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PREPARATION OF SEVERAL LACTAMS AND CORRELATION OF THEIR STRUCTURE WITH THEIR INFRARED SPECTRA

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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Approved by William B. Martin, Jr.

December 1, 1955

Acknowledgments

I wish to thank Dr. William B. Martin, whose guidance made this thesis possible. Dr. Martin's knowledge, patience and cooperation have been greatly appreciated, and it has been an inspiration to have worked with him.

Thanks are due also to Mr. Robert W. Schaefer, Dr. Howard E. Sheffer and Mr. Roman Slysh for their many helpful suggestions as well as their physical contributions.

Last, but far from least in importance, I should like to thank Mrs. Dorothy M. Heckeler, my wife. She not only contributed but actually sacrificed her time and ambitions to give help and encouragement to my work.

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Introduction

Simple amides are neutral compounds with infrared absorptions characterized by a strong carbonyl absorption, N-H absorptions, and other less significant and unassigned absorptions. Lack of basic nature of amides has been attributed to strong resonance of the unshared pair of electrons on nitrogen with the C=O double bond. This stabilizes the molecule to an extent not possible when the electron pair on nitrogen is protonated, since resonance stabilization of such an ammonium structure is no longer possible.

It seemed of interest to see what effect ring size might have on the nature of cyclic amides (lactams). The use of infrared spectrophotometry was deemed of prime importance, as it should perhaps differentiate between strong amide-type resonance and lack of it by the location of the carbonyl absorption. This should logically follow from the fact that without resonance, the higher force constant between the C and O atoms of the carbonyl group should absorb energy of lower wave length (higher frequency) than in the case where amide-type resonance is strong.

Furthermore, enol form of the carbonyl should perhaps be detectable in any cases in which such a tautomer is present in any large percent.

Historical

When a beam of light of nearly monochromatic nature but of continuously increasing wave lengths (ranging from 1 to 100 microns) is passed through a sample of material, an infrared spectrum is produced due to varying amounts of quantized energy absorbed by the sample. The spectrum will show absorptions of this monochromatic light at fixed wave lengths caused by different modes of vibration and rotation of the atoms within the material being analyzed. The pure rotational spectra of molecules will occur at very long wave lengths, beyond 25 μ (known as the "far infrared"). At shorter wave lengths (the "near infrared" region of 1 μ to 25 μ) the light has sufficient energy to cause changes in the vibrational as well as the rotational levels of the molecule. It is this shorter wave length region which will be discussed in this paper.

The number of modes of vibration possible for a particular molecule is mathematically fixed by the formula 3n-6 for cyclic or aromatic compounds and 3n-5 for linear ones where "n" is the number of atoms in the molecule. For example, toluene would have 3(15)-6 or 39 possible modes of vibration and rotation. If a molecule is highly symmetrical, as is the case with benzene, fewer than the theoretical number of absorptions may be noted. When symmetrical vibrations of parts of a molecule occur which result in no change in dipole moment due to these vibrations, no absorption of infrared light energy at that wave length will occur. There can, however, never be more fundamental absorptions than the various modes of vibration and rotation. On careful examination one may often find that what appears to be an "extra" absorption in reality is nothing but a harmonic (overtone) of a fundamental absorption. The exact

location of some of the fundamental absorptions may be mathematically determined (1). This method has been found to be quite complex (2) and, consequently, comparison of large numbers of absorption spectra of similar compounds has been found to be more practical. Also, further complexity of absorption spectra may result due to combination tones (the sum of two or more different absorption frequencies) and difference tones (the difference between two frequencies).

It has been mentioned previously that in the "near infrared" the energy of the light is sufficiently high to cause changes in the rotational and vibrational energy levels of the molecule. The atoms of any molecule are constantly oscillating about their positions of equilibrium, and these oscillations are of the same range of frequencies as the infrared radiation. When the incident monochromatic light is of exactly the same frequency as one of the molecular vibrations, a change of dipole moment occurs caused by the absorption of all or part of the infrared radiation, thus causing an absorption of the infrared light.

The infrared spectrum of a particular compound is a record of that compound's absorption of infrared radiation of varying wave lengths from 1 to 100 microns. Since no two compounds can ever have exactly the same modes of rotation and vibration, the infrared radiation cannot interact in the same manner for both, and absorptions will be located at different wave lengths in each compound. It is obvious then that the infrared spectrum of any pure compound is unique for that substance and serves as a "fingerprint" method of qualitative analysis.

The amount or percent of the initial infrared intensity absorbed at one particular wave length serves as a quantitative measure of the oscillation

causing the absorption. For example, an infrared beam having a wave length of approximately 2.90 microns will be absorbed by O-H stretching vibration; the amount of light absorbed by ethyl alcohol at that wave length is proportional to the amount of hydrogen bonded O-H present, providing none of the impurities contain this same bond. Except for special cases where intermolecular action occurs, the amount of light transmitted by a sample is governed by Beer's law:

$$\frac{I}{I_o} = e^{-kcx}$$

"I_o" is the intensity of the beam incident on the sample; "I" is the intensity of the beam transmitted by the sample; "k" is the absorption coefficient of the material being analyzed; "c" is the concentration of the material; and "x" is the thickness of the sample. The absorption coefficient "k" is primarily a function of molecular structure, but the physical state of the material being analyzed does cause some slight variations due to interactions with neighboring molecules. Temperature and pressure have practically no effect on "k". Since infrared absorption obeys Beer's law, it enables quantitative analysis of pure organic compounds or simple mixtures.

A great deal of information concerning the configuration of a molecule may also be obtained by a careful investigation of its absorption spectrum. Such information includes cis-trans or ortho-, meta-, and para- isomerism, hydrogen bonding, and keto-enol tautomerism. For example, the spectrum of a pure ketone will show a very strong absorption at approximately 5.85 microns due to the stretching vibration of the C=O bond. If an absorption also appears around 2.90 microns which is separate from any harmonic of the C=O

absorption, an O-H bond is present and the pure ketone exists in both the enol and keto forms. This subject of the configuration will be considered in this thesis.

The portion of the infrared spectra used for the configuration determinations is usually limited by the optical equipment available. The standard infrared spectrophotometer is normally equipped with a sodium chloride prism which has been found to be a fair monochromater over the infrared range of 2 to 15 microns—a region of great importance when studying organic molecules. Many of the important bond stretching vibrations in the region of 2 to 7.3 microns include O-H, N-H, C-H, C=O, C=N, and C=C. The region of 7.3 to 15 microns, known as the "fingerprint" area, is also of importance as it contains other organic bond stretching vibrations as well as bond bending and rocking absorptions. Although the sodium chloride prism allows investigation in only a small segment of the infrared spectrum, this portion is very important and is the spectrum area most completely understood.

Experimental

1. Preparation of Cyclopentanone

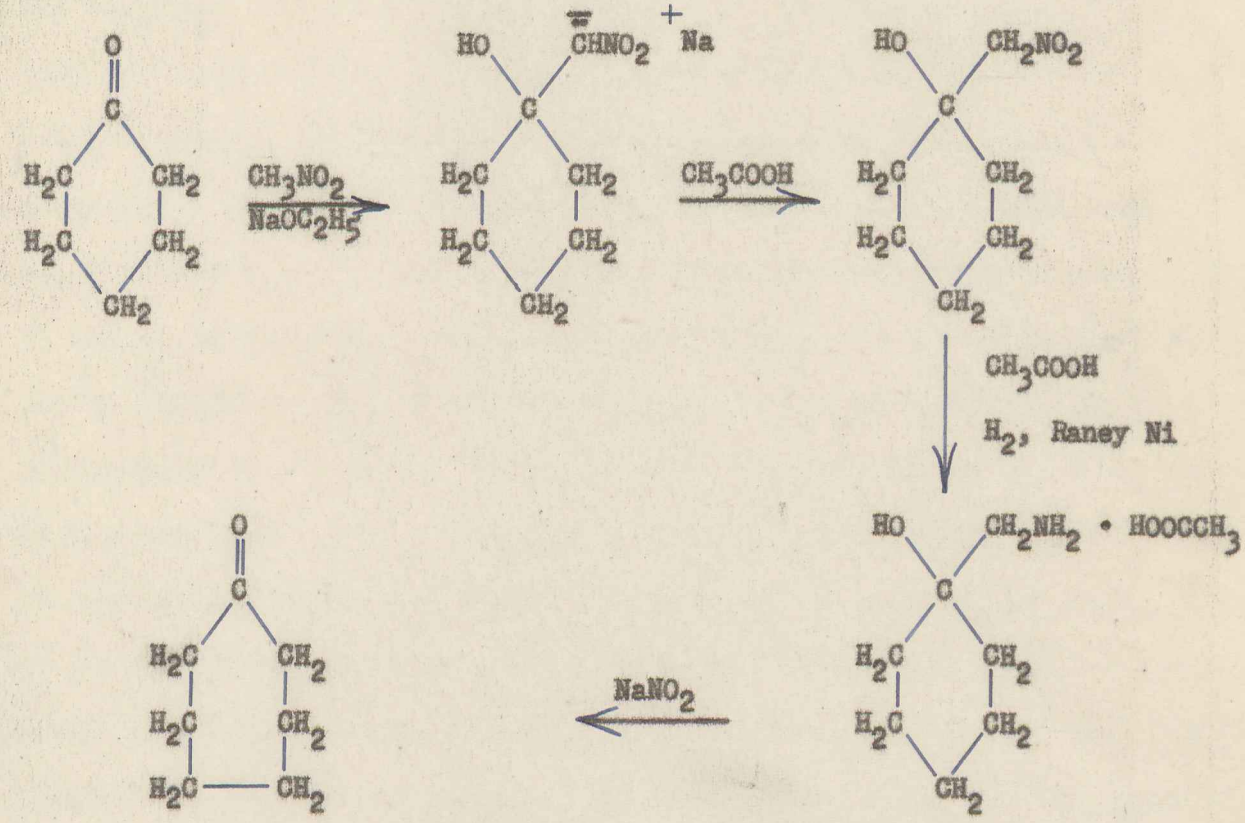
The method used for the preparation of cyclopentanone was that of Thorpe and Kon (3):

In a 1-liter distillating flask, fitted with a thermometer reaching within 5 mm. of the bottom, was placed an intimate mixture of 189 g. (1.26 moles) of powdered adipic acid and 10 g. of finely ground, crystallized barium hydroxide. Since a fusible alloy bath was not available, the mixture was gradually heated by a carefully controlled flame to 285-295°. (If the temperature goes above 300°, the adipic acid begins to distill quite rapidly.) It has been found best to hold the temperature as near 290° as possible, until only a small amount of dry residue remains in the flask. This required about 3½ hours. The cyclopentanone distilled slowly, accompanied by small quantities of adipic acid.

The ketone layer was separated from the water and the aqueous layer was extracted with a little ether. The ketone and ether extract were washed with a little aqueous alkali and then with water, dried over calcium chloride, and distilled through a good fractionating column. Cyclopentanone is somewhat volatile with ether vapor, and careful fractionation was necessary. The fraction boiling at 129-130° C. was cyclopentanone. The yield was 72 g. (66.3% of the theoretical amount).

