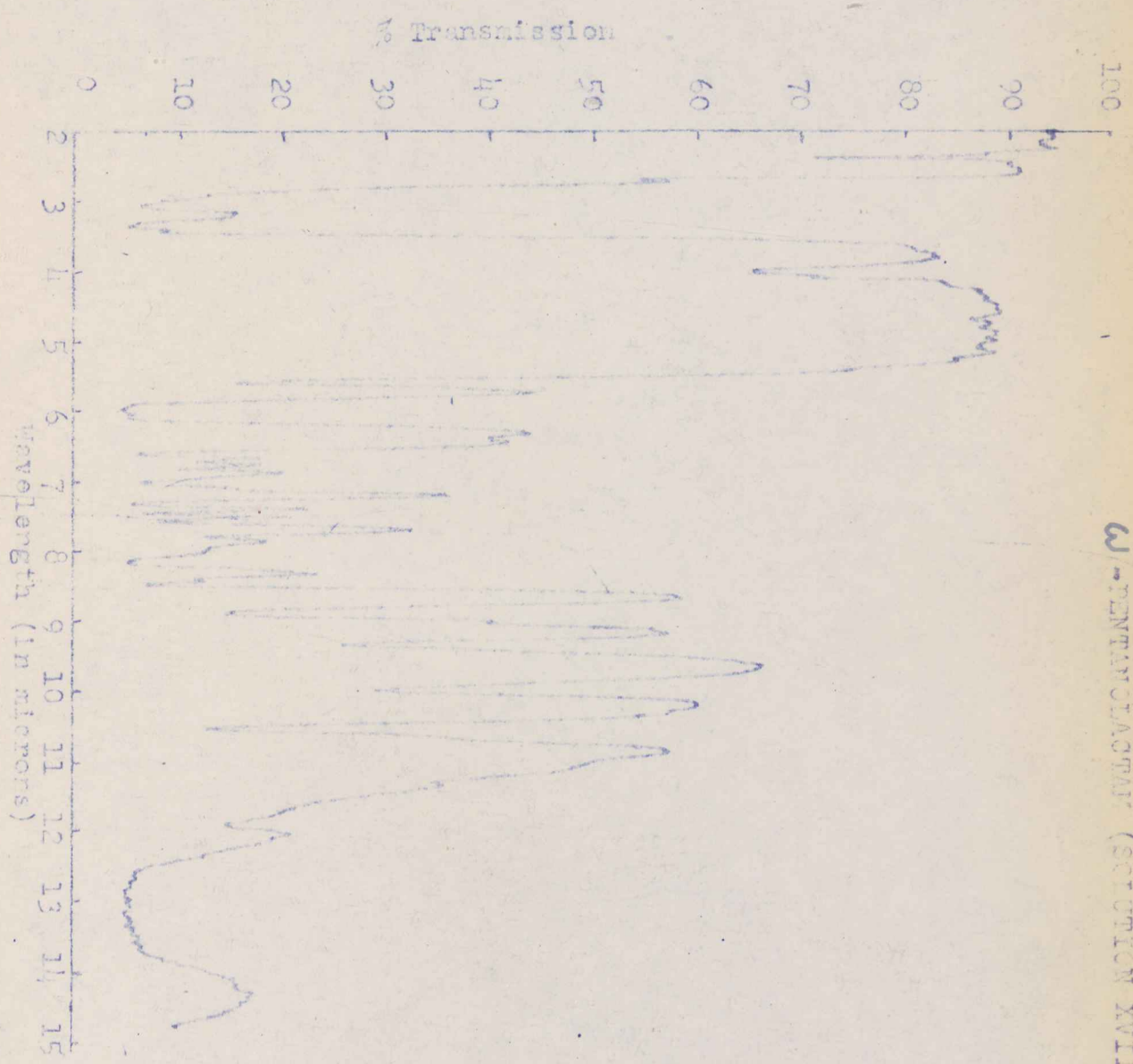
ω-hexanolactam has the following structure:

% Transmission

ω-PENTANOLACTAM (NEAT .025 mm)

Wavelength (in microns)

% Transmission.

ω - PENTANOLACTAM (SOLUTION XVI)

% Transmission

ω - PENTADECALACTONE (SOLUTION XVII)

ω - PENTANOLLACTAM (SOLUTION XVIII)

% Transmission

wavelength (in microns)

% Transmission

Wavelength (in microns)
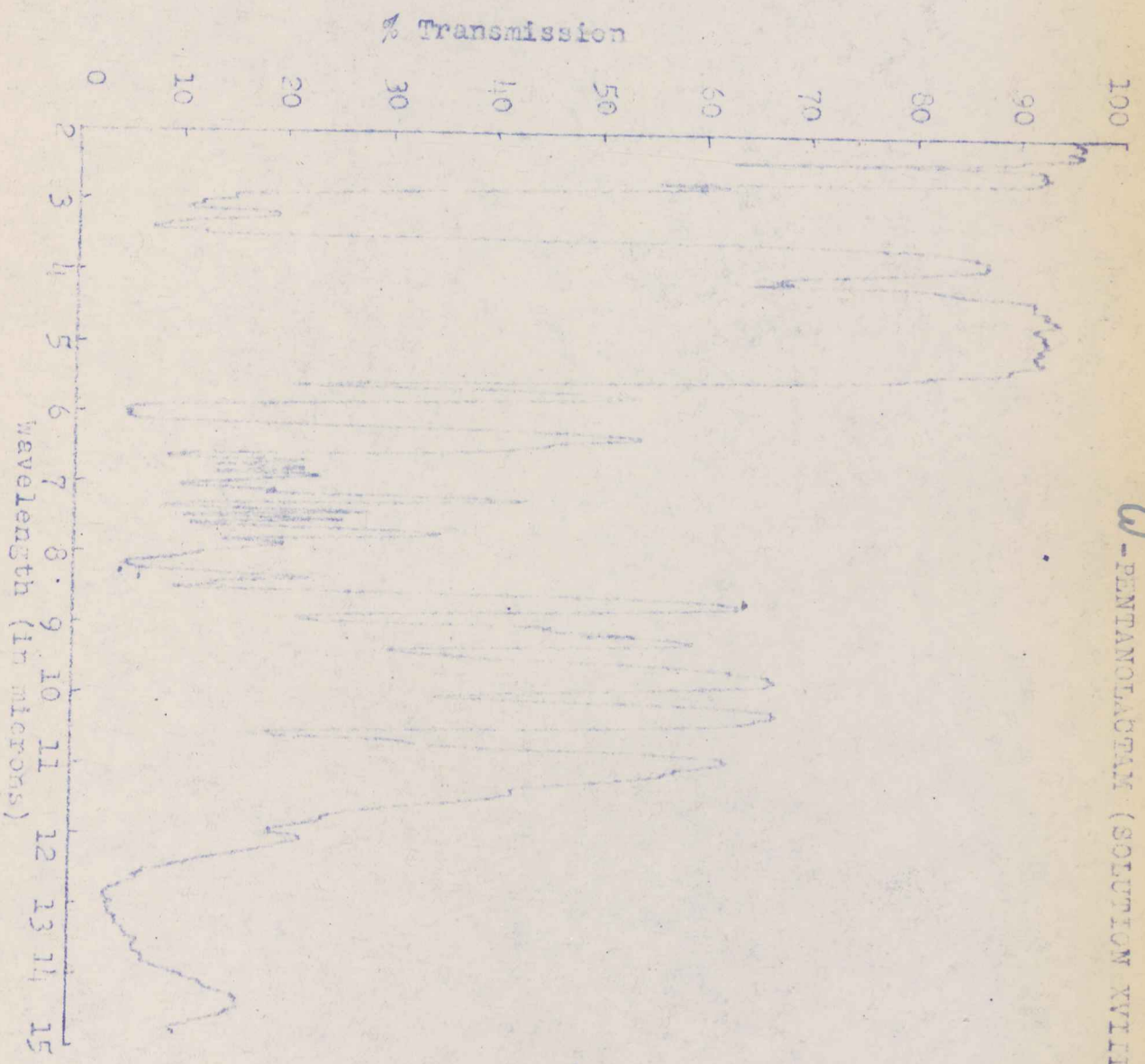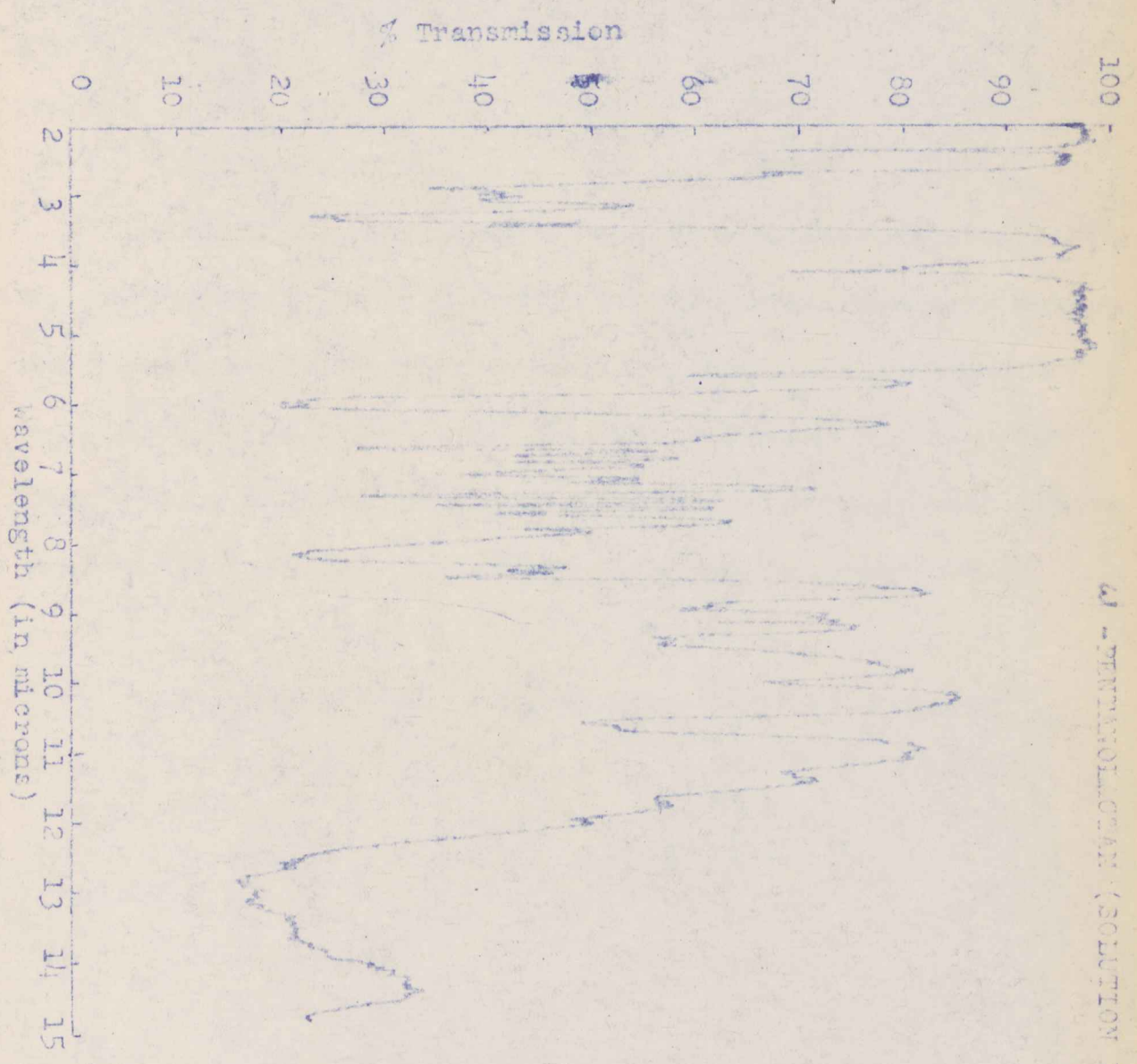
3 - THIOGLYCOLLANI (SOLUTION XIX)

Table 7 shows the quantitative changes in the absorption due to NH

bonding at 3.1μ.

Table 7

Quantitative Study of the ω-Hexanolactam 3.1μ
Absorption Using Peak at 10.2μ as Referance

Solution Concentration (mole ratio)	Peak Height in Absorbance Units		Ratio of Peak Heights
	at 3.1μ	at 10.2μ	
neat	.443	.348	.785
1-1	.810	.360	.445
1-10	.295	.143	.505
1-20	.152	.102	.670

As can be seen from Table 7, the ratio of the NH absorption peak

at 3.1μ to the base peak at 10.2μ was again increasing. This again meant

that the amount of NH bonding increased upon dilution. In the infrared

spectra of ω-Hexanolactam, there were many variations in intensity of

absorption for different wavelengths at the different concentrations. These

were all listed, together with their suggested raasons or explanations

in Table 8.

The 8-member ring of ω-heptanolactam was the last lactam
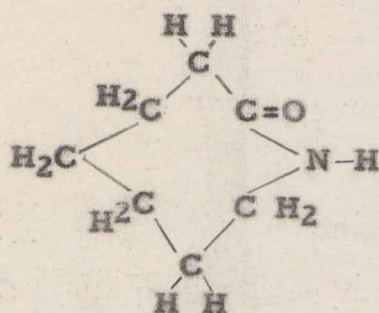
studied. It's structure is:

Table 8 shows the quantitative study of the NH bond at 3.1μ.

% Transmission

0 10 20 30 40 50 60 70 80 90 100

Wavelength (in microns)

2 3 4 5 6 7 8 9 10 11 12 13 14 15

ω-HEXANOLLACTAM (NEAT .025 mm)

ε-HEXANOLACTAM (SOLUTION VIII)

% Transmission
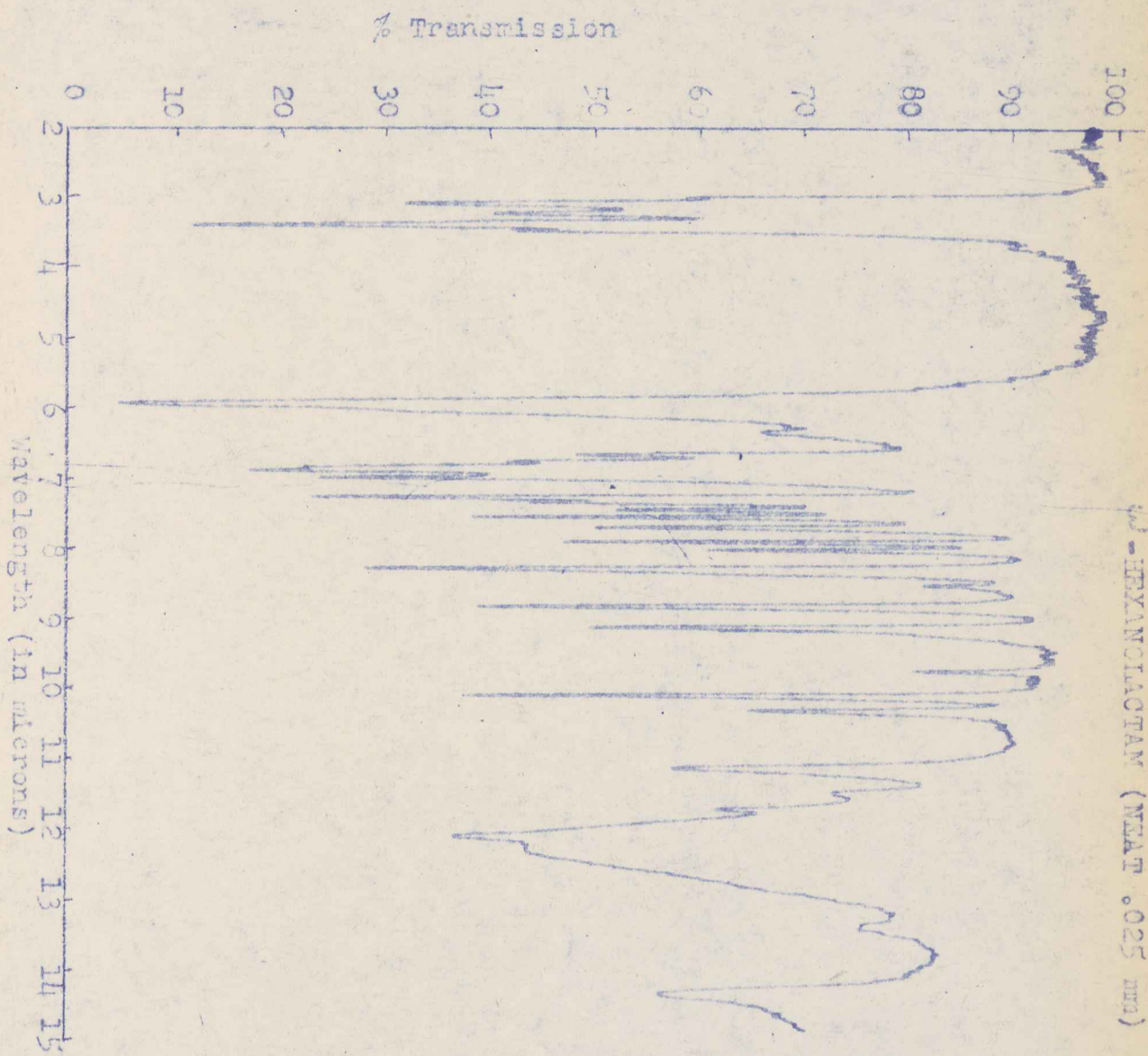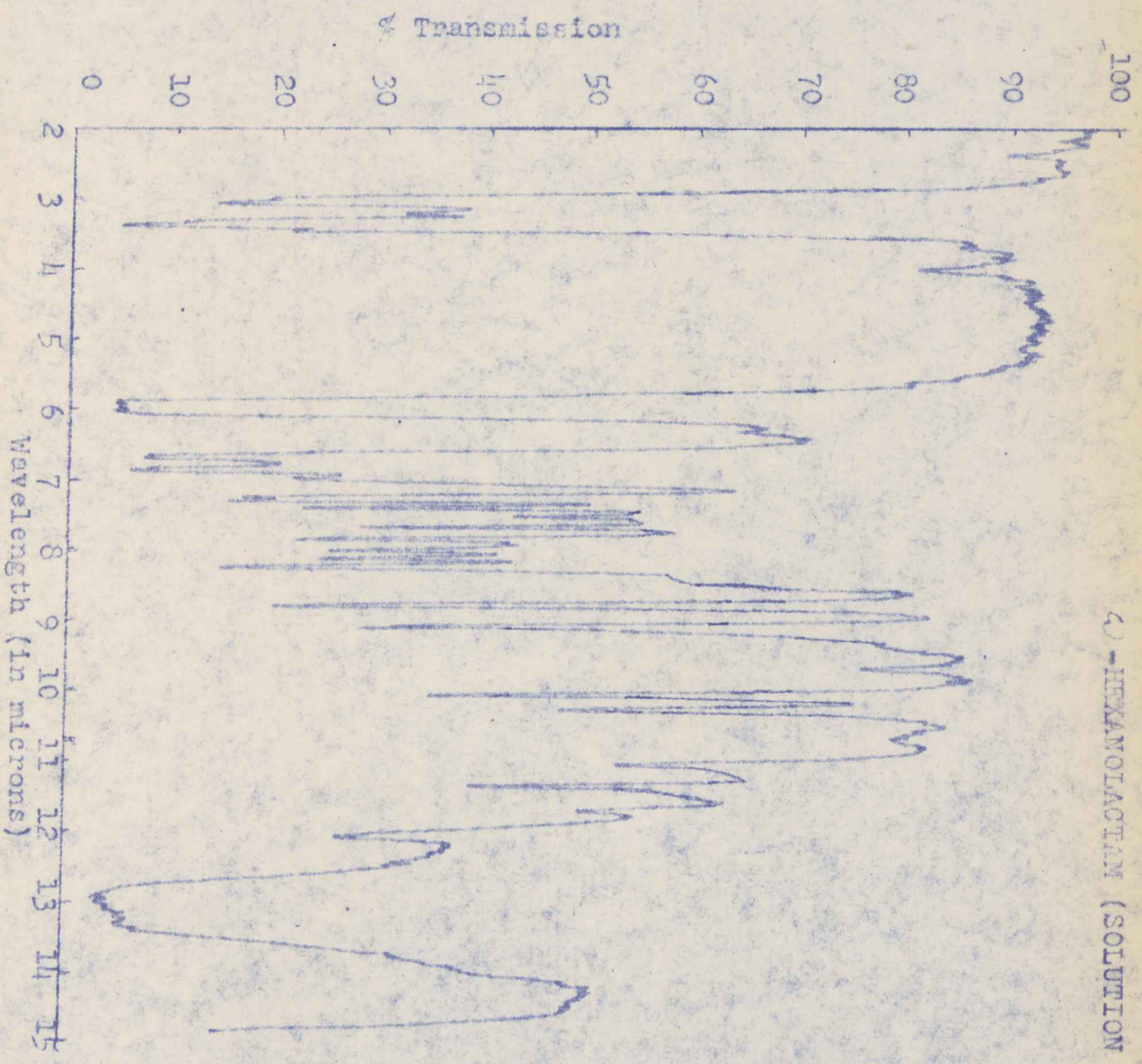
ω-HEXANOLACTAM (SOLUTION XIV)

Wavelength (in microns)
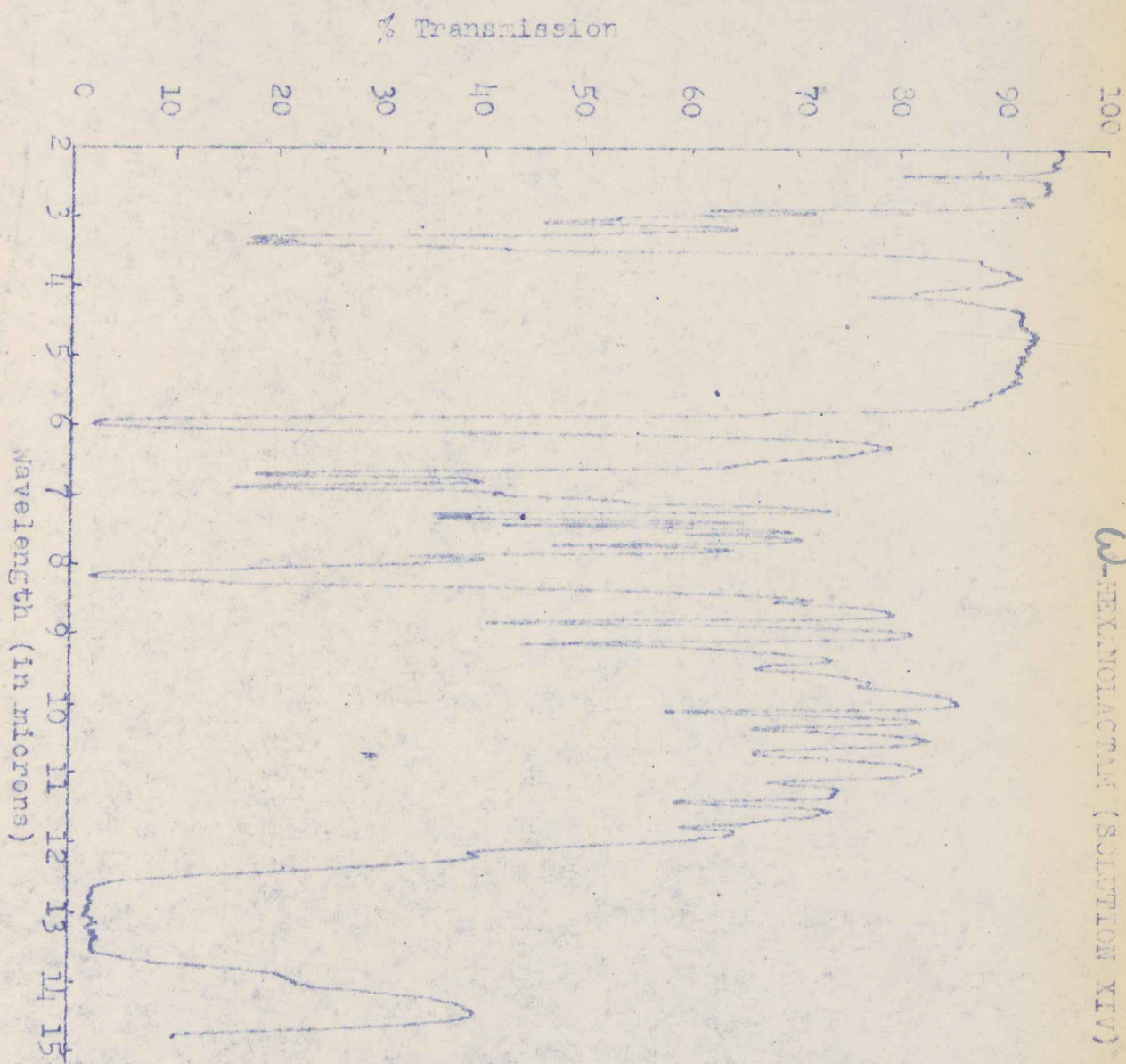
ω-HEXANOLACTAM (SOLUTION XV)

Table 8

Quantitative Study of ω-Heptanolactam at 3.1μ
With Peak at 10.05μ as Reference

Solution Concentration (mole ratio)	Peak Height in Absorbance Units		Ratio of Peak Heights
	at 3.1μ	at 10.05μ	
neat	.94	.28	.30
1-1	.70	.16	.23
1-5	.54	.14	.26
1-10	.43	.14	.34
1-20	.08	.04	.54