2. Preparation of Cycloheptanone

The method used for the preparation of cycloheptanone is that of Dauben, Ringold, Wade, Pearson, and Anderson (4):



A solution of sodium ethoxide was prepared by adding 19.2 g. (0.83 gram atoms) of clean sodium to 400 ml. of absolute ethanol in a 1-liter three-necked flask equipped with a reflux condenser fitted with a drying tube, a sturdy sealed stirrer, and a dropping funnel. After the sodium had dissolved, the solution was cooled to 40° and the condenser was replaced by a thermometer extending into the liquid. A mixture of 82 g. (86.5 ml.) (0.83 moles) of cyclohexanone and 66 g. (58 ml.) (1.80 moles) of nitromethane was added dropwise with vigorous stirring over the course of about three

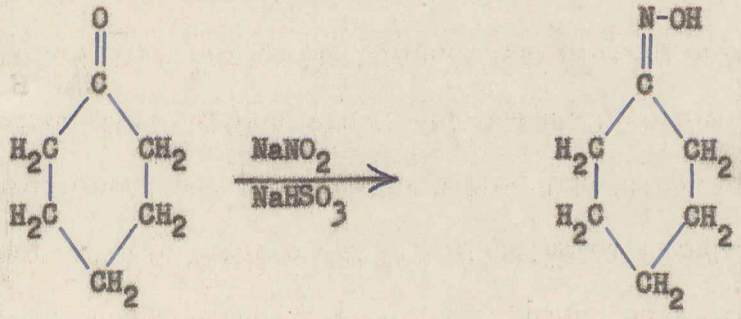
hours at a rate that maintained an internal temperature of 45 ± 3°. After addition was complete, the white, pasty mass was stirred for an additional three hours without cooling or heating and then was allowed to stand overnight. The resulting suspension was cooled with an ice bath, and the white sodium salt of 1-(nitromethyl) cyclohexanol was collected on a Büchner funnel and dried by suction for about one hour. The sodium salt cake was broken up and transferred to a 2-l. beaker equipped with a stirrer and immersed in an ice bath. A cold solution of 61 g. (58 ml., 0.97 moles) of glacial acetic acid in 420 ml. of water was added in a single portion, and the mixture was stirred for 30 minutes to complete dissolution. The oily layer of 1-(nitromethyl) cyclohexanol was separated, and the aqueous layer was extracted with three 50-ml. portions of ether. The ether extracts and the 1-(nitromethyl) cyclohexanol were combined, dried briefly over magnesium sulfate, and concentrated by distillation from a steam bath with a water aspirator at 70 mm. to remove ether and excess nitromethane. The crude, undistilled 1-(nitromethyl) cyclohexanol was dissolved in 150 ml. of glacial acetic acid in an externally cooled glass hydrogenation bottle. W-4 Raney nickel catalyst was added, and the mixture was shaken with hydrogen at 40-45 p.s.i. with cooling to maintain the temperature below 35°, until about 90% of the theoretical amount (2.5 moles) of hydrogen was taken up and absorption ceased. The catalyst was separated by filtration with suction through Filter-Cel, and the green filtrate containing the acetic acid salt of 1-(aminomethyl) cyclohexanol was used directly in the next step.

The filtrate was transferred to a 2-l. round-bottomed flask, immersed in an ice-salt mixture, and equipped with a stirrer, a thermometer, and a

dropping funnel. The solution was diluted with 770 ml. of ice water; then an ice-cold solution of 97 g. (1.4 moles) of sodium nitrite in 250 ml. of water was added dropwise during a period of about one hour with stirring and cooling (ice-salt bath) to maintain the temperature at 0°. The mixture was stirred for an additional period of one hour and then allowed to come to room temperature overnight as the ice in the cooling bath melted. The acetic acid in the reaction mixture was neutralized by the addition of small portions of solid sodium bicarbonate, and the neutral (to litmus paper) solution was then steam-distilled until about 700 ml. of distillate was collected. The oily cycloheptanone layer was separated, the aqueous layer was extracted with three 50 ml. portions of ether, and the combined organic layers were dried briefly over magnesium sulfate. Most of the ether was removed by distillation through a short, glass bubble-cap column at atmospheric pressure. The residue was then distilled through the same column, and the fraction boiling at 75-80° at 22 mm. was collected. The yield of cycloheptanone was 37.4 g. (39.9%).

3. Preparation of Cyclohexanone Oxime

The method used for the preparation of cyclohexanone oxime is that of Eck and Marvel (5):



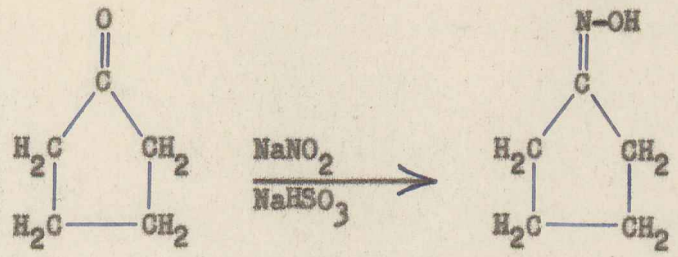
In a 2-l. flask, fitted with an efficient mechanical stirrer and a 7 mm. glass inlet tube reaching to within 5 cm. of the bottom of the flask, were placed 500 g. of cracked ice and a solution of 61 g. (0.83 moles) of technical sodium nitrite (95%) in 170 ml. of water. The flask was placed in an ice-salt mixture, and a cold (-8°) solution of sodium bisulfite was added; this was prepared by saturating with sulfur dioxide a solution of 48 g. (0.45 moles) of anhydrous sodium carbonate in 200 ml. of water. While the temperature was kept below 5°, a moderate stream of sulfur dioxide was passed into the mixture until it was acid to congo red and then just enough longer to remove the dark color which appeared shortly before the solution became acid.

To this solution were added 72 g. (0.74 moles) of technical cyclohexanone and 170 ml. of 85% ethyl alcohol. The cooling bath was replaced by a steam bath, the stirrer started, and the mixture heated to 75°. The flask was then packed in sawdust and allowed to cool slowly, with effective stirring, for 48 hours. The solution at room temperature was exactly neutralized to litmus with a 50% solution of sodium hydroxide, with cooling and stirring. About 150 g. of sodium hydroxide was required (large amounts of inorganic sodium salts separated from solution).

The aqueous solution was extracted with three 75 ml. portions of ether. The ether and other impurities were removed by distillation from a 125 ml. claisen flask having a 15 cm. fractionating tube. It was found that the boiling point and melting point of cyclohexanone oxime at 10 mm. are quite close. The cyclohexanone oxime was purified by recrystallization from petroleum ether until a melting point of 85-87° was obtained for the 50 g. yield (60.2%).

4. Preparation of Cyclopentanone Oxime

The method used for the preparation of cyclopentanone oxime was the same method used for the preparation of cyclohexanone oxime (5):

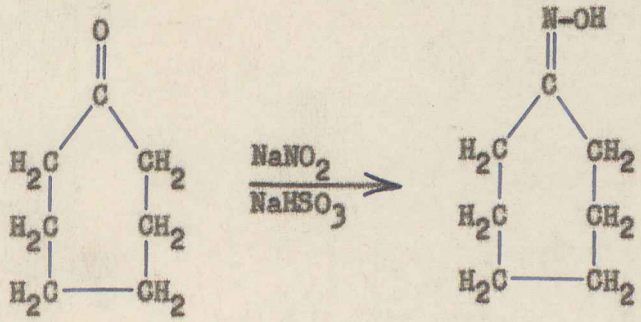


The preparation of cyclopentanone oxime was also carried out using the same molar amounts of chemicals and the same equipment as were used in the previous preparation. Again during the neutralization with sodium hydroxide, large amounts of inorganic sodium salts were noted separating from solution. The cyclopentanone oxime did not separate from the aqueous solution as an oily layer either, but was finally separated by the ether extraction.

63 g. of cyclopentanone was used to prepare the 29 g. (39.2% yield) of cyclopentanone oxime which was found to have a boiling point of 90-92° at 10 mm. and a melting point of 57.5-58.5°.

5. The Preparation of Cycloheptanone Oxime

The method used for the preparation of cycloheptanone oxime is the same method used for the preparation of the other oximes (5):

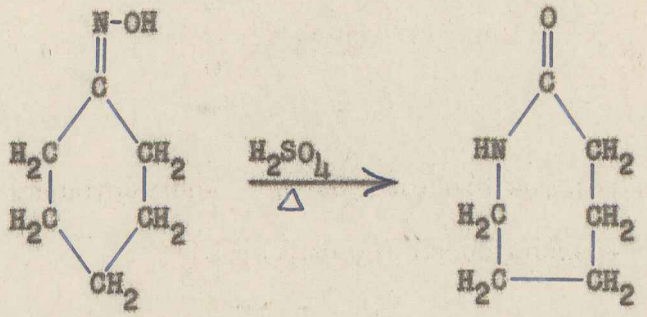


The preparation of cycloheptanone oxime was carried out with one-half the molar amounts of chemicals (and proportionally sized equipment) which were used in the preparation of the previous two oximes. The cycloheptanone oxime did separate from the aqueous solution as an oily layer after the neutralization; however, large amounts of inorganic sodium salts also separated.

37.4 g. of cycloheptanone was used to prepare 29.9 g. (70.4% yield) of cycloheptanone oxime which was found to have a boiling range of 112-116° C. at 10 mm. and a melting point of 12° C.

6. Preparation of ω-Hexanolactam (Caprolactam)

The method used for the preparation of ω-hexanolactam is that of Marvel and Eck (6):



The Beckmann rearrangement of 30 g. (0.26 moles) of pure cyclohexanone oxime was carried out in three 10 g. portions in a 1-l. beaker with 20 ml. of 85% sulfuric acid with each sample of the oxime. The beaker was heated with a low flame until bubbles first appeared. The beaker was then removed from the flame immediately, and the violent reaction, which lasted a few seconds, was allowed to subside.

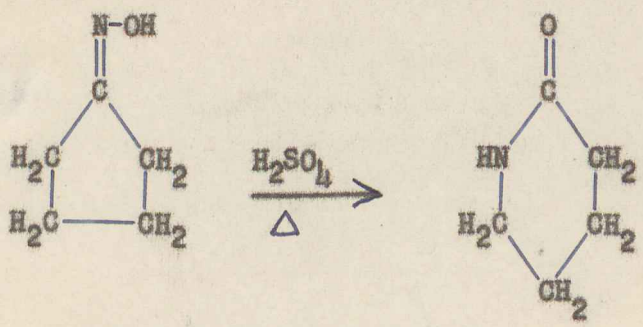
The acid solutions of ω-hexanolactam from the three runs were combined in a 1-l. round-bottomed flask which was fitted with a mechanical stirrer and a separatory funnel and packed in an ice-salt mixture. The solution was cooled to 0° and carefully made faintly alkaline to litmus by the addition of 24% potassium hydroxide, added slowly over a period of about three hours with good cooling. About 400 ml. of the alkaline solution was needed. The temperature was kept below 10° to avoid hydrolysis during this stage of the preparation.

The potassium sulfate which had separated was then removed by filtration and washed with two 50 ml. portions of chloroform. The faintly alkaline aqueous solution was extracted with about five 50 ml. portions of chloroform. (Some trouble was encountered with emulsions believed to be caused by the fairly high water solubility of ω-hexanolactam.)

The combined chloroform solutions were washed once with 20 ml. of water to remove any alkali. The chloroform was then distilled and the product fractionated under reduced pressure. The yield of ω-hexanolactam, boiling at 137-139° C. at 10 mm. pressure and melting at 67-68°, amounted to 15.3 g. (51.0% of the theoretical amount).

7. Preparation of ω-Pentanolactam (Valerolactam)

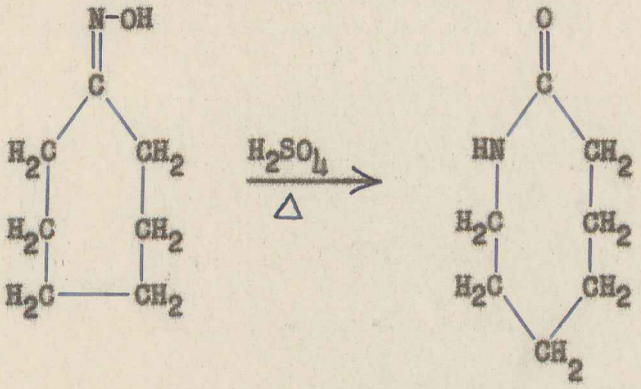
The method used for the preparation of ω-pentanolactam is the same method used for the preparation of ω-hexanolactam (6):



The preparation was carried out with 17 g. of cyclopentanone oxime and two-thirds of the molar amounts of chemicals (in proportionally sized equipment) which were used in preparation of ω-hexanolactam. A great deal of difficulty with emulsions was noted during the chloroform separation. 2.6 g. (15.3% yield) of ω-pentanolactam was prepared and was found to have a boiling range of 128-139° at 10 mm. and melted at 38-40°.