In the 6.0μ area of ω-heptanolactam, the carbonyl absorption bond had no shouldres and was located at 5.98μ. In the 1-20 mole ratio solution, 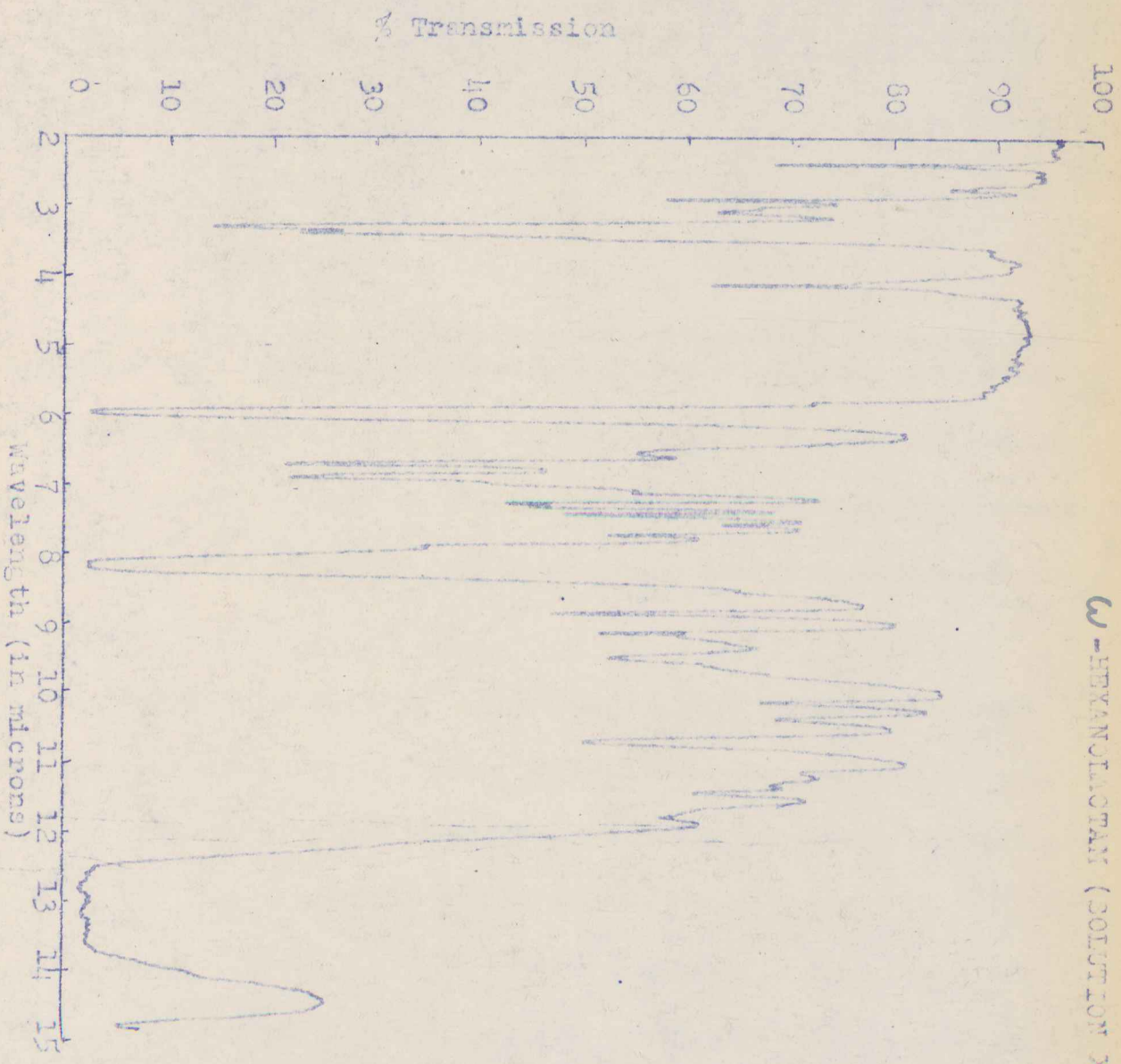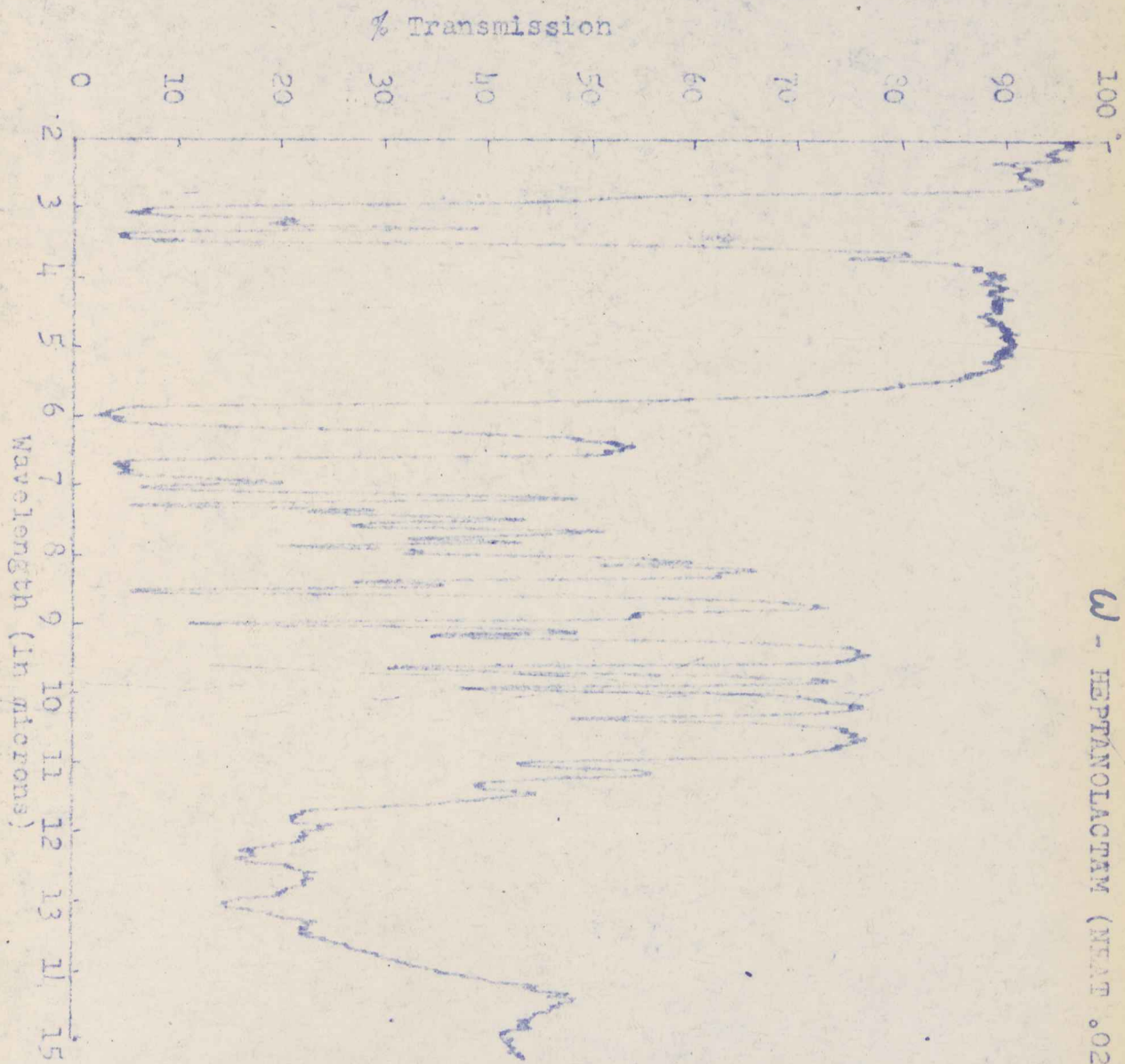a second bond appeared at 6.02μ, and the original 5.98μ bond was not as strong as before. This seemed to be a gradual building of another absorption peak near the original 5.98μ peak, with the loss of importance of the original peak.

Another peak appeared on dilution at 9.56μ. There was no peak in the neat solution, and as the dilution increased, the peak at 9.56μ appeared. This was probably due to OH absorption and suggests that on dilution the enol form of ω-heptanolactam becomes more important.

Table 9 gives a summary of either increasing, decreasing or shifting of absorption peaks in the lactams. The suggested reasons for this are also given.
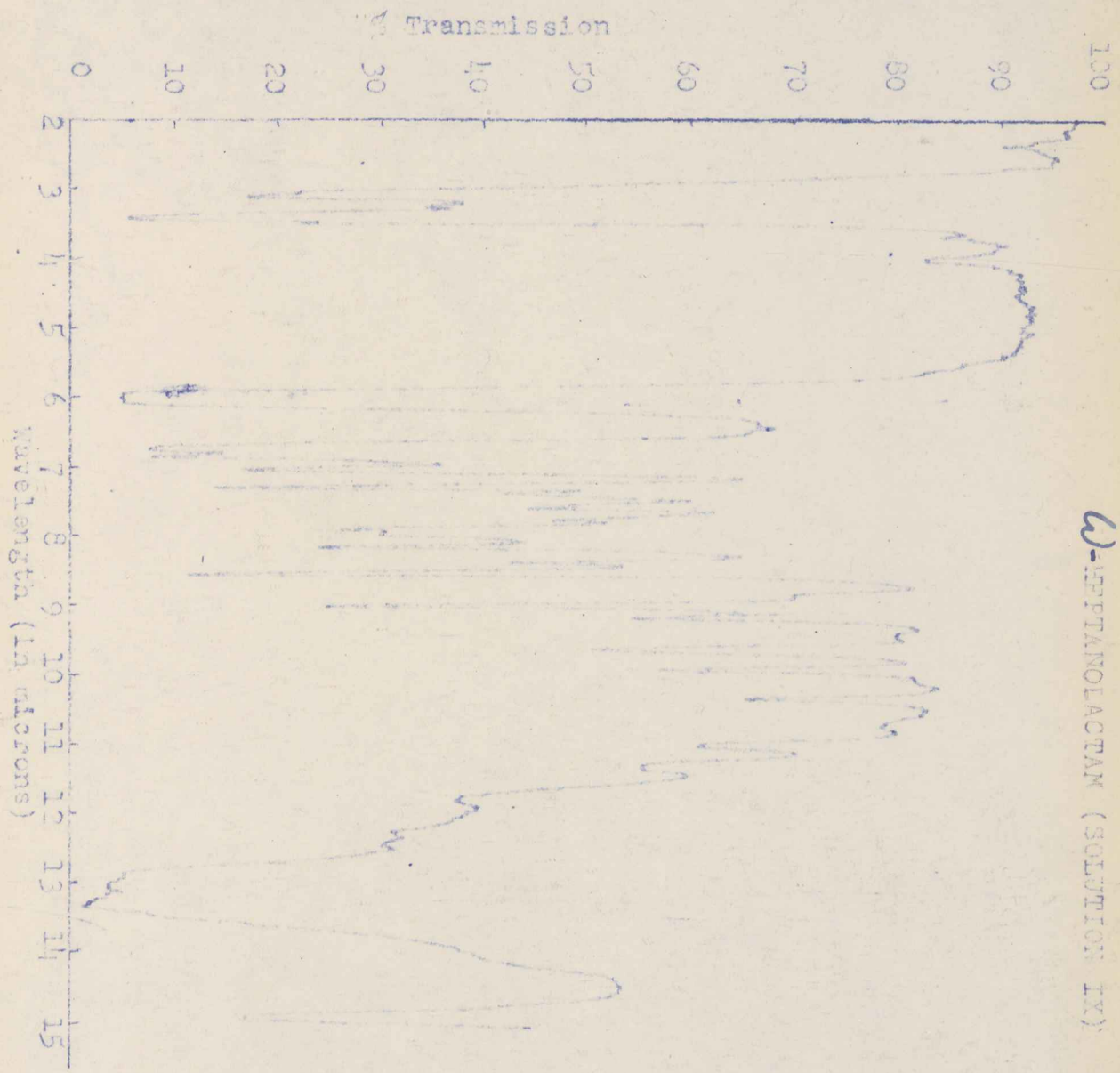
% Transmission

Wavelength (in microns)

ω - HEPTANOLACTAM (NEAT .025 mm)

ω-HEPTANOLACTAM (SOLUTION IX)

% Transmission

Wavelength (in microns)

% Transmission

Wavelength (in microns)

ω-HEPTANOLACTAM (SOLUTION X)

ω-HEPTANOLACTAM (SOLUTION XI)

% Transmission

Wavelength (in microns)
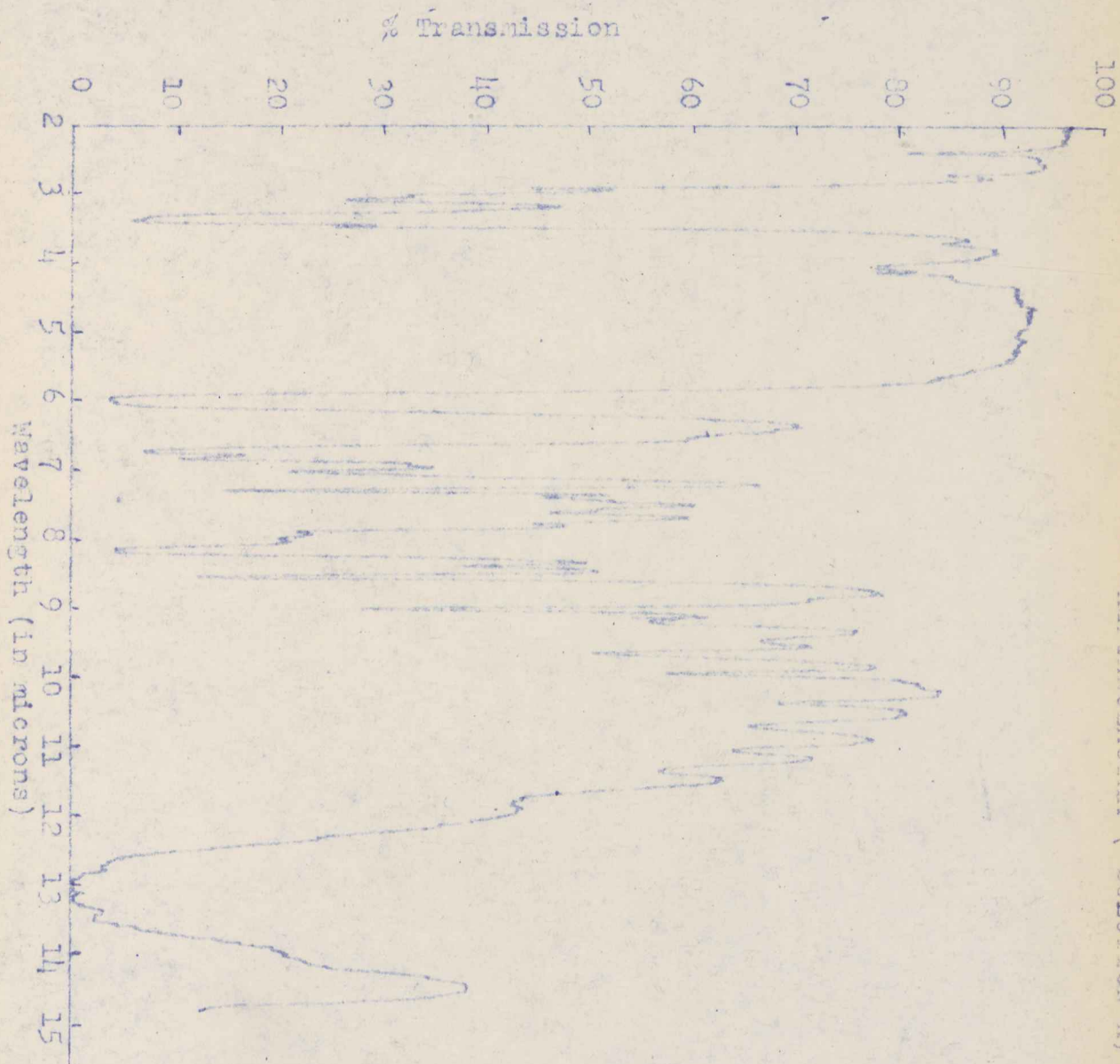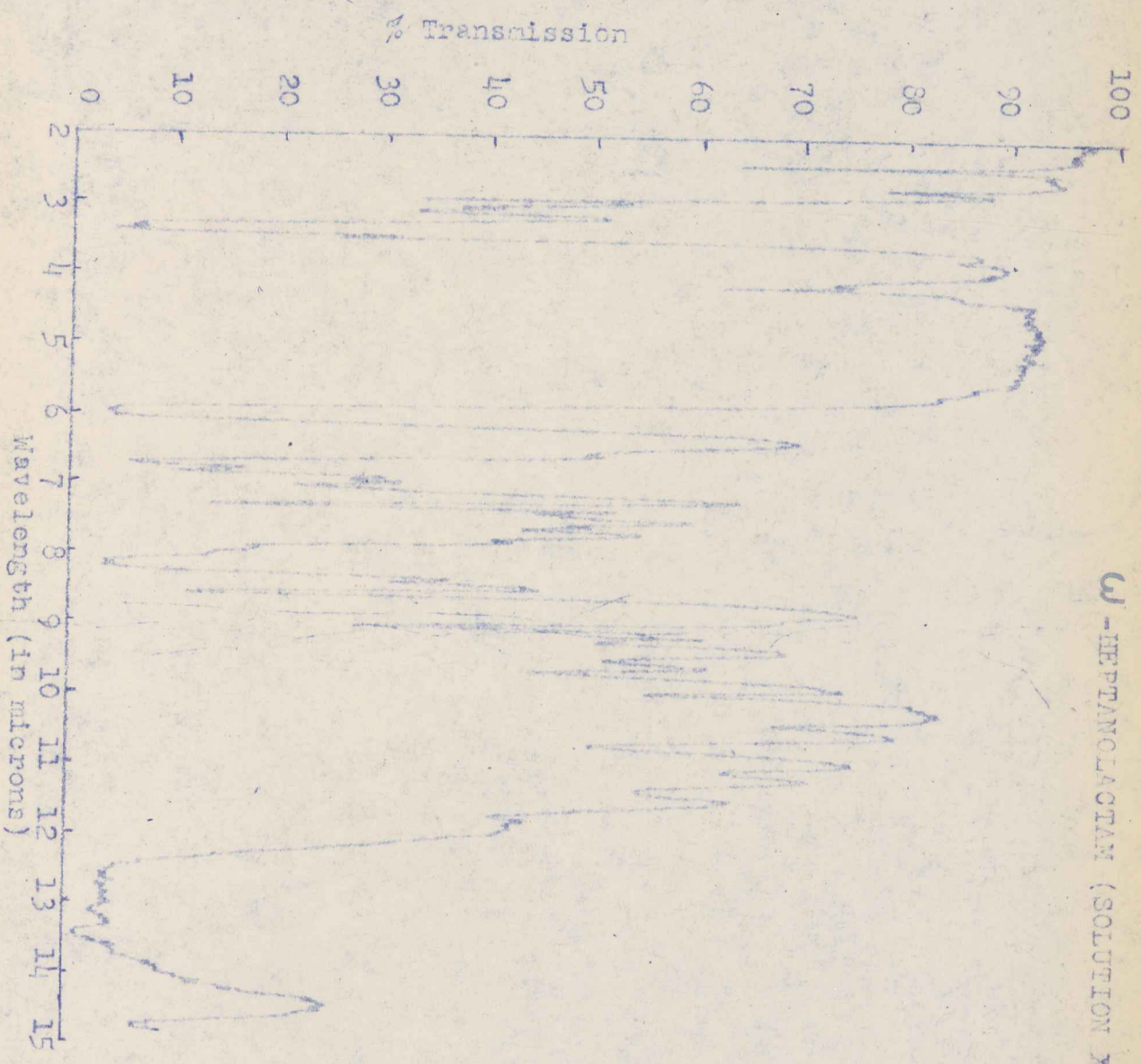
β-METHOXYLON- (SOLUTION XIII)
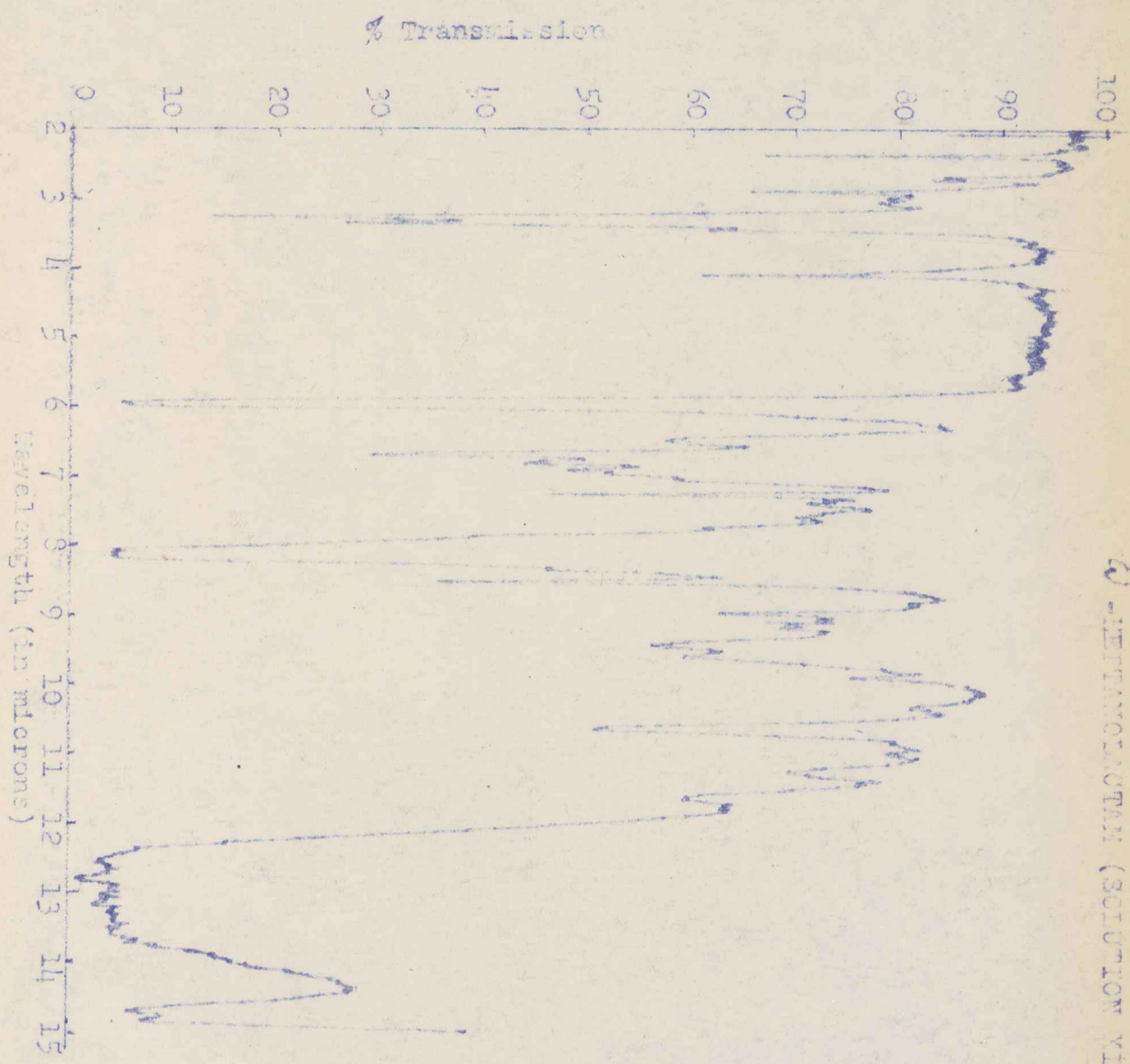
Table 9

Wave Length (μ)	Wave No. cm^{-1}	A	B	C	D	Suggested Reason
2.9	3454	x	x	x	x	NH (bonded & unbonded)
4.08	2451	x	x	x	x	uncertain
6.0	1666				x	large ring lactam
6.23	1602				x	NH bond, C=N
6.6	1516			x		C-N stretch
6.70	1492	x	x		x	uncertain
6.77	1476				x	uncertain
6.80	1471				x	C-H deformation
7.1	1408	x		x	x	C-H deformation
7.25	1380	x				text OH or carbonyl
7.37	1356				x	alcohols (enolic)
7.77	1270	x				alcohols (enolic)
8.49	1178		x		x	tert alcohol (enolic)
8.8	1136	x	x		x	tert alcohol (enolic)
9.5	1052	x	x		x	uncertain
10.69	935		x			uncertain
11.82	846		x			uncertain
12.25	815			x		c=c

A - Pyrrolidone
B - ω-Pentanolactam
C - ω-Hexanolactam
D - ω-Heptanolactam

Section C

The polarizing unit, set at 0° had an absorbance of optical density of

.4 plus or minus a little at all wavelengths except between 2μ and 3.5μ and

between 12.5μ and 15μ where it changed in both cases to .6. The polarizer,

set at 45° rotation, produced a line parallel to the 0° line but having an

% Transmission

Wavelength (in microns)

CHLOROACETIC ACID (CRYSTAL)

% Transmission

0   10   20   30   40   50   60   70   80   90   100

2   3   4   5   6   7   8   9   10   11   12   13   14   15

Wavelength (in microns)

POLARIZING UNIT ALONG 0° ROTATION

% Transmission

100 90 80 70 60 50 40 30 20 10 0

2 3 4 5 6 7 8 9 10 11 12 13 14 15

Wavelength (in microns)