8. The Preparation of ω-Heptanolactam

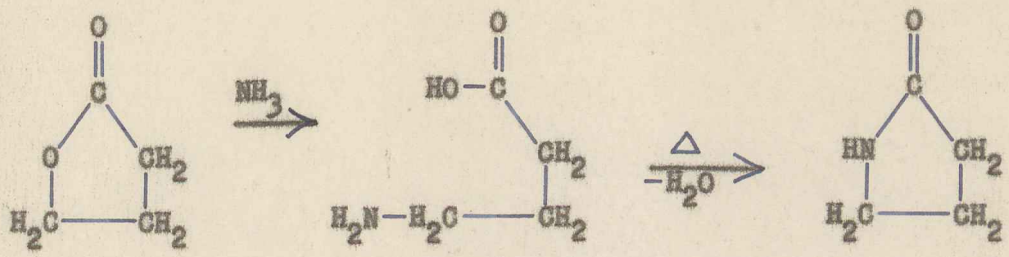
The method used for the preparation of ω-heptanolactam is the same method used for the preparation of the previously mentioned lactams (6):



The preparation of ω-heptanolactam was carried out using 20 g. of cycloheptanone oxime with proportional molar amounts of those chemicals used in the previous preparations. Practically no difficulty was encountered with emulsions during the chloroform separation. 12.5 g. (62.5% yield) of ω-heptanolactam was prepared and was found to have a boiling range of 153-155° and melted at 27-28°.

9. Preparation of ω-Butyrolactam (2-Pyrrolidone)

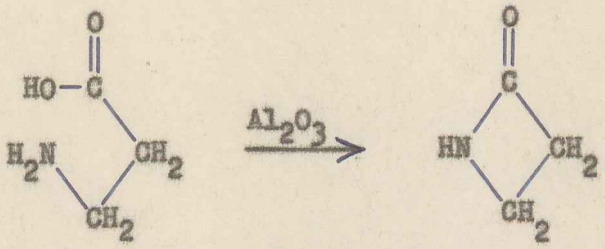
Numerous attempts were made to prepare ω-butyrolactam from butyrolactone as shown by the following equation:



Various solvents were tried including water, acetonitrile, tert-butanol, and the butyrolactone itself at temperatures ranging from 6 to 203°; none yielded γ-amino butyric acid. The method of Gresham & Shaver (7) for the preparation of β-amino propionic acid was tried with no more success. It was believed that the hydroxy amide was prepared rather than the amino acid, although this was not proved as the hydroxy amide would reconvert to the lactone on heating, liberating ammonia.

Since the first step of the ω-butyrolactam preparation was unsuccessful, γ-amino butyric acid was employed. 0.8 g. of this material was slowly heated in a test tube to 200° and held at this temperature until the bubbling ceased (liberation of water vapor). The remaining liquid, ω-butyrolactam, which was prepared in nearly 100% yield, was found to have a melting point of 25° C. (This was desiccated and its spectrum taken without further purification. Justification of lack of recrystallizations seems probable from its spectrum.)

An attempt was made in preparing ω-propriolactam. A mixture of β-alanine and alumia was heated to 270° in a sealed tube by means of a sand bath. It seemed possible that the following reaction might occur if ammonia were not allowed to escape:



Instead, the aluminum salt of acrylic acid was believed to have been produced by elimination of NH_3. The gummy mass removed from the sealed tube was insoluble in chloroform but did dissolve in concentrated hydrochloric acid. The acid solution was extracted with ether. After the ether was removed, a yellow liquid was found having a melting point of 10° which was believed to be acrylic acid.

Several compounds which were not synthysized were obtained from chemical supply houses for infrared spectra comparisons.

The procedure followed in studying the infrared light absorption was to prepare solutions of one molar concentration of each of the lactams (as well as the oximes) in chloroform. These were placed in sodium chloride cells of 0.1 mm. sample thickness. The ketones were placed as neat liquids in a 0.025 mm. sample cell (sodium chloride windows) for their absorption spectra. The spectrophotometer used was the Perkin Elmer model 21 infrared spectrophotometer, a gift to Union College by the Schenectady Varnish Company.

Discussion

The purpose of the lactam investigation was to ascertain information concerning the structure of this type of compound by means of infrared spectra. It was hoped that examination of the spectra would lead to conclusions concerning the degree of amide resonance as influenced by the lactam ring size. The infrared spectra of these compounds might also indicate the existence of enol-keto tautomerism of the carbonyl grouping in amides.

In studying the family of cyclic amides known as lactams, the investigator is met with an immediate problem--lactams are not available from the common sources of chemical supply. It was, therefore, found necessary to prepare the needed compounds. There are several methods for the preparation of lactams, but the most practical and the most universally used method is the Beckman rearrangement of the corresponding cyclic oximes. Since the oximes are also rather uncommon, it is often necessary to prepare them from their corresponding cyclic ketones. As one may have already concluded, the cyclic ketones are not to be found on every laboratory shelf either.

The infrared absorption spectra of nearly all organic compounds are very complex. It should be emphasized that to understand the cause of all absorptions of any common organic substance is an impossibility at the present state of knowledge about this subject. While the spectra of the compounds prepared for this thesis are recorded for the range of 2 to 14 μ, the discussion will be limited largely to the region of 2 to 7.3 μ and will not include the "fingerprint" area. The interest in the region which is considered here is based on the fact that this is the region where most of the bond stretching vibration frequencies of functional groups will be located.

The actual absorption spectra used as the basis for the following discussion are to be found in the Union College Chemistry Department Infrared Library, and where cited, the number of a reference spectrum will be given after the name of that compound. The absorption spectra included in this thesis are reproductions of the reference spectra.

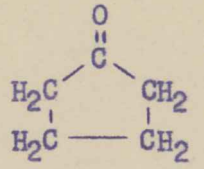
In studying infrared absorption of lactams, it seems worthwhile first to investigate absorptions of the corresponding cyclic ketones and their oxime derivatives which were used in the lactam syntheses.

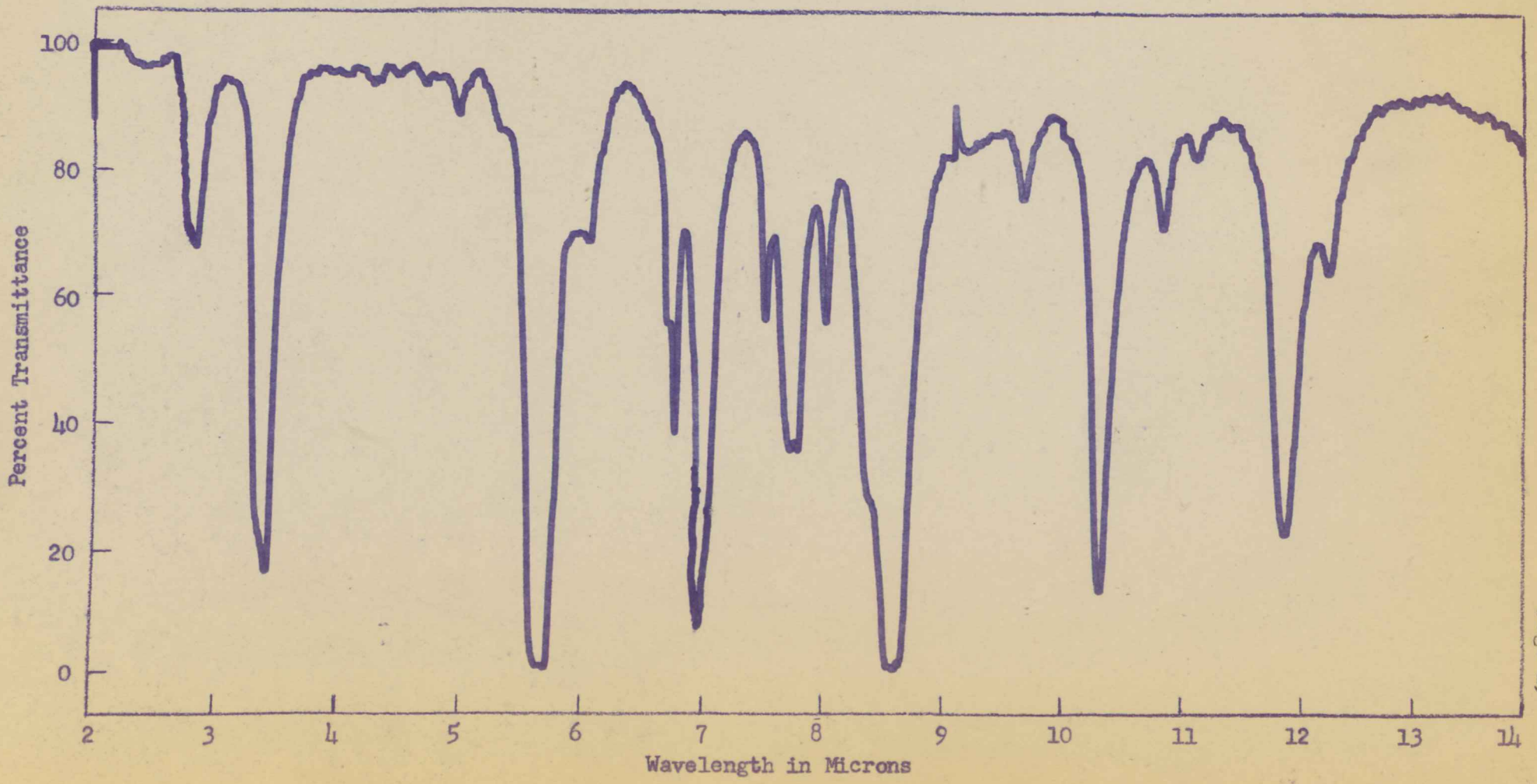
Cyclic Ketones

One of the most obvious absorptions in the spectrum of a ketone is that of the C=O carbonyl stretching vibration. In the case of cyclopentanone (55-1), cyclohexanone (55-14), and cycloheptanone (55-13), this C=O stretching absorption appears at 5.75, 5.82, and 5.90 μ respectively. The slight shift to shorter wave lengths with decreasing ring size is believed to be caused by corresponding increasing ring strain which in turn strengthens the C=O bond (8). Since this bond would have become stronger with increased ring strain, it would require more energy to cause a change in its dipole moment and absorb at a shorter wave length where quanta of light have higher energy.

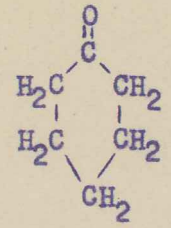
One might expect these three ketones to exist as an equilibrium mixture of the enol and the keto form. At first glance it appears that such equilibrium exists because of the weak absorption in the 2.90 μ wave length region where the O-H stretching absorption occurs. However, on close examination it will be noted that this absorption is actually a harmonic of the very strong C=O stretching absorption. In the case of cyclopentanone the harmonic is located at 2.87 μ, in cyclohexanone it may be either of two absorptions at 2.85 and 2.92 μ, and in cycloheptanone it is found at 2.91 μ.