POLARIZING UNIT ALONE 45° ROTATION

% Transmission

POLARIZING AZONE 90° ROTATION

Wavelength (in microns)
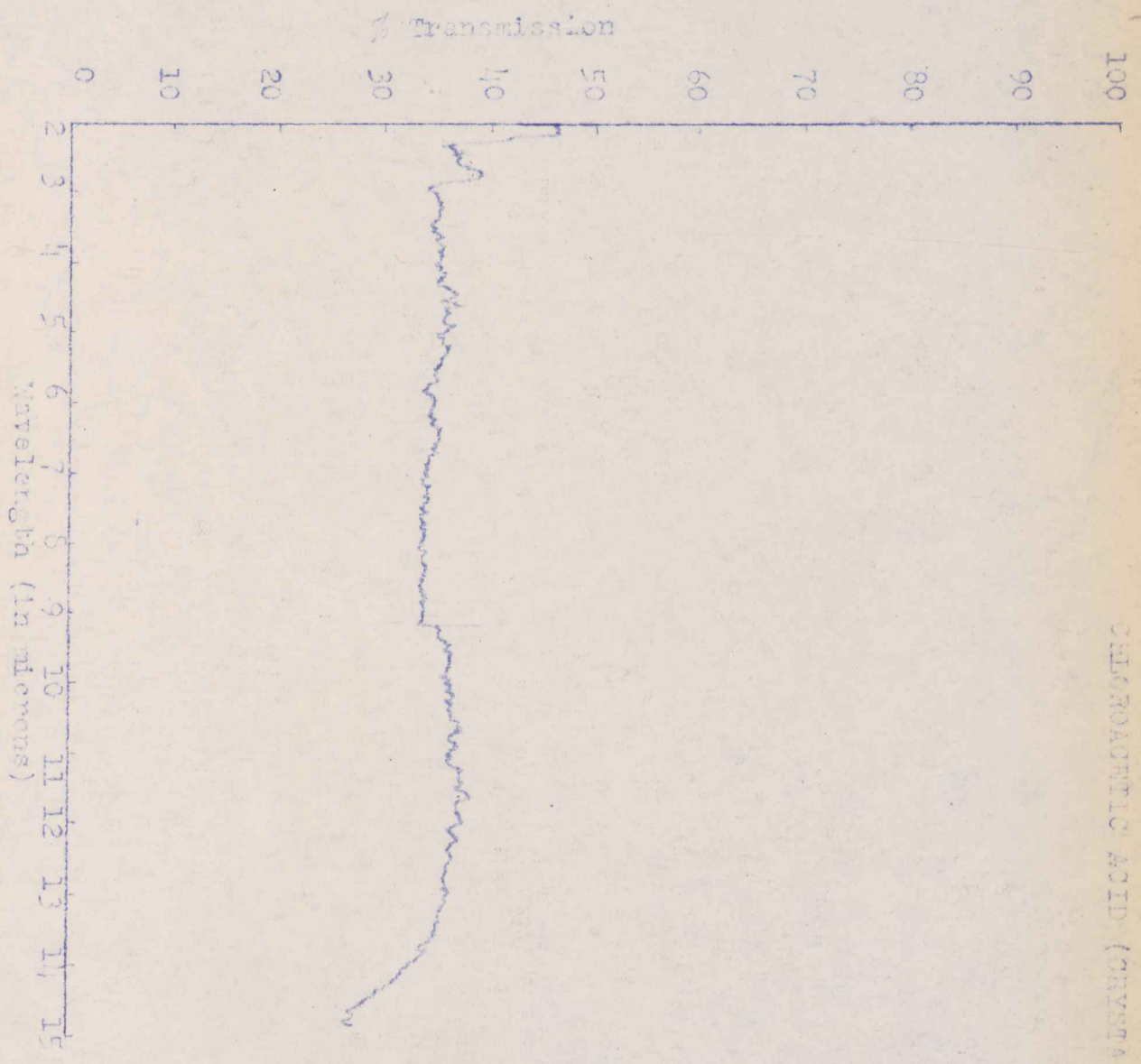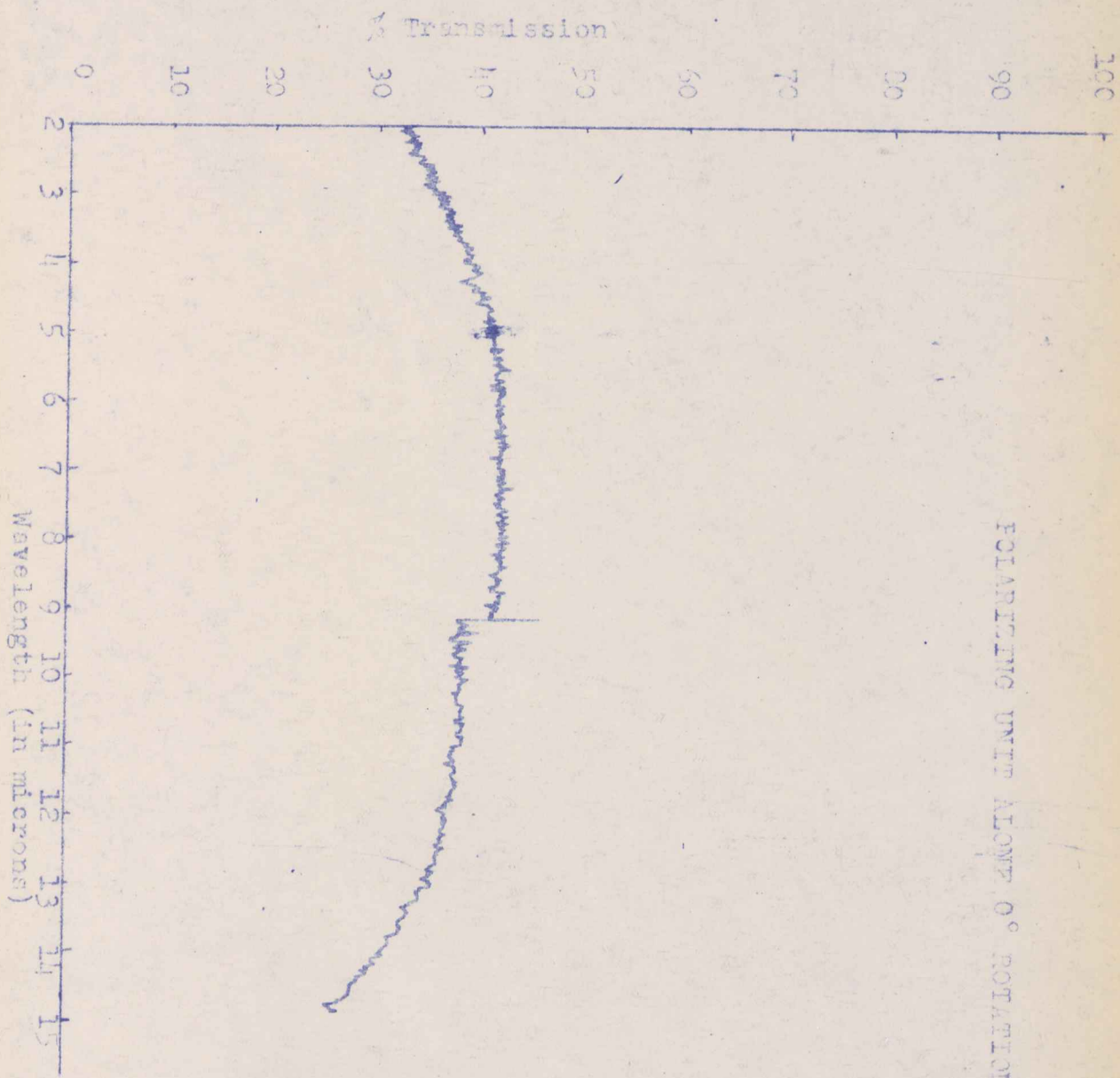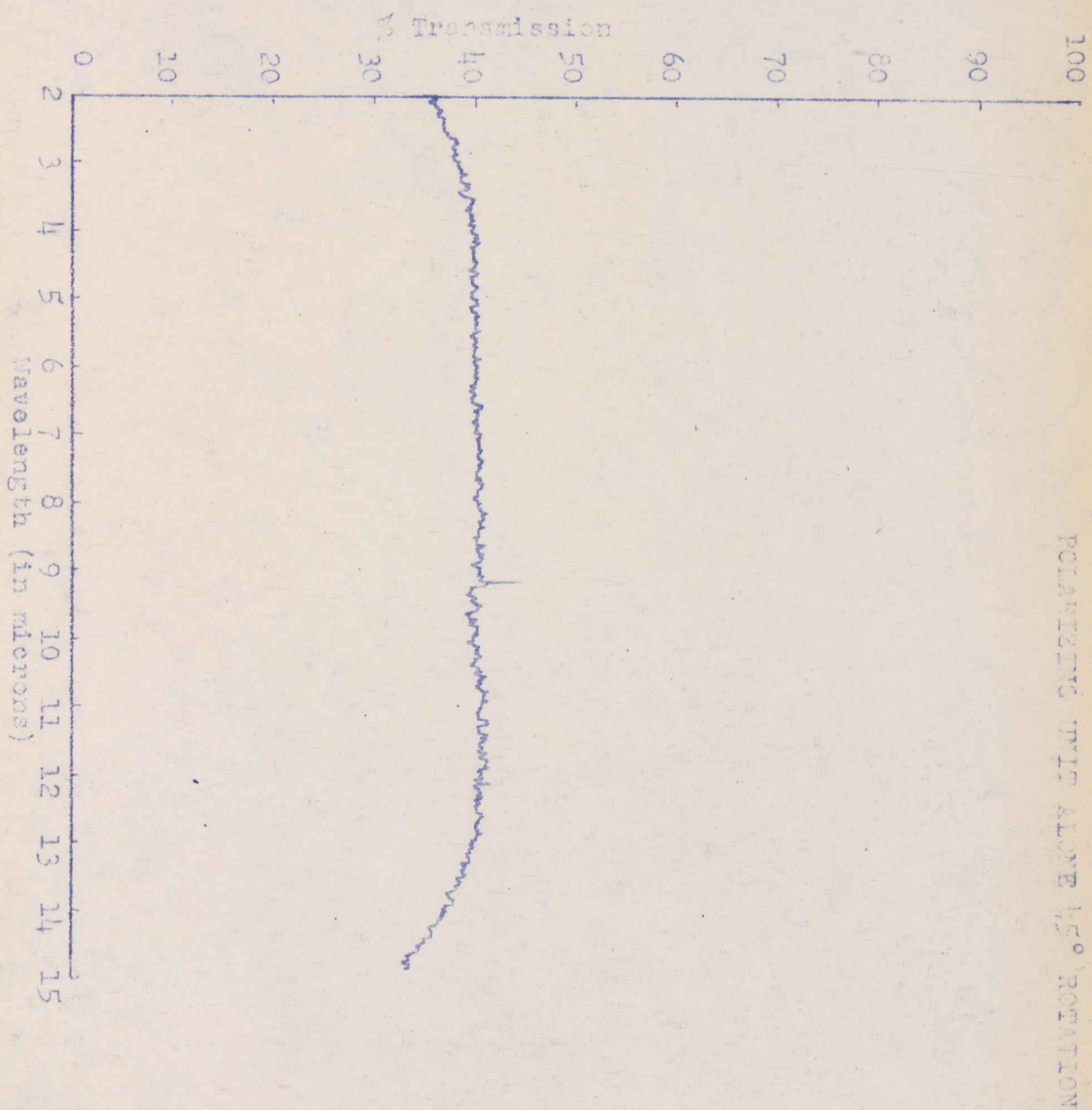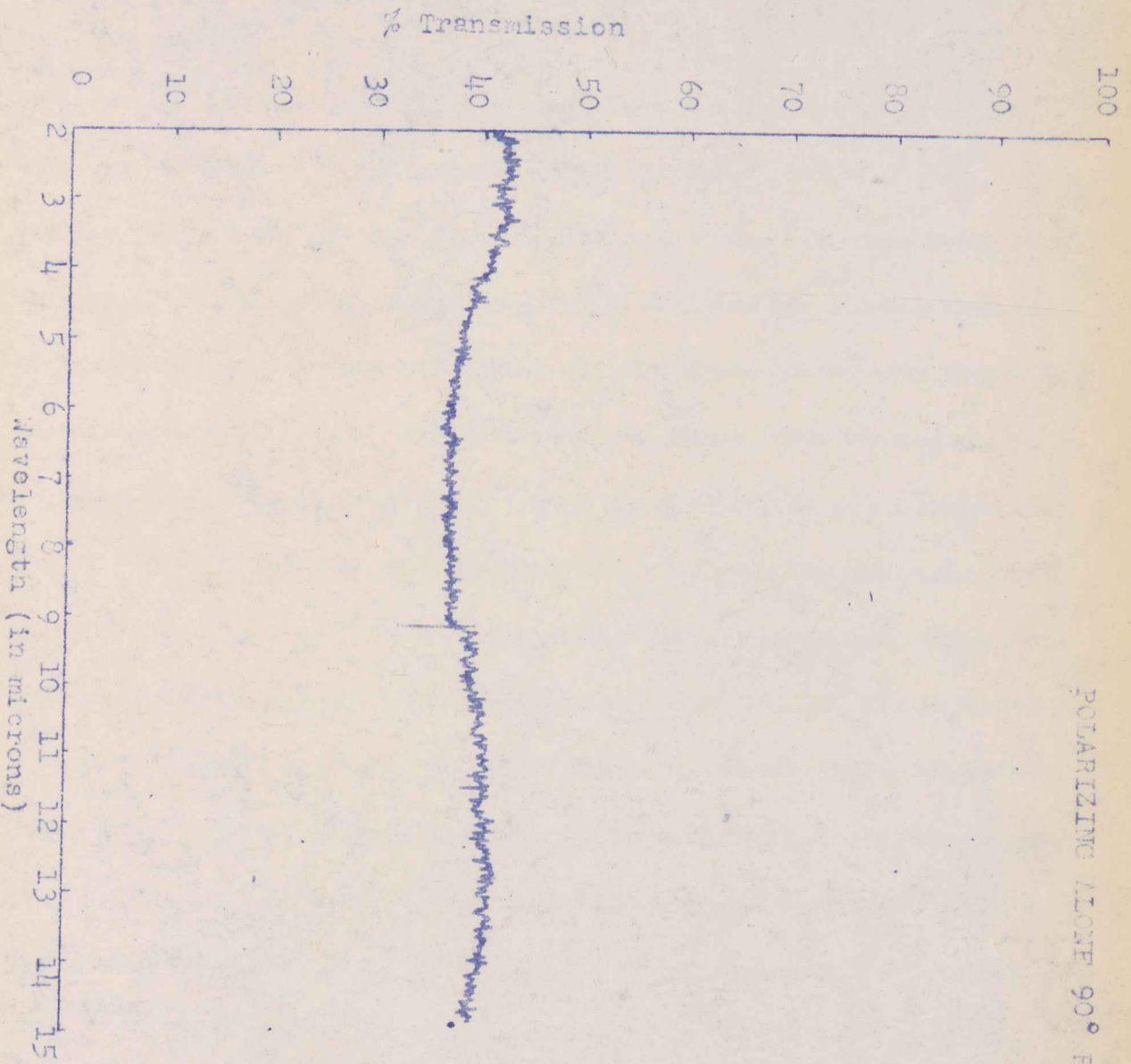
optical density of about .1 absorbance units less. At 90° rotation, the polarizer had an optical density of .37. This was fairly constant over all wavelengths. Between 4.5μ and 9.1μ the instrument shows some internal polarization of optics as evidenced by the cross over of the absorption lines.

The absorption graphs are given for cis-stilbene-α, β, -diol-diacetate with the plane of polarized light rotated 0°, 45° and 90°. The graph of the cis-stilbene-α, β, diol-diacetate without the polarizing unit was also included for comparison. Table 10 shows the variations in the absorption curves for cis-stilbene-α, β, diol-diacetate in comparison to the absorption curves for the polarizing unit alone. The strongest absorption peaks were noted together with the comparison of the absorption peak for the 0°, 45° and 90° plane rotation with what the polarizer itself absorbed as shown in the absorption curves for the polarizing unit alone. If a zero appears for the peak at a given angle of rotation, the absorption line is in the same respective position as in the standard and, therefore, there has been no change on rotating the incident light. The zero degree line was taken as a reference line and, therefore, it always had a zero. If the absorption line for the rotated light was higher or above where they were in the standard run (the polarizer alone), in other words the absorption was less, a plus sign was assigned. If the absorption were greater, or the absorption line were below where the corresponding line for the same degree of rotation of light by polarizer in the reference curves, a minus sign was noted.