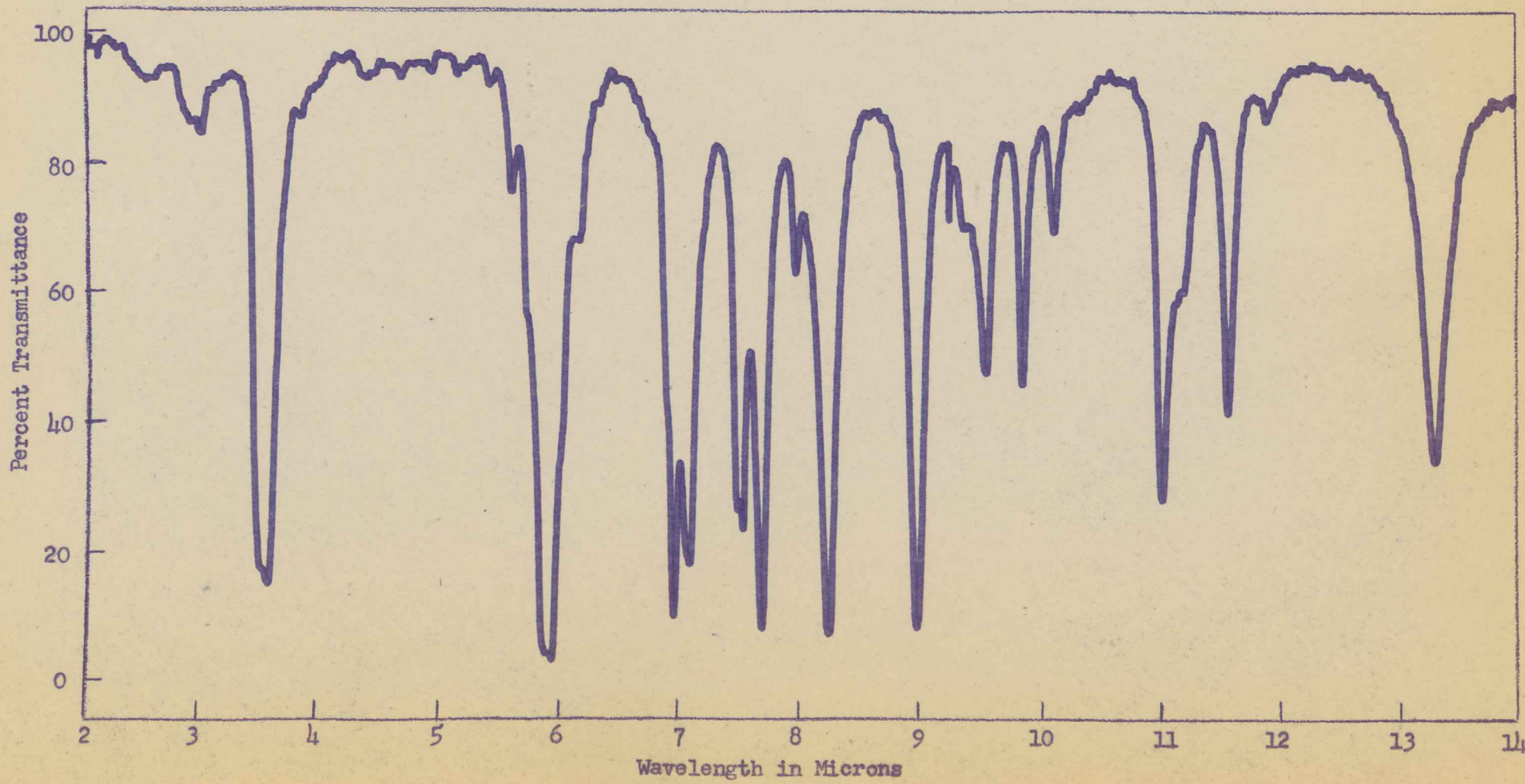
CYCLOPENTANONE



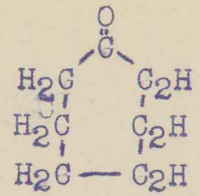


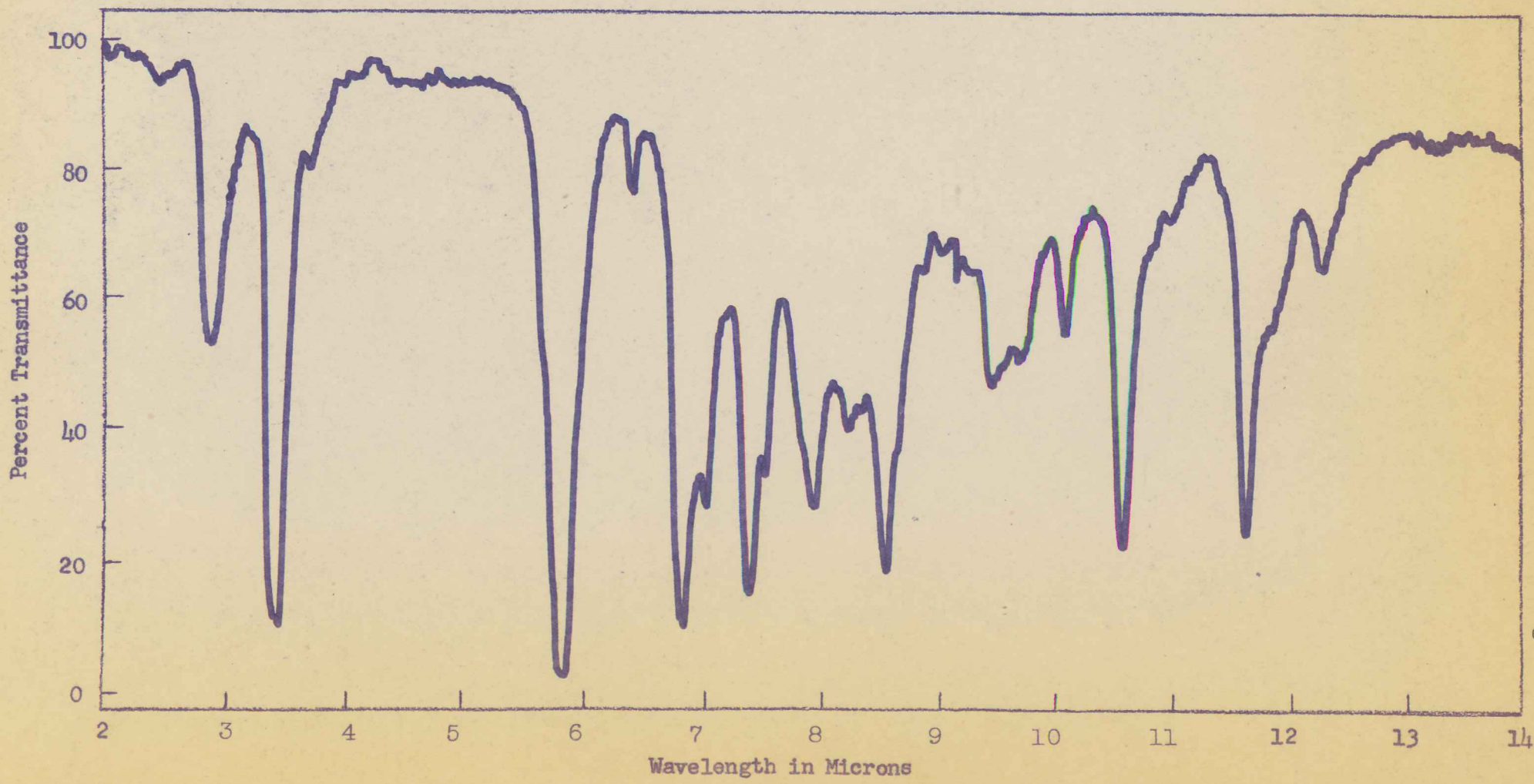
CYCLOHEXANONE





CYCLOHEPTANONE





The spectra indicate that no appreciable percent of enol form exists for cyclopentanone and cycloheptanone. For cyclohexanone, the two absorptions near 2.9 μ appear to be harmonics of the doublet absorption in the carbonyl region near 5.8 μ. The presence of a carbonyl doublet is hard to explain here unless due to some impurity, but such a large percent as the doublet would imply seems highly unlikely; one may rather be an additive absorption of two other frequencies of absorption. At any rate, the stabilization of cyclohexanone by forming its enol tautomer seems unlikely according to a check with Hirschfelder atomic models.

When investigating organic compounds the C-H stretching absorption is perhaps the most common of all absorption maxima. In studying the three ketones it was evident that two distinct C-H stretching absorptions were present for each compound: at 3.38 and 3.47 μ for cyclopentanone, 3.43 and 3.48 μ for cyclohexanone, and 3.44 and 3.50 μ for cycloheptanone. These two absorptions correspond to the in-phase and out-of-phase stretching vibrations of the hydrogen atoms, a phenomenon characteristic of compounds containing $-CH_2-$ groups (9).

Not only is the C-H stretching absorption present in the region of infrared investigation, but also the C-H bending (deformation) absorption. For cyclopentanone the C-H bending absorptions occur at 6.80 and 6.86 μ, for cyclohexanone at 6.82 and 6.88 μ, and for cycloheptanone at 6.87 and 6.92 μ. The fact that two absorptions exist for this one type of vibration can perhaps best be explained similarly to the case of two C-H stretch absorptions, namely, in-phase and out-of-phase bending in this case.

Still another C-H bending absorption will be located at approximately 7.10 μ which is caused by the CH_2 group adjacent to the carbonyl. This group exhibits a shift to a longer wave length as a result of activation due to a double bond (10). For example, in cyclopentanone this absorption is located at 7.10 μ, in cyclohexanone at 7.02 μ, and in cycloheptanone at 7.10 μ.

If the enol form should not exist for these three ketones, the C=C stretching vibration should not appear in the infrared spectra. The main absorption for this particular vibration would be partially hidden by the stronger C=O absorption and would appear as a "shoulder" of the stronger one. Such a C=C absorption may occur in the cyclopentanone spectrum at 6.15 μ, cyclohexanone spectrum at 6.10 μ, and cycloheptanone at 6.02 μ. The shift with ring size may be caused by one of two phenomena or a combination of the two: the relative strain of the ring in question or vibrational interference from the C=O absorption. Again, these are only speculations and there is no proof to support either theory.

Cyclic Ketoximes

The increase in yield with the increase in ring size of the oximes can be explained by their water solubilities. The polar portion of the ring remains the same while the size of the hydrocarbon grouping increases causing increasingly lower water solubility with increased ring size. Thus, the molecules of higher molecular weight are more completely extracted from the aqueous layer by the ether. It will be noted that of the three oximes only the one of highest molecular weight was insoluble enough in water to separate as an oily layer while the other two were completely dissolved in the aqueous solution.

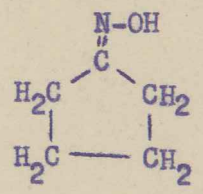
The oxime derivatives of the previously mentioned cyclic ketones exhibit strong O-H stretching absorptions as would be expected. For example, cyclopentanone oxime (55-16), cyclohexanone oxime (55-15), and cycloheptanone oxime (55-17) produce extremely strong O-H stretching absorptions at 3.11, 3.13, and 3.20 μ respectively. Strong shoulders on the latter two O-H absorptions are not readily explained unless as some addition tone. These three O-H absorptions indicated hydrogen-bonded O-H (to $\ddot{N}$ of adjacent molecules).

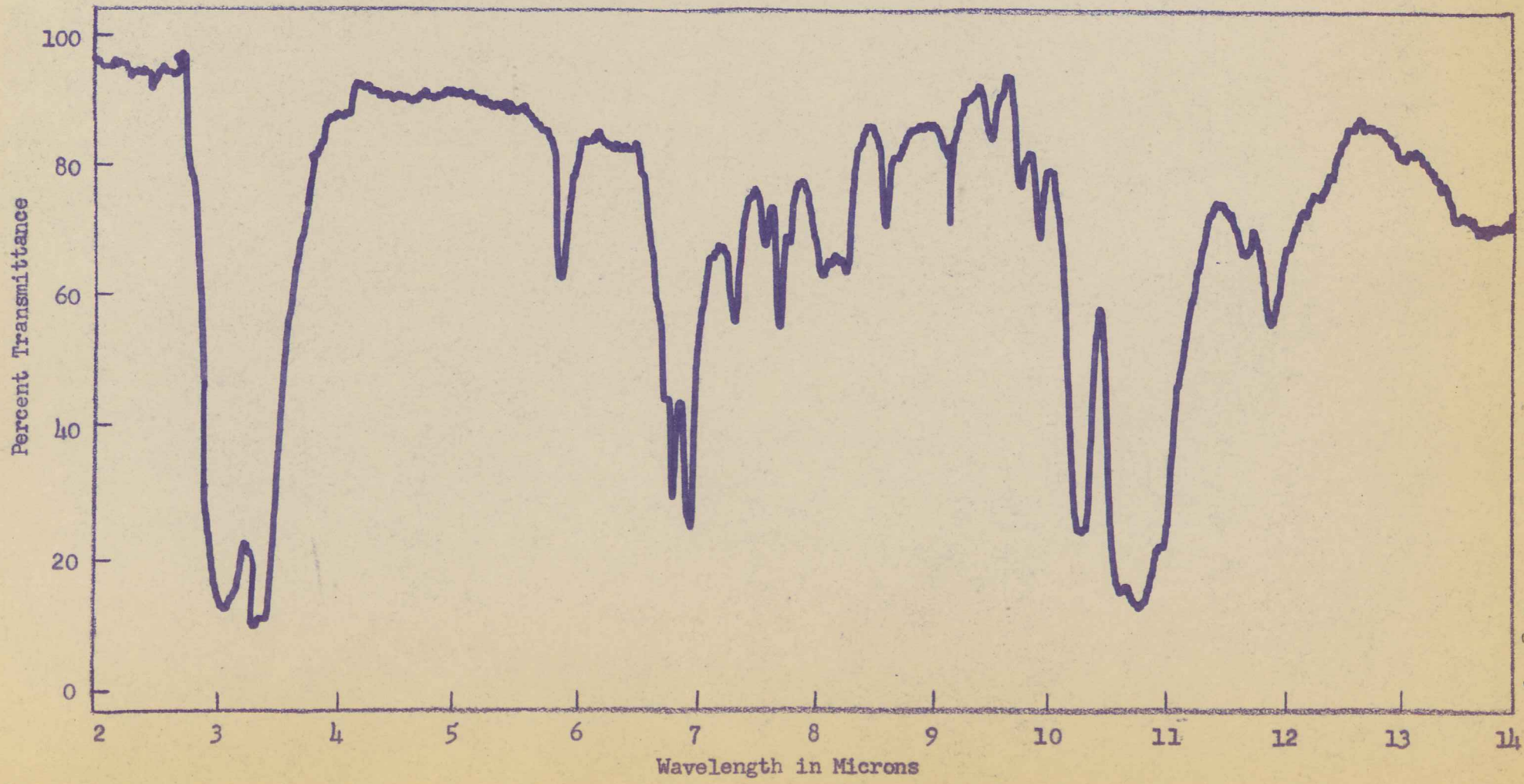
The C-H stretching vibrations of the three oximes appear as two distinct absorptions as they did in the spectra of the cyclic ketones for the same reason; that is, in-phase and out-of-phase stretching (9). For cyclopentanone oxime the two absorptions are located at 3.39 and 3.47 μ, for cyclohexanone oxime at 3.45 and 3.50 μ, and for cycloheptanone at 3.45 and 3.50 μ.

Since the oxime derivatives do not affect the C-H bond structure of the cyclic ketones, it is not surprising to find the corresponding C-H bending absorptions in the oxime spectra, too. These appear at 6.87 and 7.02 μ in the cyclopentanone oxime spectrum, 6.90 and 6.96 μ in the cyclohexanone oxime, and 6.90 and 7.00 μ in cycloheptanone oxime.

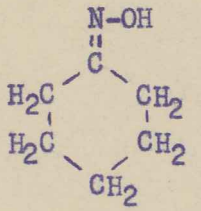
A bond found in the oximes, which is not present in the ketones, is the C=N double bond. The stretching vibration of this bond causes absorption at 5.91, 6.00, and 6.07 μ for cyclopentanone oxime, cyclohexanone oxime, and cycloheptanone oxime respectively. The steady increase in the wave length (absorptions of energies of lower levels) with increase in ring size is similar to the C=O absorption shift of the cyclic ketones and may be due to the decrease in ring strain (11). The fact that the location of these absorptions is roughly the same as in the corresponding ketones suggests that there is

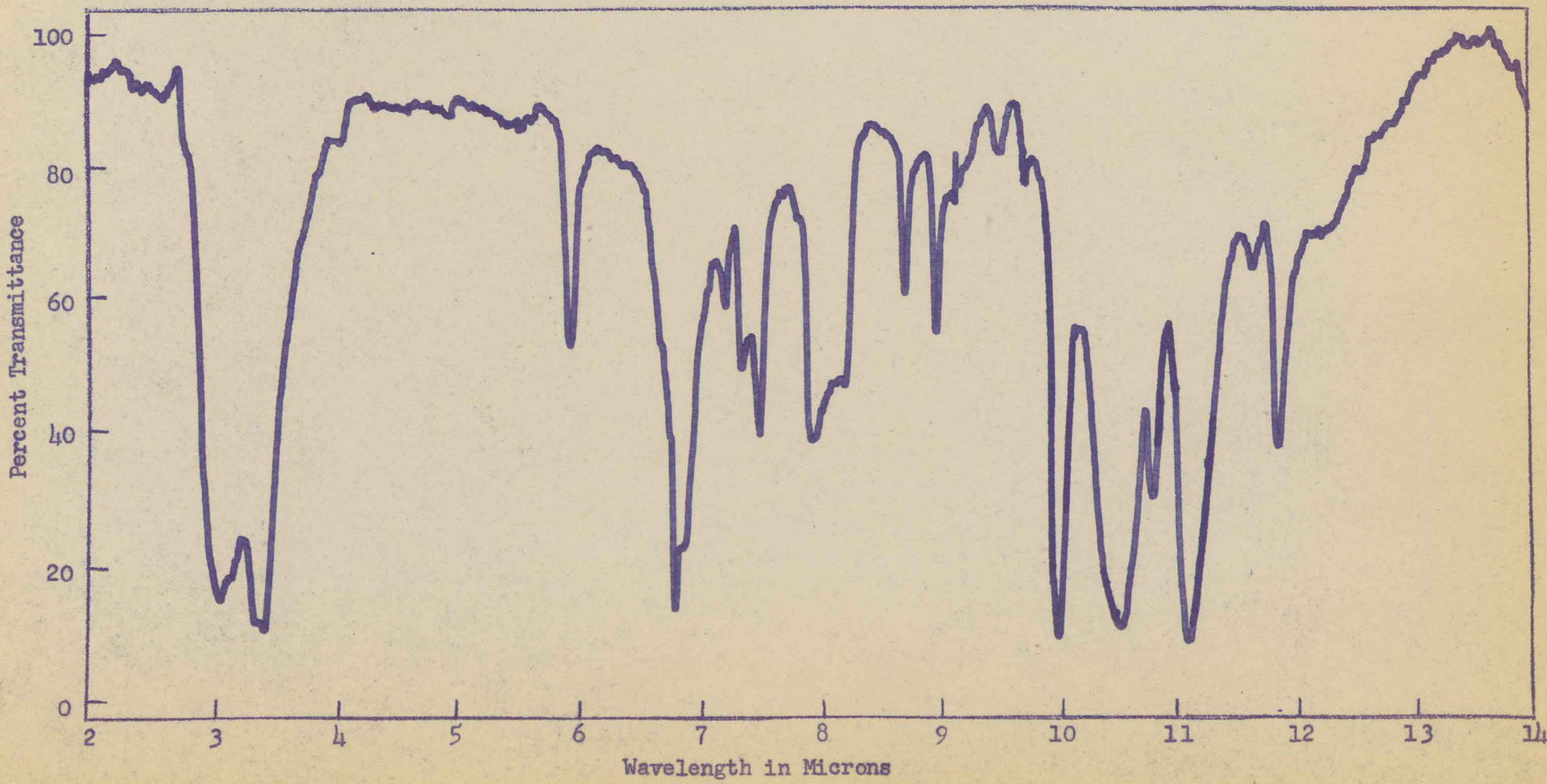
CYCLOPENTANONE OXIME





CYCLOHEXANONE OXIME





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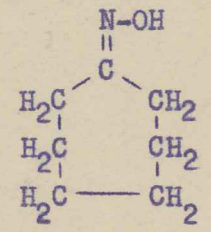
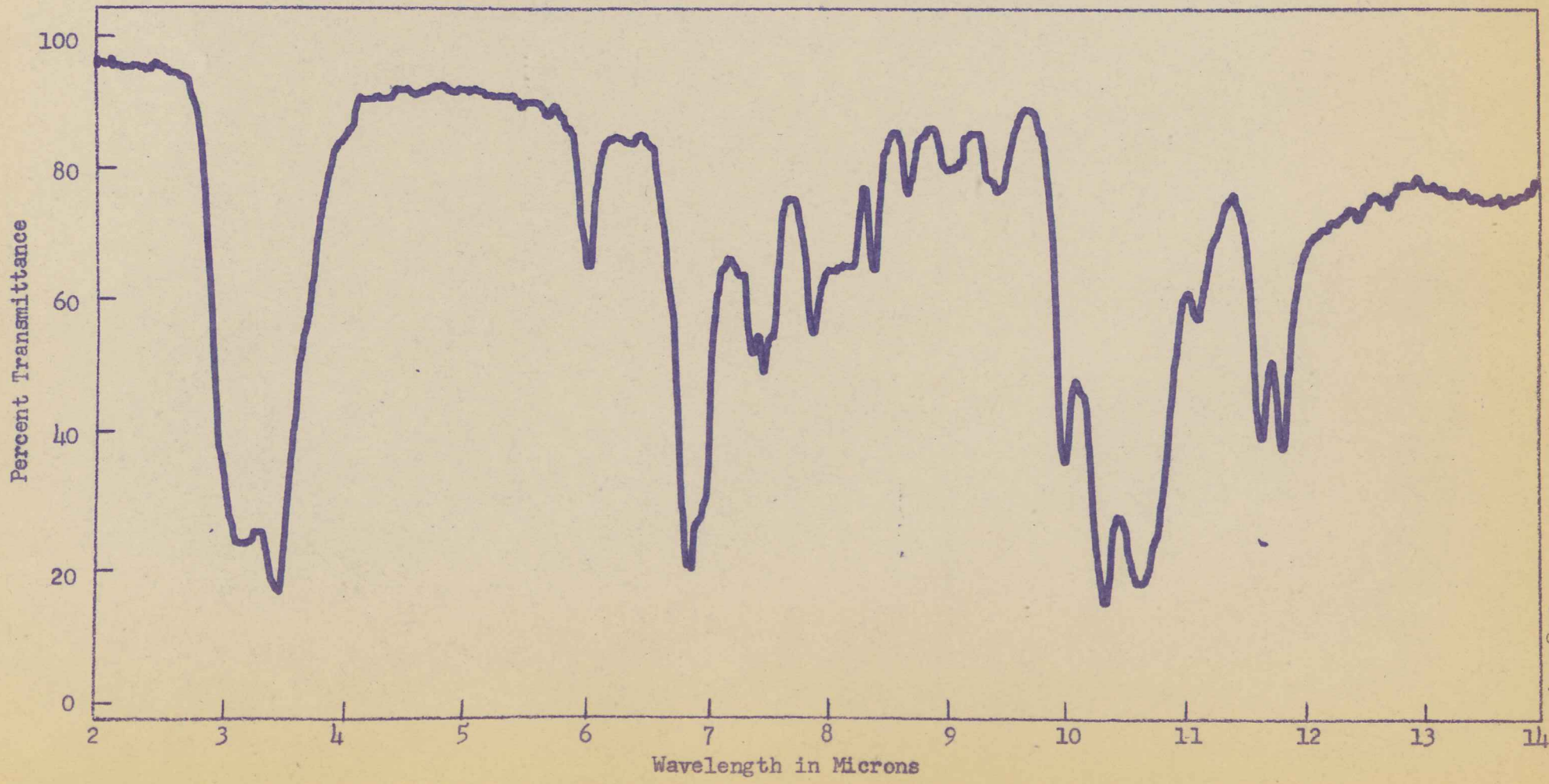




some correlation between the carbonyl absorption and the oxime absorption. This would bring to mind the possibility of a keto tautomer of the oxime (i.e., ). However, since nitroso alkanes are highly colored this seems unlikely since oximes are colorless.

The N-O absorption is found at 10.70 μ for cyclopentanone oxime, 10.62 μ for cyclohexanone oxime, and 10.66 μ for cycloheptanone oxime (12).

It was first believed that absorption located in the 4.12 μ region was caused by intermolecular hydrogen bonding of the hydroxyl group to the unshared electrons of the nitrogen of another molecule. During further investigation, however, this same absorption was found in the spectrum of a disubstituted amide where hydrogen bonding would be impossible. The present theory concerning this absorption, therefore, is that it is probably a harmonic of a fundamental located at approximately 8.15 μ. In the case of cyclopentanone oxime the harmonic appears at 4.10 μ and the fundamental at 8.13 μ, in cyclohexanone oxime at 4.12 μ and 8.14 μ, and in cycloheptanone oxime at 4.11 μ and 8.15 μ.

Lactams

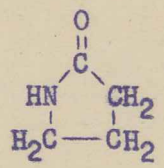
The problem of emulsions during the chloroform separation of the three lactams prepared by the Beckman rearrangement can be explained by water solubilities: as the molecule becomes larger, its water solubility decreases and its emulsifying power lessened. Further indication of decreasing water solubility with increasing molecular weight (or ring size) is the relative yields of these three compounds where their isolation depends on a chloroform extraction from an aqueous solution.