Table 10

Cis-Stilbene-α, β, Diol Diacetate

Wavelength (in microns)	Degree of Rotation of Incident Light		
	0°	45°	90°
3.3	0	0	0
5.6	0	0	0
6.7	0	0	0
7.35	0	00	0
9.6	0	-	-
10.8	0	-	-
11.45	0	-	-

Table 11

Trans-Stilbene-α, β, Diol Diacetate

Wavelength (in microns)	Degree of Rotation of Incident Light		
	0°	45°	90°
5.7	0	-	0
6.25	0	0	0
6.35	0	-	0
6.7	0	0	+
7.3	0	-	0
11.45	0	0	0
11.85	0	0	0
12.60	0	0	0
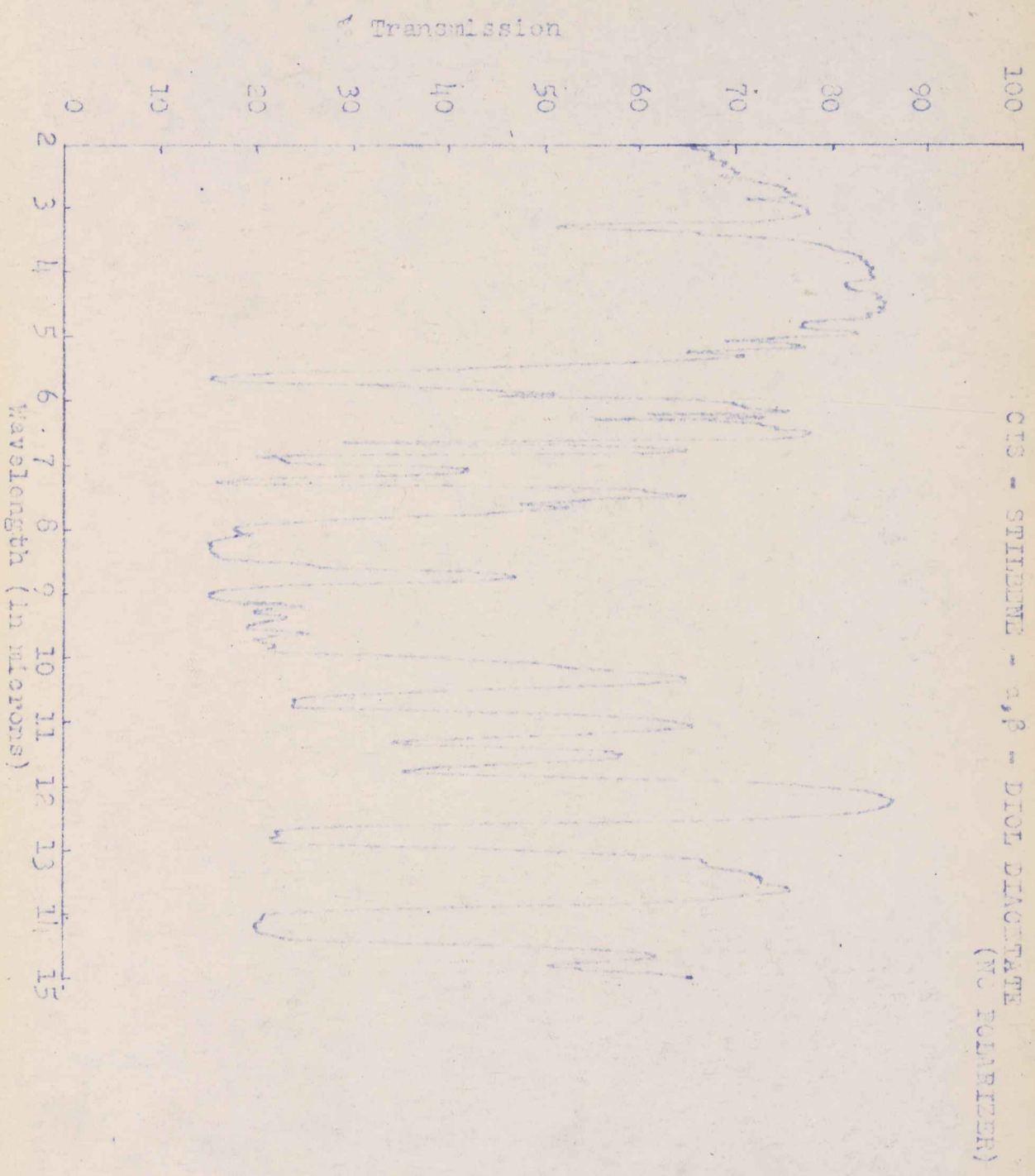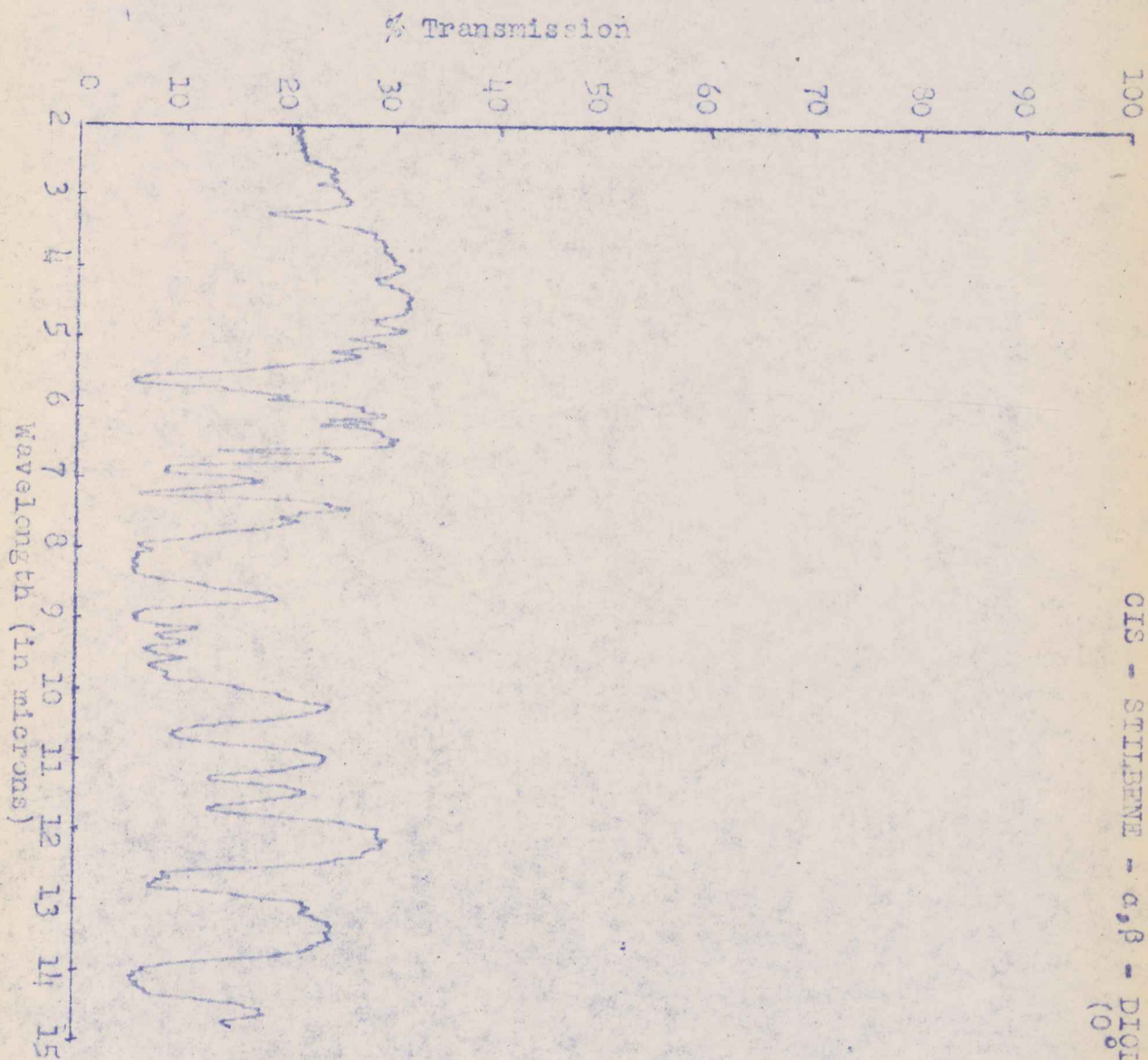
% Transmission

CTS - STILBENE - α,β - DIOL DIACETATE (NO POLARIZER)

Wavelength (in microns)

% Transmission — Wavelength (in microns)

CIS - STILBENE - α,β - DIOL DIACETATE (0° ROTATION)

51

% Transmission

CIS - STILBENE - α,β - DIOL DIACETATE
(45° ROTATION)

CIS - STILBENE - α,β - DIOL DIACETATE
(90° ROTATION)

% Transmission

% Transmission

100 90 80 70 60 50 40 30 20 10 0

TRANS - STILBENE - ,B - DIYL DIACETATE
(0° ROTATION)

Wavelength (in microns)