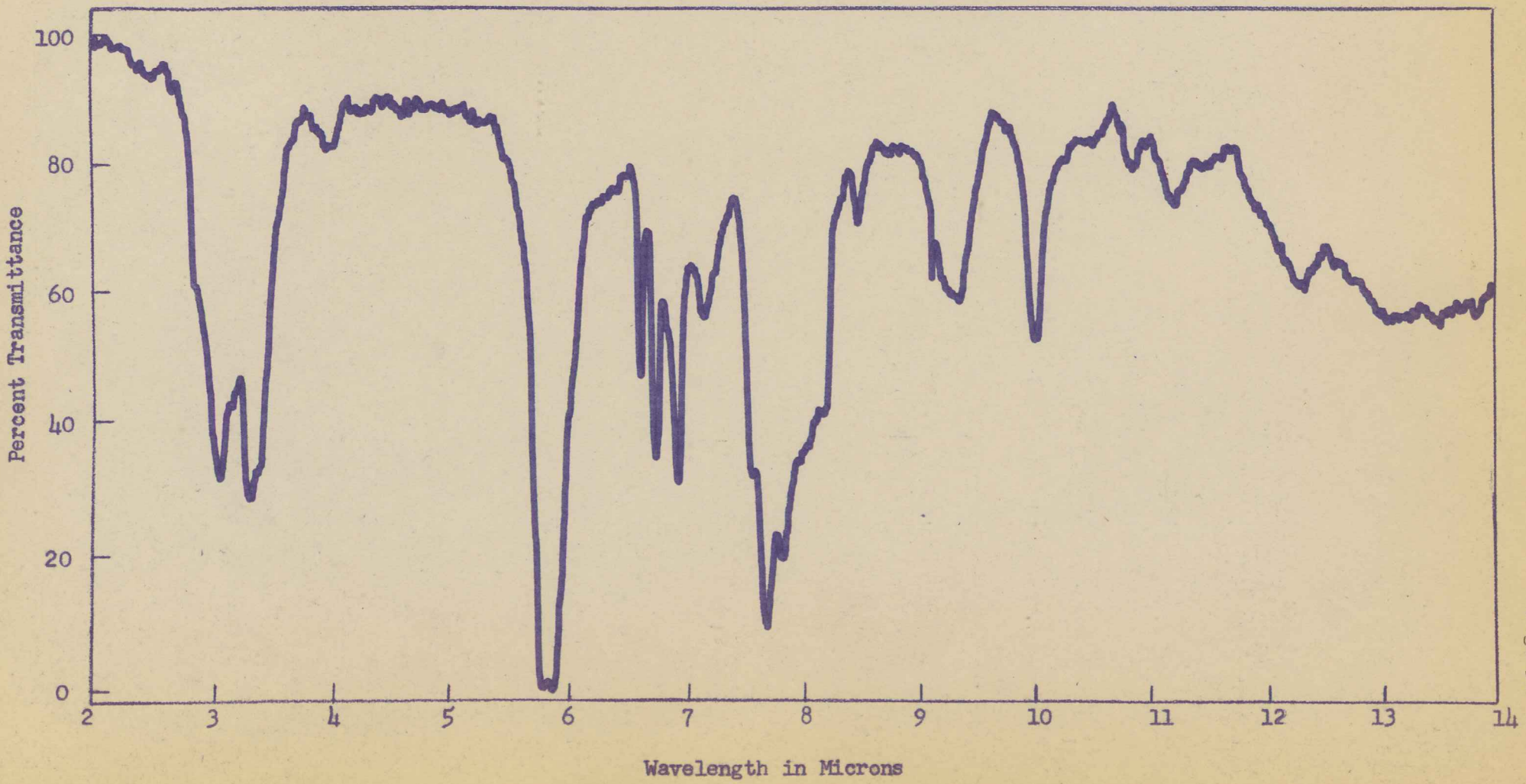
Previous work with infrared spectra of lactams concerned only the location of the carbonyl stretching absorption (13).

The carbonyl C=O stretching vibration of the lactams absorbs energy of a longer wave length than that of the corresponding cyclic ketones. For example, the carbonyl absorption is located at 5.90 μ for ω-butyrolactam (55-29), at 6.05 μ for ω-pentanolactam (55-19), at 6.00 μ for ω-hexanolactam (55-18), and at 6.05 μ for ω-heptanolactam (55-20). Since all amides exhibit a very strong carbonyl absorption in the range of 6.0-6.2 μ (14), the values for the three largest lactams agree well with regular amide carbonyl absorptions even though there is a definite shift toward longer wave length as compared with the carbonyl absorption in the corresponding ketones. The smallest lactam studied shows this absorption to be below the lower limits expected for amides and is probably attributable to ring strain. The lower wave length absorption of the carbonyl group in ω-butyrolactam shows that there is more C=O double bond character, and therefore less amide resonance, due without doubt to ring strain inhibiting this resonance. The fact that N-methyl-2-pyrrolidone has a carbonyl more nearly that of the other lactams would indicate that the inductive effect of the methyl group overcomes this lowered resonance to some degree.

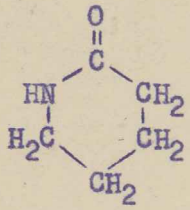
In studying the lactams it is not surprising to find that the harmonics of the carbonyl stretching absorptions appear in the lactam spectra as they do in the cyclic ketone spectra. The harmonic absorptions are located at 2.90 μ in the spectrum of ω-butyrolactam, at 2.94 μ in ω-pentanolactam, at 2.94 μ in ω-hexanolactam, and at 2.94 μ in ω-heptanolactam. From the spectra it appears uncertain if any enolization occurs in the lactam carbonyl since

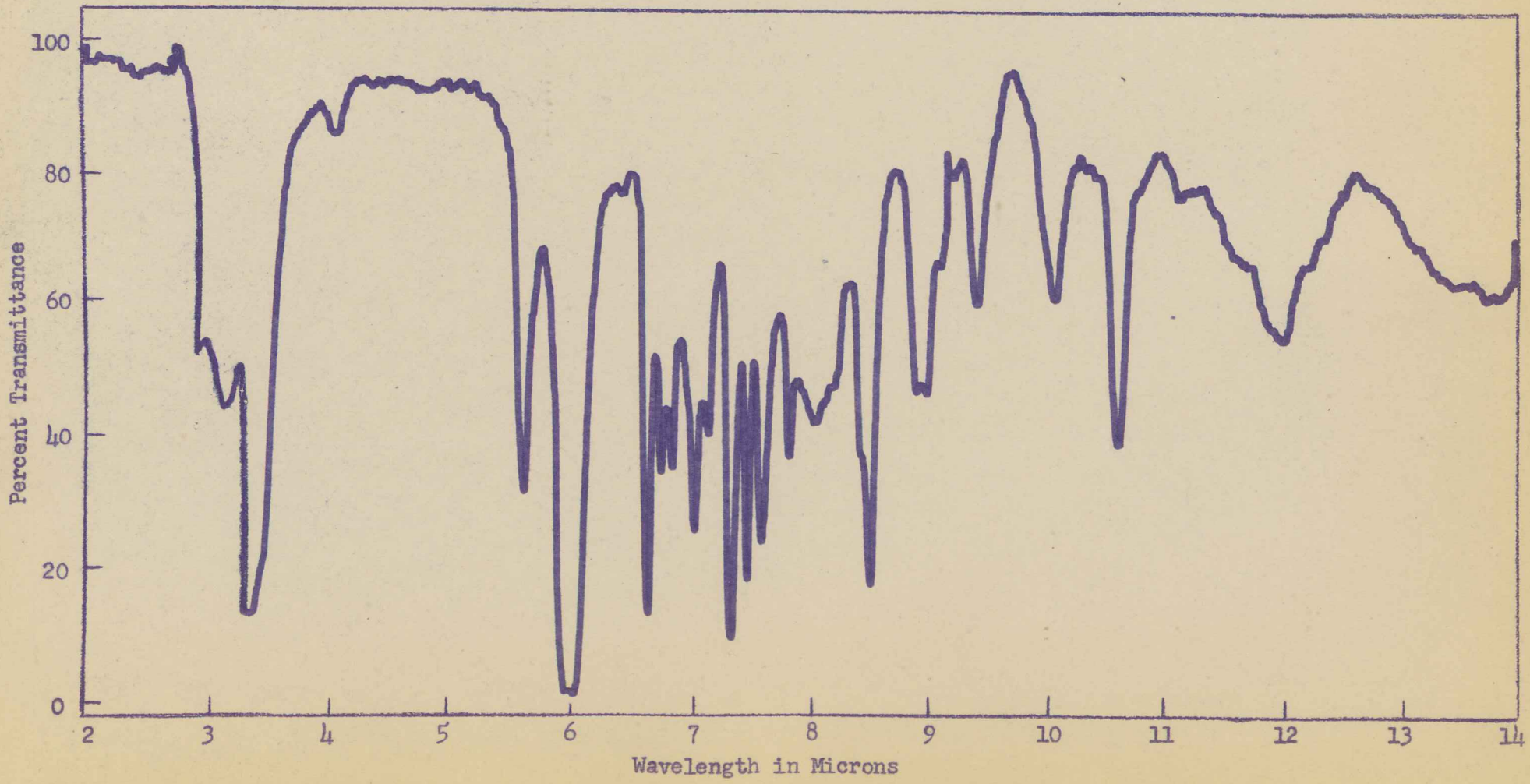
ω — BUTYROLACTAM
(2-PYRROLIDONE)



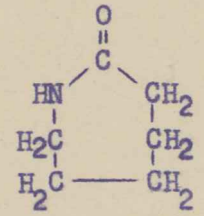


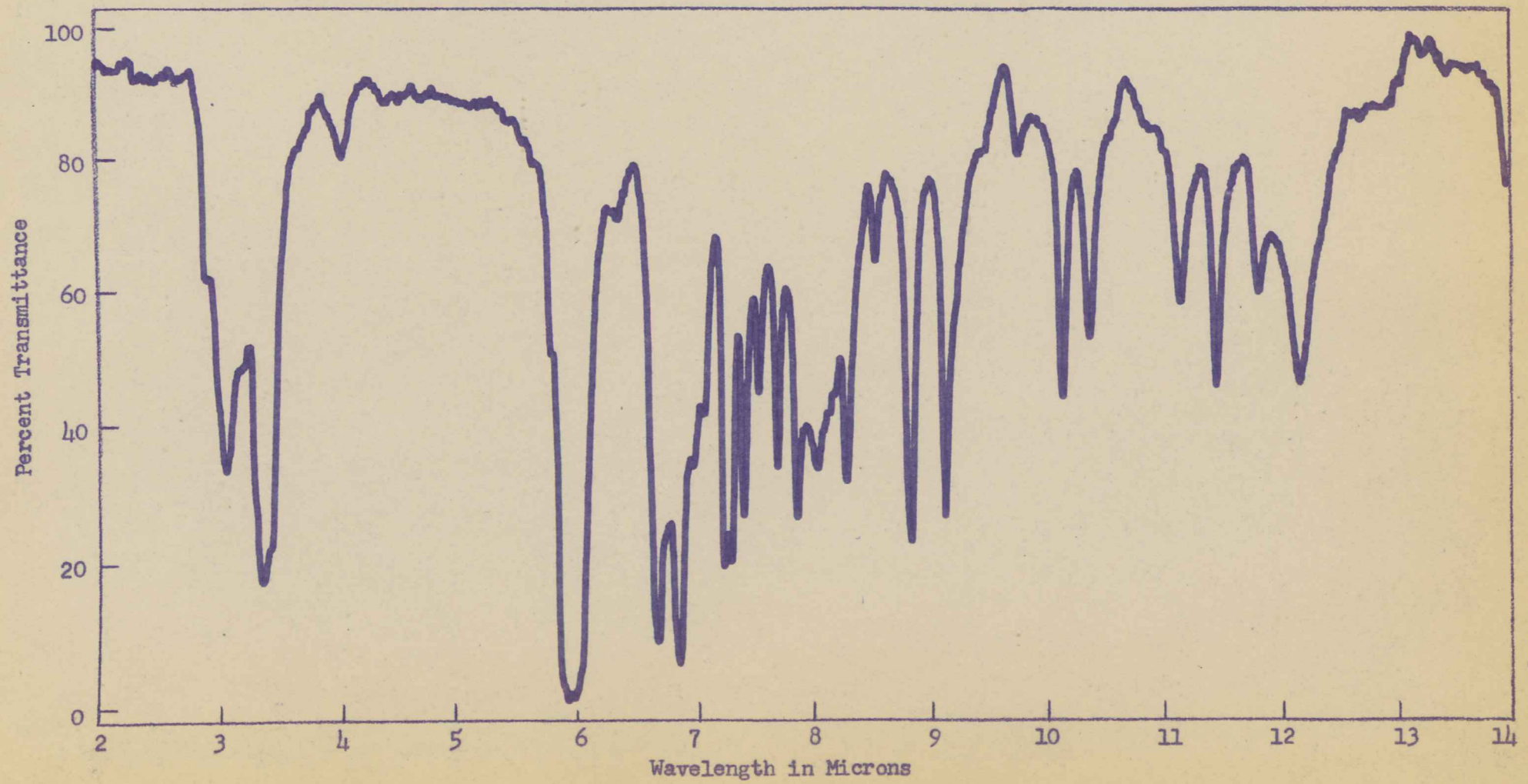
ω – PENTANOLACTAM
(VALEROLACTAM)