2 3 4 5 6 7 8 9 10 11 12 13 14 15
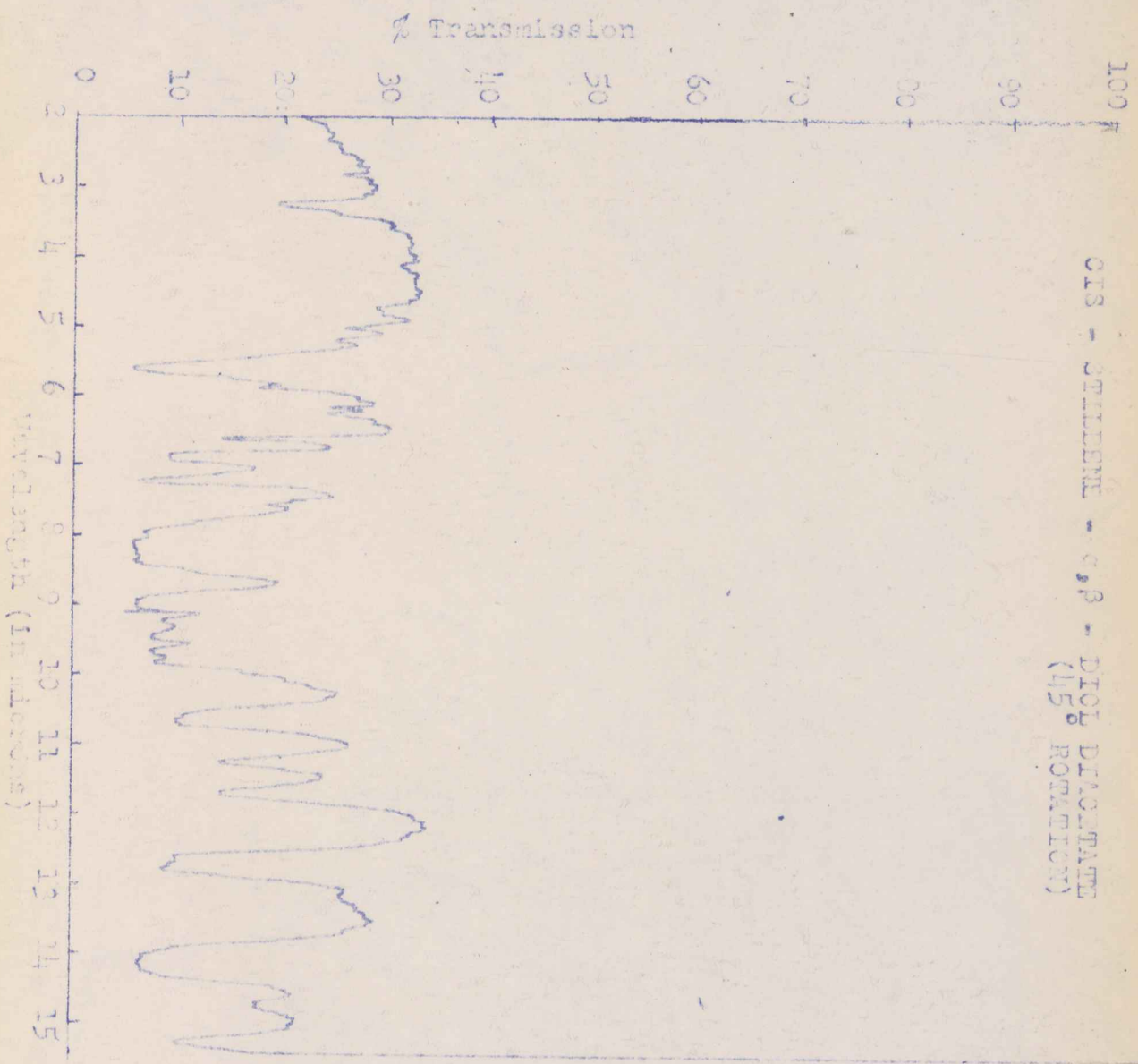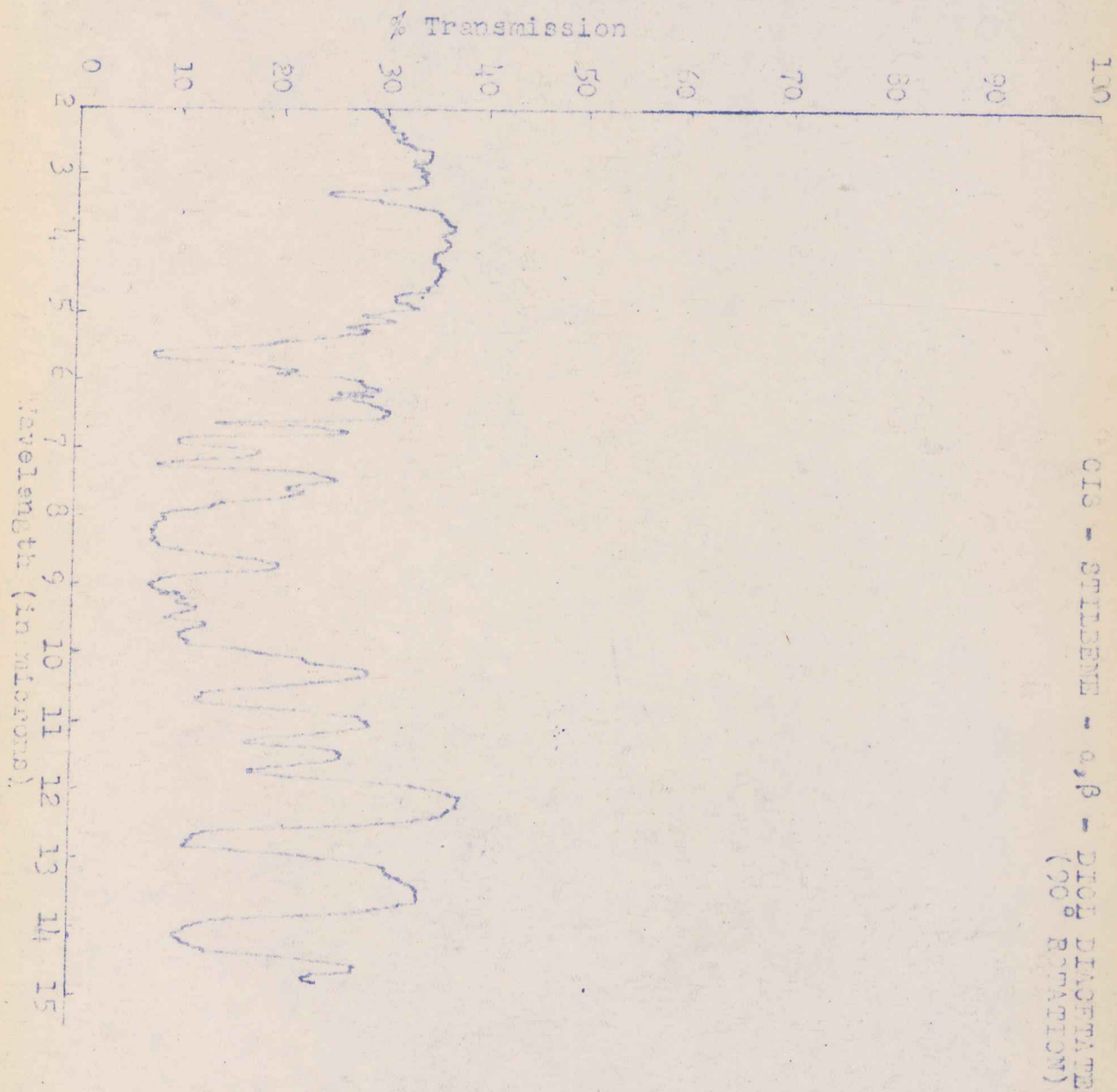
TRANS - STILBENE - α,β - DIOL DIACETATE
(45° ROTATION)
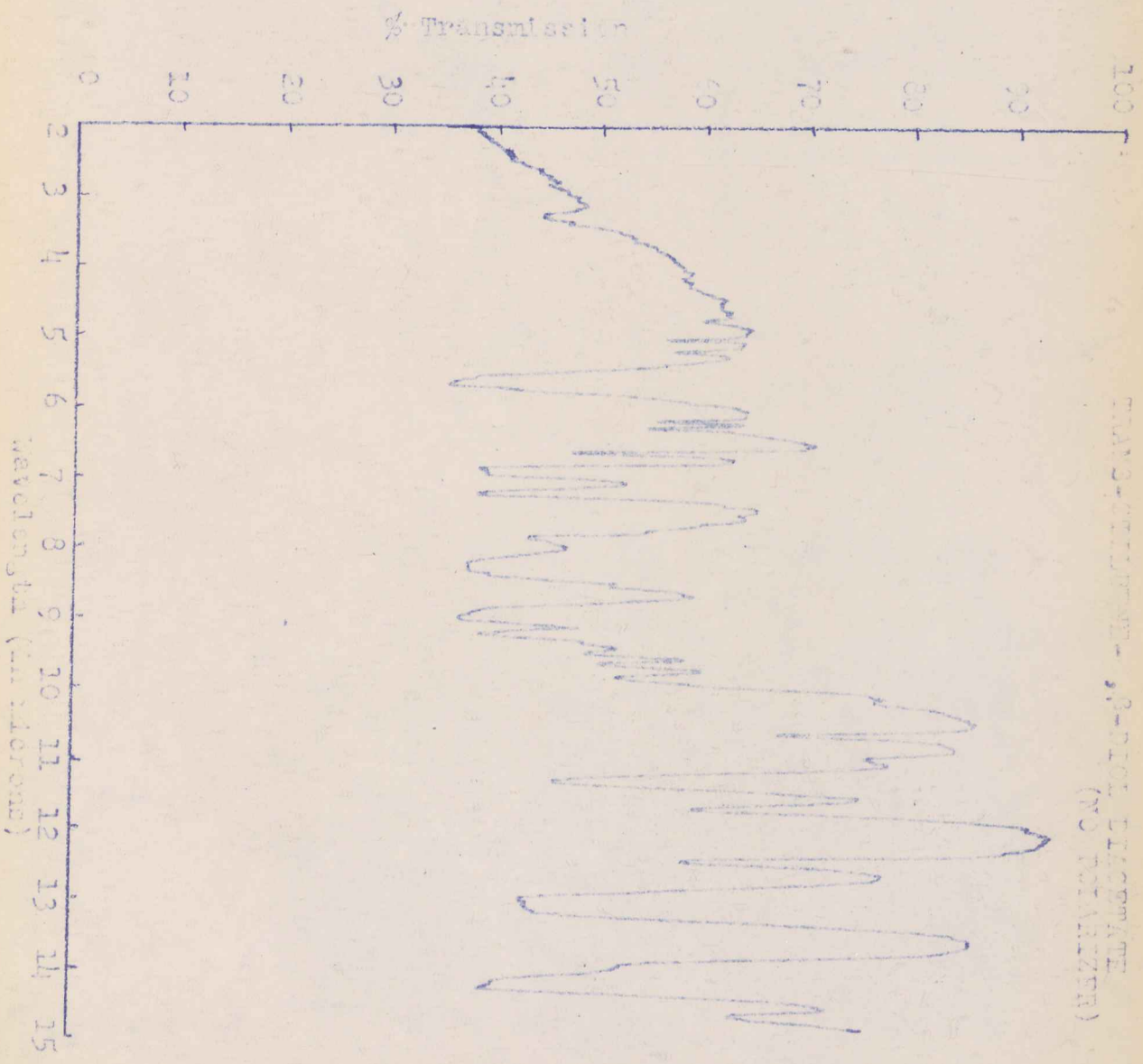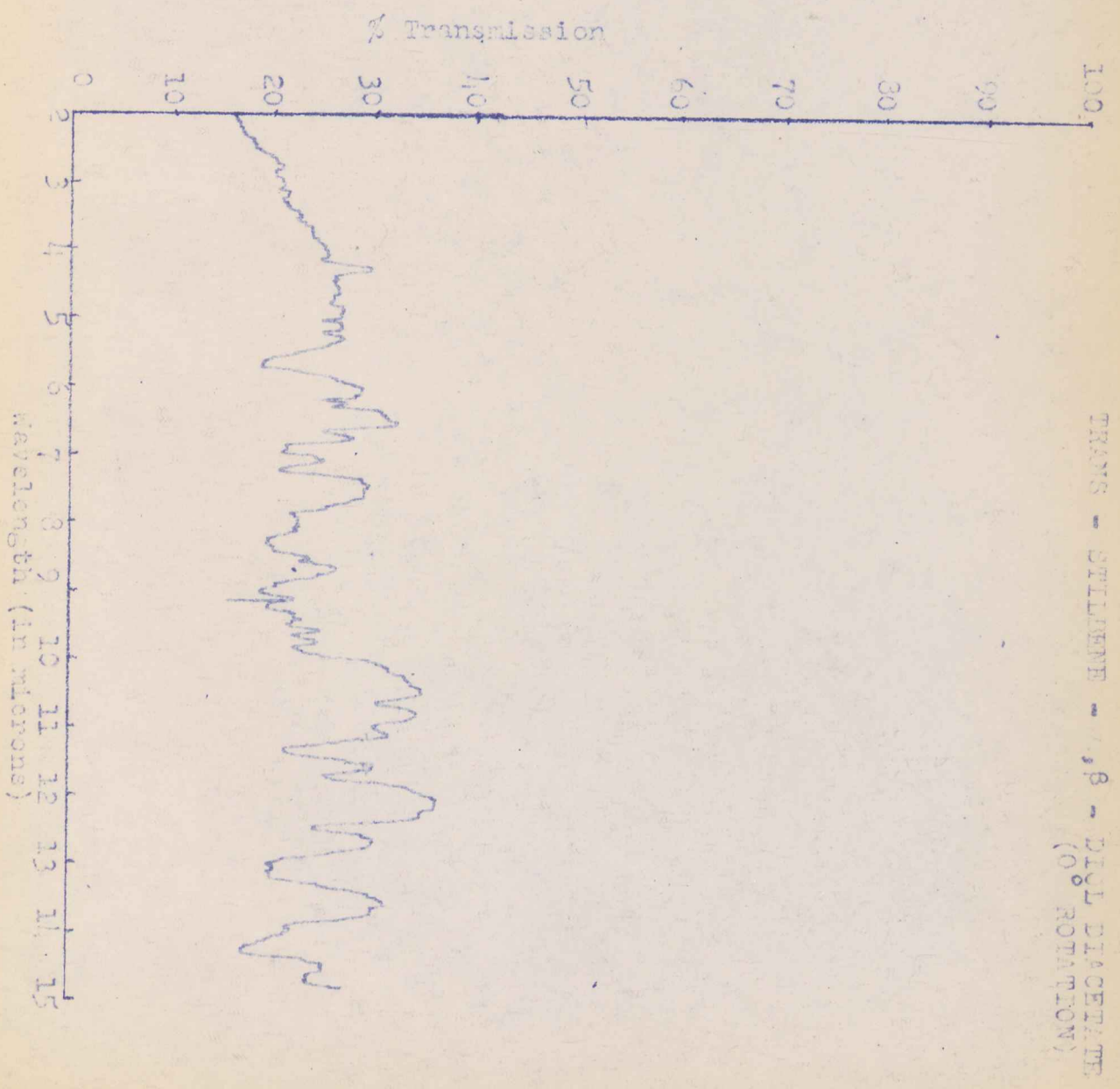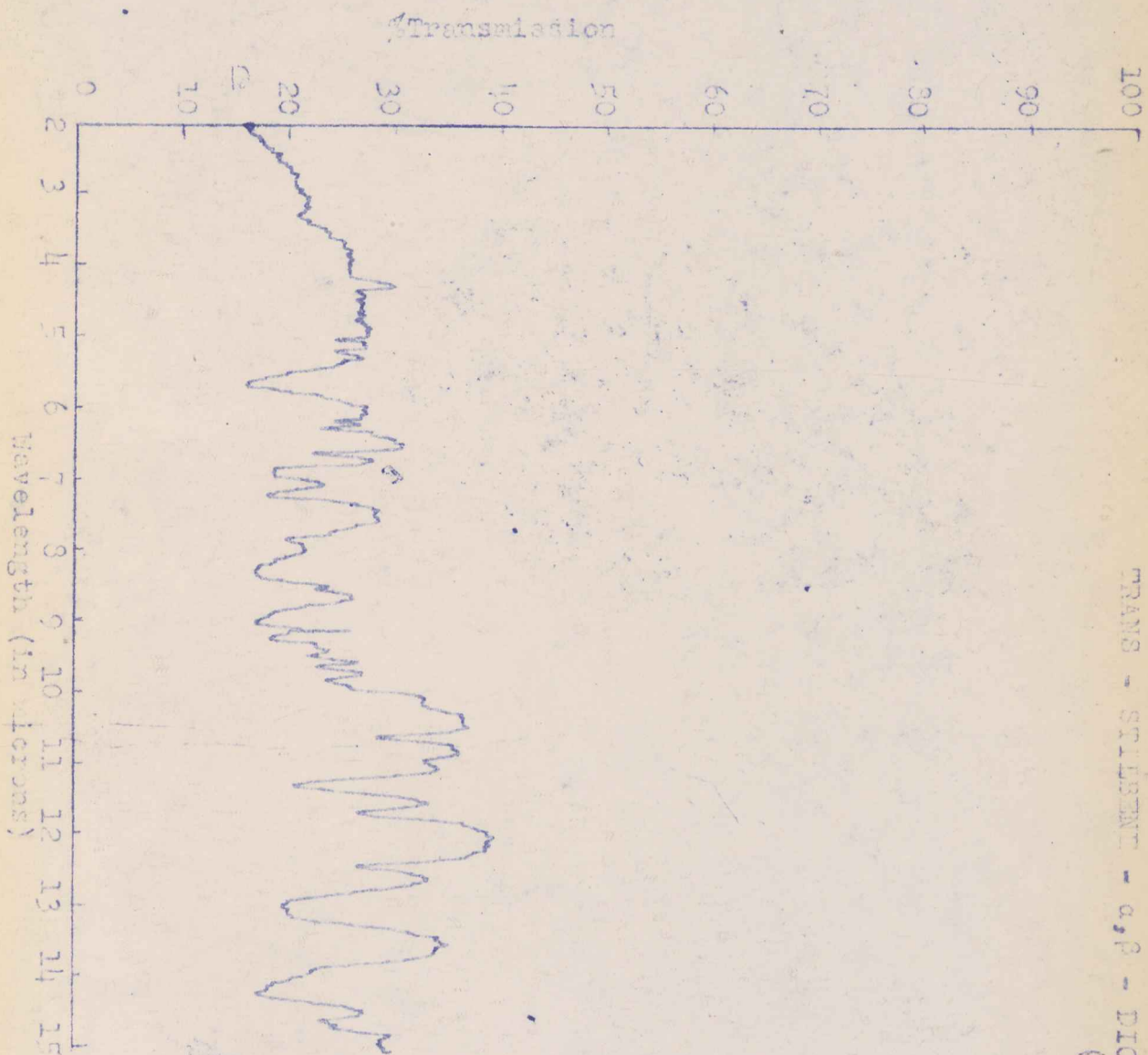
TRANS - STILBENE - α,β - DIOL DIACETATE
(90° ROTATION)
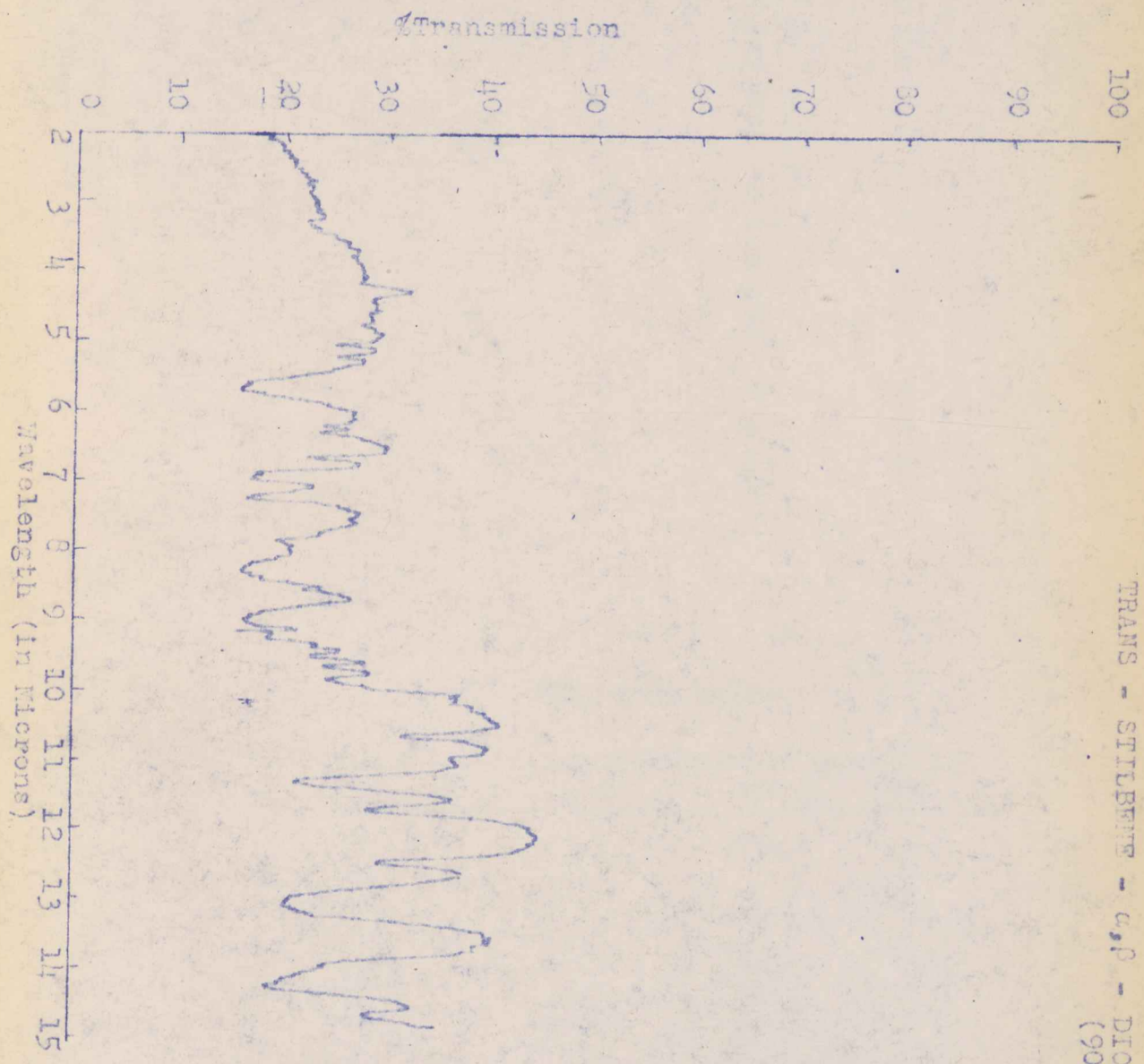
Table 12