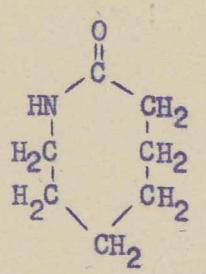


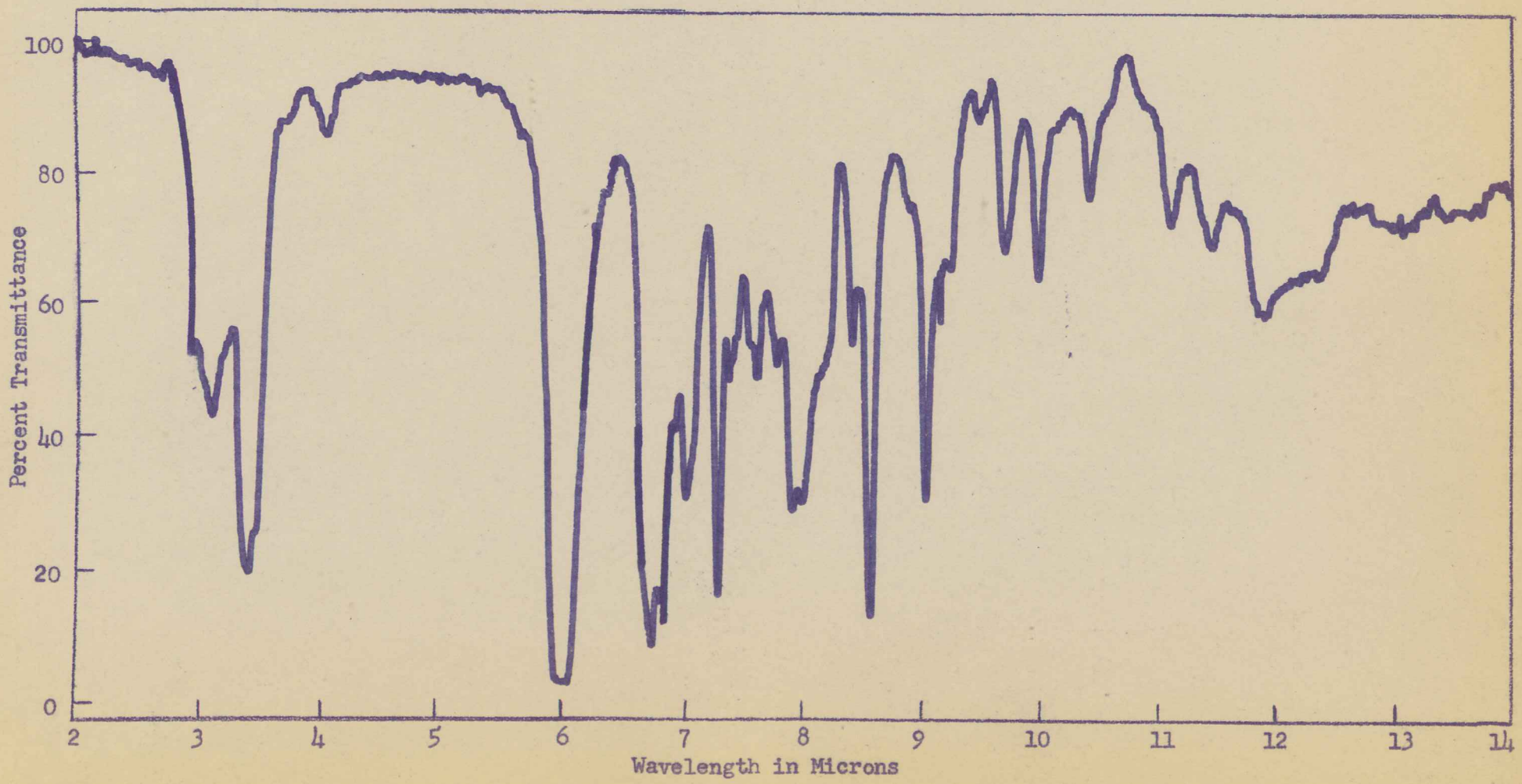
ω – HEXANOLACTAM
(CAPROLACTAM)





ω – HEPTANOLACTAM





the only absorption that could possibly be associated with an O-H vibration would appear at the same location as the harmonic of the carbonyl absorption.

An absorption which has not been encountered earlier during this investigation of the ketones or oximes is the absorption caused by the N-H stretching vibration in the lactams. In reality there are usually two absorptions for secondary amides in concentrated solution--one caused by the free unassociated N-H stretching vibration and a second at a longer wave length caused by the associated (intermolecular hydrogen bonded) N-H stretching vibration. In the case of ω-butyrolactam the free absorption and the associated absorption are located at 3.02 and 3.12 μ respectively; similarly these occur in ω-pentanolactam at 3.05 and 3.13 μ, in ω-hexanolactam at 3.05 and 3.10 μ, and in ω-heptanolactam at 3.05 and 3.12 μ.

Not only is the N-H stretching vibration to be found within the region of investigation, but also the N-H bending vibration. Whether this vibration causes an absorption in the case of cyclic lactams is a subject of much question (15) (16). In the case of primary amides, the N-H bending vibration causes absorption close to the carbonyl absorption and usually on the side of longer wave length, but some compounds show the location to be of lower wave length than the carbonyl (17). It appears that such a shift may exist in these lactam spectra. If this were the case, what had appeared to be an absence of the absorption might actually be a shift to an unpredicted location. On the basis of this theory the N-H bending absorption might appear at 6.08 μ in ω-butyrolactam, at 5.65 μ in ω-pentanolactam, at 5.84 μ in ω-hexanolactam, and at 6.23 μ in ω-heptanolactam. The shift of the N-H bending absorption

might be caused by the interference of the C-H groupings neighboring the N-H, therefore allowing the N-H of ω-heptanolactam more freedom for bending than that of the more hindered ω-pentanolactam. However, this is only speculation, and these absorptions might be addition or difference tones.

The absorption caused by the C-N stretching vibration is a little better understood and will usually be located within the range 6.4-6.6 μ (18). In all four lactams being investigated absorption appears at slightly longer wave length (6.69 μ), which may be due to C-N stretch.

The absorptions caused by the C-H stretching and bending vibrations are located in the expected positions. In ω-butyrolactam the stretching vibrations absorb at 3.38 and 3.46 μ while the deformation absorptions are located at 6.82 and 7.00 μ; in ω-pentanolactam the stretching absorptions appear at 3.40 and 3.47 μ and the bending absorptions at 6.80 and 6.90 μ; in ω-hexanolactam the stretching absorptions appear at 3.43 and 3.50 μ while the deformation absorptions are located at 6.75 and 6.95 μ; and in ω-heptanolactam the stretching absorptions appear at 3.44 and 3.50 and the bending absorptions at 6.80 and 6.90 μ.

The bending absorptions of the C-H bonds in the CH_2 group adjacent to the carbonyl also appear in the lactams as they did in the case of the cyclic ketones. In ω-butyrolactam this absorption appears at 7.03 μ, in ω-pentanolactam at 7.08 μ, in ω-hexanolactam at 7.05 μ, and in ω-heptanolactam at 7.08 μ.

As in the spectra of the oximes, the 4.10 μ absorption appears in the lactams, too. In ω-butyrolactam this absorption is located at 4.06 μ, in ω-pentanolactam at 4.05 μ, in ω-hexanolactam at 4.07 μ, and in ω-heptanolactam

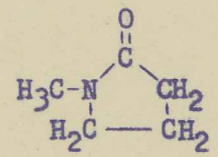
at 4.06μ . These absorptions can be explained as harmonics of the fundamental absorptions located in the 8.15μ region.

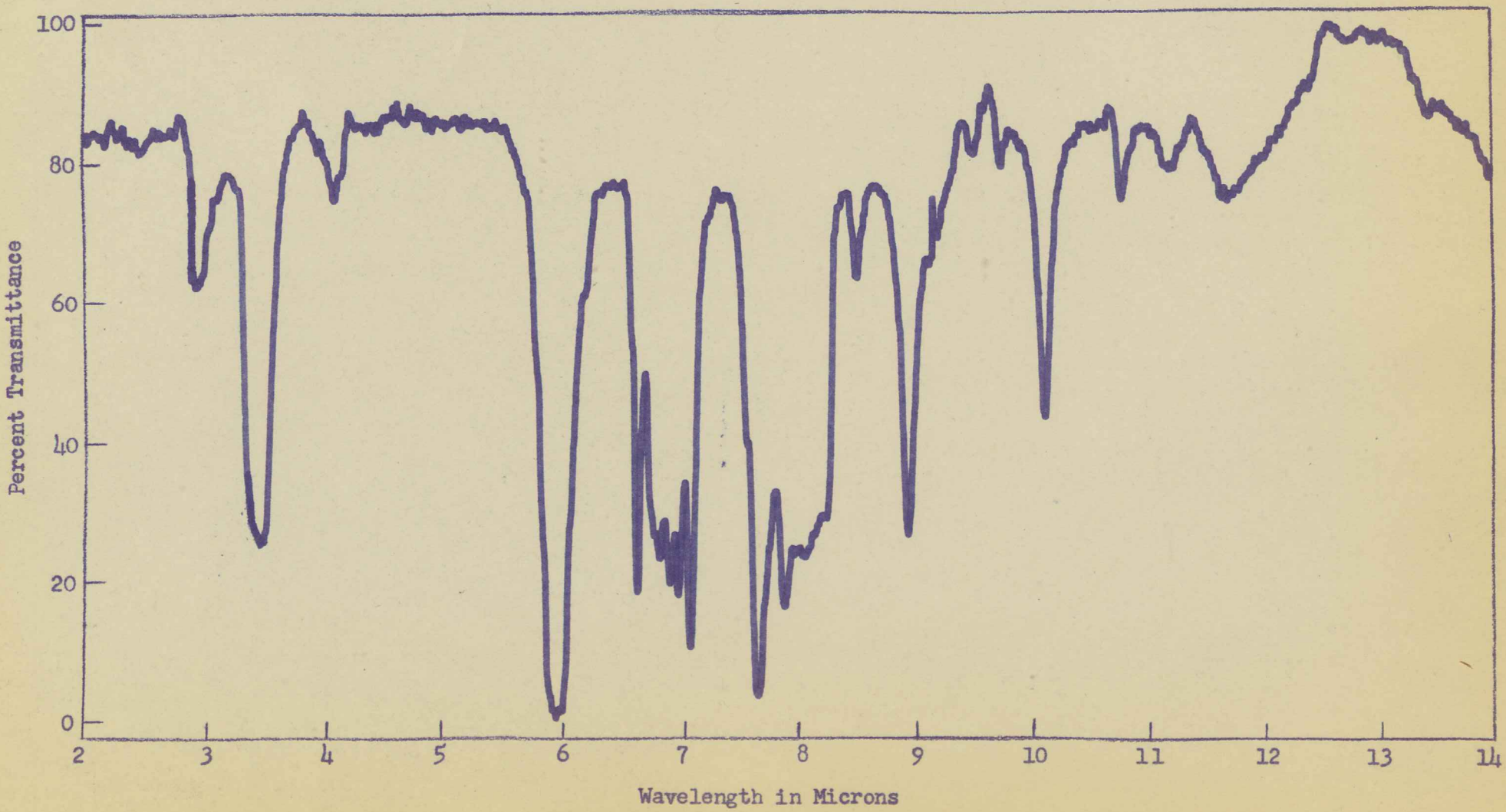
For purposes of comparison the spectra of two other amides were made. N-methyl-2-pyrrolidone was used, as a 1.00 molar solution in chloroform, and acetamide was used as both a .714 molar solution and .200 molar solution in chloroform. As would be expected, the N-methyl-2-pyrrolidone (55-30) shows no N-H vibrational absorptions since it is a disubstituted amide. The .714 molar acetamide (55-31) does show the free N-H absorption at 3.02μ and the associated N-H absorption at 3.15μ . The reduction in concentration of the acetamide to .200 molar (55-32) shows that both the unassociated and the associated N-H bonds still are present at 3.00μ and 3.16μ respectively.