Propriophenone

Wavelength (in microns)	Degree of Rotation of Incident Light		
	0°	45°	90°
3.4	0	0	0
4.3	0	-	-
5.95	0	0	+
6.25	0	0	+
6.31	0	0	+
6.91	0	0	+
7.09	0	+	0
7.27	0	0	+
7.42	0	0	+
8.5	0	0	0
9.3	0	0	0
9.9	0	0	0
10.0	0	0	0
10.55	0	0	0

Table 13

Cyclohexanoxime

Wavelength (in microns)	Degree of Rotation of Incident Light		
	0°	45°	90°
6.-1	0	-	0
6.95	0	0	+
8.03	0	-	0
8.20	0	-	0
8.73	0	0	0
9.08	0	-	0
10.12	0	-	-
11.26	0	-	-
11.93	0	-	-

% Transmission

100 90 80 70 60 50 40 30 20 10 0

PROPIOPHENONE, 0°, 45°, 90°.

2 3 4 5 6 7 8 9 10 11 12 13 14 15

Wavelength (in microns)
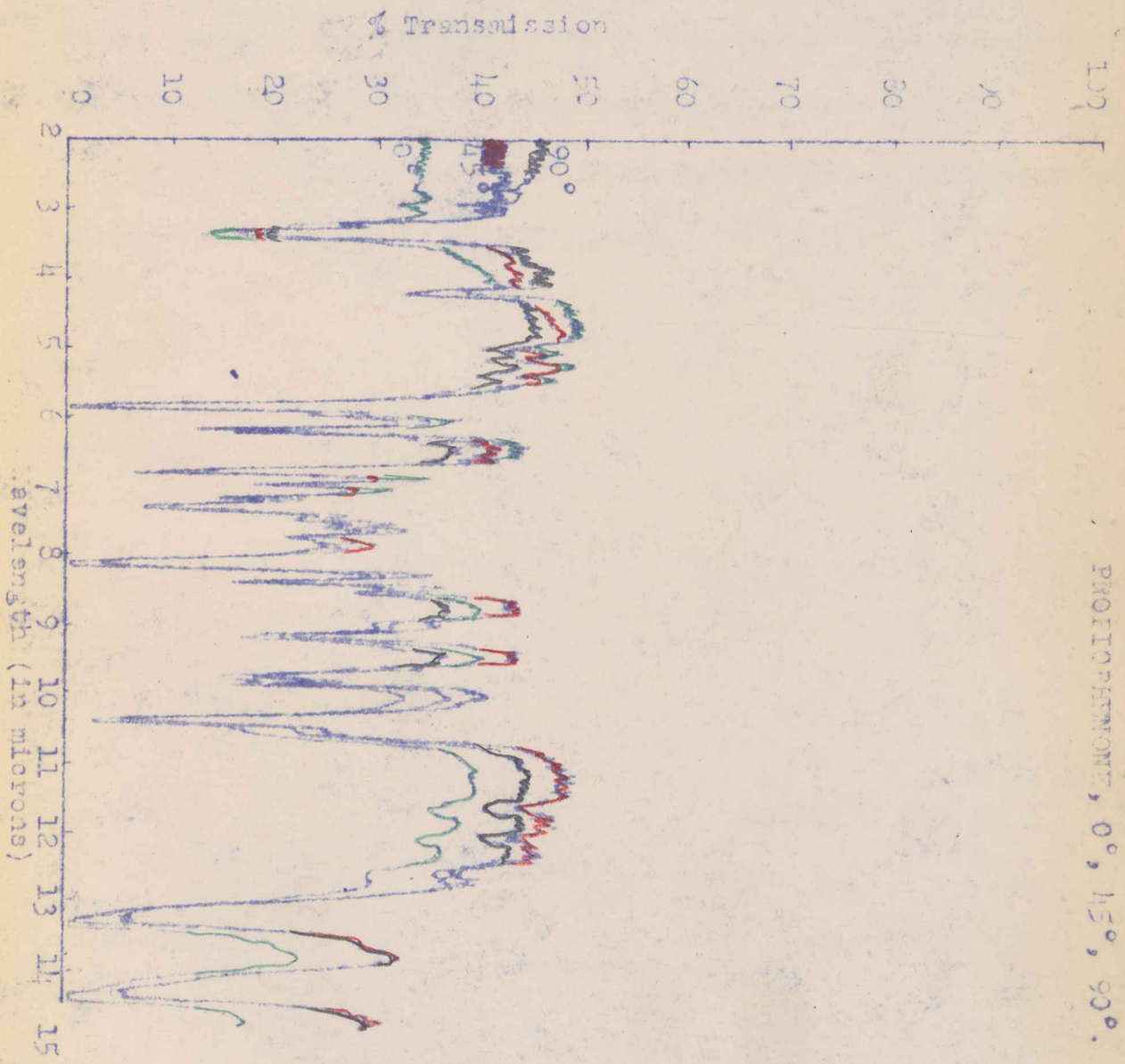
The NaCl plates used to support these substances had been polished using rouge and propyl alcohol. The NaCl was rubbed in one direction only so that the fine scratches lined up fairly parallel and very close together. The distance between the scratches was so small in comparison to the thickness of the NaCl block, that a good estimate of the width of the scratches were not readily available; probably the fine rouge particle average diameter would be about the width of the largest scratch groove.

Table 12 shows the comparison for propiophenone, a liquid, and the standard absorption for the polarizing unit.

Discussion:

Section A

It seemed as though rolled silver chloride plates made the best cell windows of all of the material experimented with, although some of the plastics could be used for some regions of the infrared, but not all.

Several mineral salts were tried but didn't work. These were the cryolite, fluorite and graphite. According to theory, a covalent bond must be present to obtain an absorption bond in the region of the infrared spectrum studied. These substances had total absorption not because of any covalent bonds, but probably because of heavy metal impurities in the material, except that carbon does have covalent bonding in graphite.

The fluorite crystals also contained impurities which effected the color of the crystals. One was pink, the other blue. It was probably these impurities, magnified by the relative thickness of the sample, that absorbed the infrared radiation and not the CaF_2 itself.

The metals experimented with all showed total absorption, including the very thin gold leaf. The molecules of the metal must be of such a nature to absorb all incident infrared radiation; metallic bonding is not very clearly understood, at any rate.

Section B

It was assumed that all of the absorption bonds picked to compare the size of the N-H absorption bond all had to do with CH_2 or ring absorption and were picked because of shape, size or location. Undoubtedly, more

consistent results would have been found if the same absorption bonds had been used.
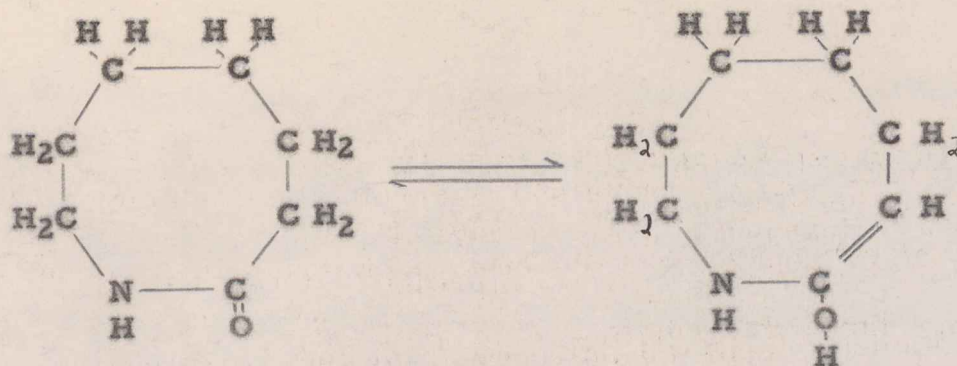
The results as tabulated in Tables 4, 5, 6, 7 and 8 showed that in all of the lactams, except N-methyl-2-pyrrolidone, as the lactam was diluted, the amount of intermolecular hydrogen bonding decreased since the unbonded N-H absorption increased.

The enolic =C-O- absorbs at 1200 cm^{-1}. The neat solution of ω-heptanolactam absorbed less at 1200 cm^{-1} than its 1-1 mole-ratio solution. These samples were both of the same thickness. If, upon dilution, the carbonyl absorbed more, it would seem that in the concentrated solution, some hydrogen bonding ties up the carbonyl, and on dilution the amount of hydrogen bonding decreased and thus the amount of carbonyl groups increase and the absorption peaks for it increased.

The large peaks at 2.9μ - 2.98μ in the ω-heptanolactam were interpreted as harmonics of the strong carbonyl absorption at 5.8 - 5.9μ.

There was another absorption at 7.37μ, possibly due to enol absorption, but the relative intensity did not change with dilution, nor did its frequency shift, but because of the gain in importance for the bonds at 6.4μ - 6.6μ, which is another enol absorption area, there was indication that, on dilution, the amount of enolization increased.

Therefore, when the solution is dilute ω-lactams may contain increasing amounts of enols.

```
   H H   H H                        H H   H H
    C------C                          C------C
   /        \                        /        \
H2C          C H2          ⇌     H2C          C H2
 |           |                    |           ||
H2C          CH2                 H2C          CH
   \        /                       \        /
    N------C                         N------C
    |      ||                        |      |
    H      O                         H      O
                                            |
                                            H
```

This enol form does not seem to exist in the concentrated solutions.
The reason for this might be that, in the concentrations, the carbonyl
oxygen is bonded to a large extent with the hydrogen from the neighboring
amine group.

Section C

The polarizing unit showed that when the sodium chloride plates are
rubbed in one direction, orientation of the molecules of the sample to be
tested does take place.

When a solid was melted on the rubbed plate and then gradually
cooled, the solid solidified first in the same direction as the rubbing.
After some of the material had begun to solidify the crystals started
growing in the direction at angles to the direction of the scratches. Enough
of the crystals grew in one direction to have some effect, but not all
crystals oriented themselves in one direction.

It was found also that the instrument itself polarized some light
by the set up of the instrument's optics. The polarization of the instru-
ment had been tested by using the polarizing unit alone.

Propiophenone, a liquid apparently had enough of its molecules
oriented in the same way as to appreciably change the absorption curve
for the 90° rotation curve. (see Table 12)

In the solid samples, cis and trans-stilbene-α, β, diol diacetate and cyclohexanoxime there was some orientation when the liquidified solid crystalized on the polished plates, but not as much as in the liquid sample of propriophenone. The scratches of the NaCl were lined up as the 0° rotation of the incident light. There was generally less absorption in the sample of propriophenone when the plane of incident light was rotated 90°. As this was especially true at 5.9μ. This suggests that many of the carbonyl groups oriented the C=O bond may not have been parallel to the surface NaCl plate and probably angled away from the sodium chloride plate.

The cyclohexanoneoxime showed that at 45° there was much greater absorption than normal and thus the carbonyl group must have lined up at about 45° to the NaCl plate grooves.

It is difficult to make any statements concerning the cis and trans-stilbene-α, β, diol diacetate samples. It seems likely that upon solidification of the melted solid on the rubbed plates not enough of the molecules oriented themselves in a uniform direction to effect differences in absorption curves on changing the angle of incidence of the plane polarized infrared radiation.

Summary:

Section A

Silicon has been very useful as a cell material, except for the fact that it must be very thin and highly polished. It's strong absorption bond at 9.1 μ may be a disadvantage but if it is balanced, this should not interfere at all.

The rolled silver chloride plates seem most desirable. They are transparent to infrared radiation, and are not effected by water.

The thin sheets of the metals tested (gold, platinum, lead, tin, tantalum and aluminum) are not transparent at all to infrared radiation.

Section B

The hydrogen bonding in the lactams has been found to increase with increased size of the lactam but, as expected, decreases upon dilution. The percent of the enol increases upon dilution, since diluted, the carbonyl oxygen H-N association becomes unbonded by solvent forces and is then free to form the enol.

Section C

Little can be said in the way of a summary for the last part of the research since it was by no means complete. It was found though that rubbing the sodium chloride crystal plates in one direction on rouge did have an effect on the orientation of the molecules of the sample, both in causing crystallization to proceed in one direction (parallel to grooves) at the onset of crystal formation, and even in liquids, as seems evident from the spectra on propriophenone.

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