The very strong C=O stretching vibration does cause the expected absorption at 6.00μ for N-methyl-2-pyrrolidone, at 6.00μ for .714 molar acetamide, and at 5.95μ for the .200 molar acetamide. There is an upward shift in the wave length of absorption in N-methyl-2-pyrrolidone as compared with ω - butyrolactam itself. This suggests that the inductive effect of a methyl group (increasing resonance stabilization of an ionic carbonyl) causes longer wave length absorption (less double bond character) of the C=O carbonyl group.

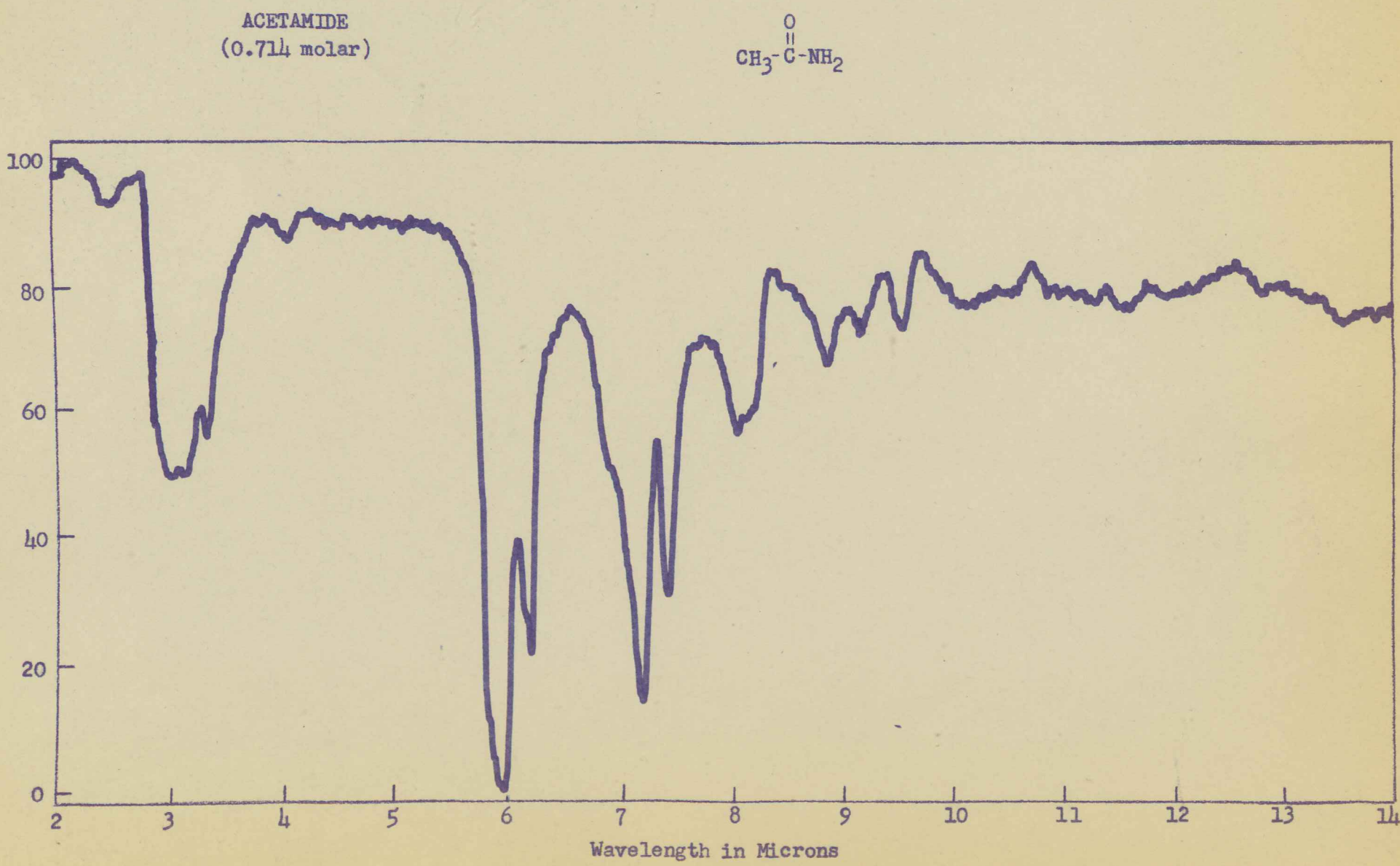
The usual two C-H stretching absorptions (in-phase and out-of-phase) appear in the spectrum of N-methyl-2-pyrrolidone at 3.43 and 3.48μ . In the case of acetamide where there are no CH_2 groupings but only CH_3, the two C-H absorptions are caused by asymmetrical and symmetrical modes of vibration rather than the in-phase and out-of-phase modes of vibration (19). For

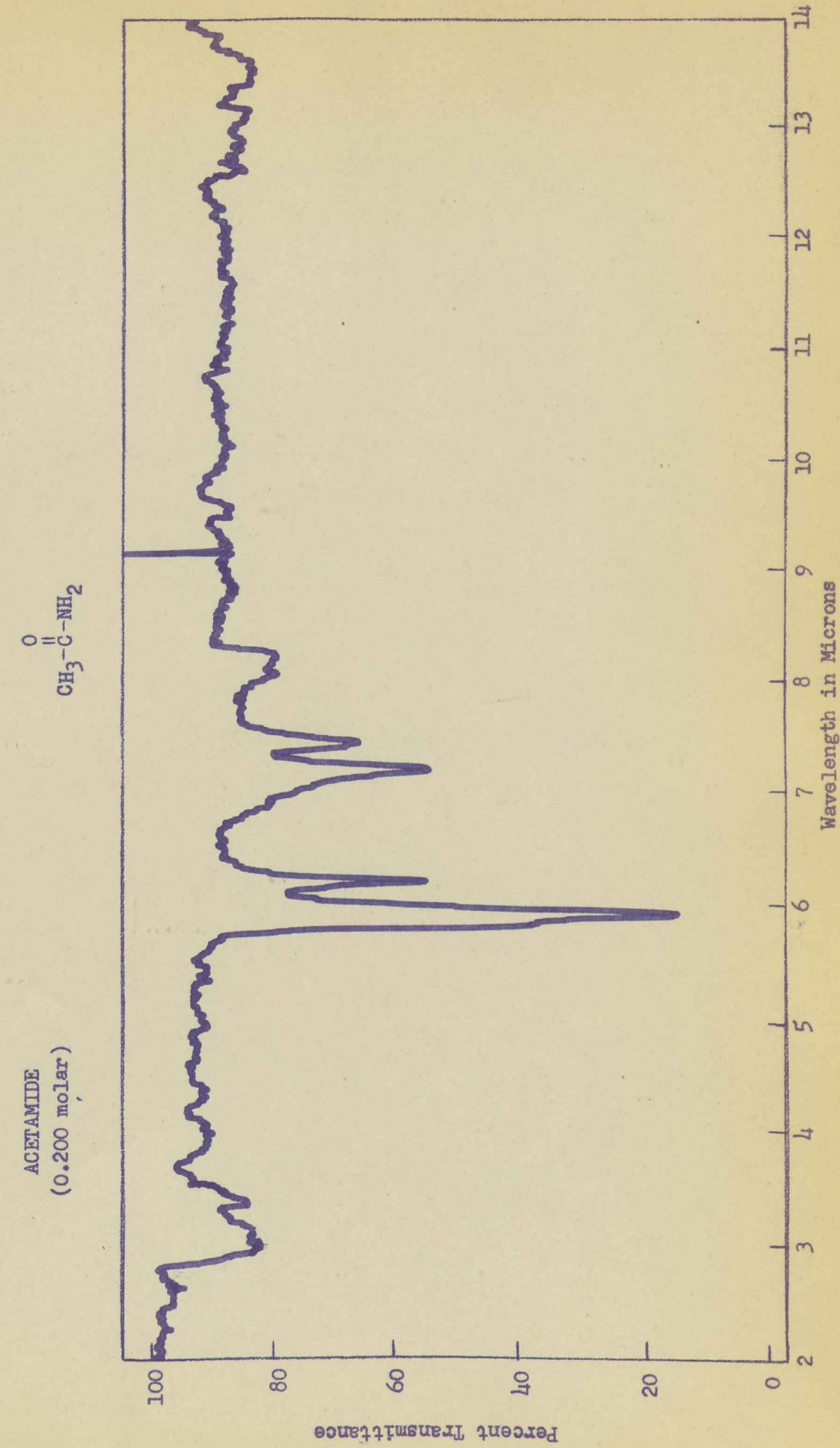
N-METHYL-2-PYRROLIDONE





ACETAMIDE
(0.714 molar)




ACETAMIDE
(0.200 molar)
O
CH3-C-NH2
Percent Transmittance
100
80
60
40
20
0
2
3
4
5
6
7
8
9
10
11
12
13
14
Wavelength in Microns

example, in the spectrum of .714 molar acetamide the two are located at 3.35 and 3.39 μ , and in .200 acetamide at 3.36 and 3.44 μ . The differences are apparently only due to solvation effects in this case of concentration differences.

The spectra of the three show the C-N absorption to be located at the expected wave length region. N-methyl-2-pyrrolidone has its C-N absorption at 6.65 μ , .714 and .200 molar acetamide solutions both at 6.71 μ .

It will be noted that the N-H bend appears in the acetamide (both concentrations) at 5.85 μ , but is naturally absent of the N-methyl-2-pyrrolidone spectrum.

The spectrum of the N-methyl-2-pyrrolidone has the 4.08 μ absorption; this supports the proposal that the 4.10 μ absorption is probably a harmonic. Since there are no N-H bonds in this compound, no hydrogen bonding can exist. This absorption appears in the unsubstituted .714 molar acetamide at 4.08 μ and in the .200 molar acetamide at 4.07 μ .

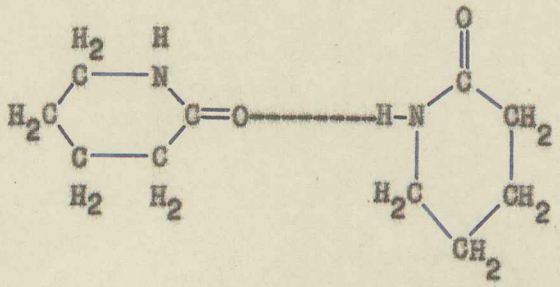
The other absorptions of these three spectra coincide well with absorptions of the ketones, oximes, and lactams previously investigated (C=O harmonics, C-H bend, etc.).

Summary and Conclusions

The following compounds have been prepared: cyclopentanone, cycloheptanone, cyclopentanone oxime, cyclohexanone oxime, cycloheptanone oxime, ω-butyrolactam, ω-pentanolactam, ω-hexanolactam, and ω-heptanolactam. Both cycloheptanone oxime and ω-heptanolactam have been prepared for the first time as far as a literature search reveals. Infrared spectra of the above compounds were made with a model 21 Perkin-Elmer Infrared Spectrophotometer.

The investigation of the infrared absorption spectra of the four lactams and related compounds has lead to several conclusions concerning their structure:

1. The infrared spectra indicate that no intermolecular hydrogen bonding (as in an enol form) exists in cyclopentanone, cyclohexanone, or cycloheptanone. On the other hand, their oxime derivatives showed almost exclusively the hydrogen-bonded O-H absorption.
2. The infrared absorption spectra indicate that the molecules of a lactam (as well as an unsubstituted amide) are held together in solution by intermolecular hydrogen-bonding:



This is true for ω-butyrolactam, ω-pentanolactam, ω-hexanolactam, ω-heptanolactam, and acetamide.

3. No definite conclusion could be reached as to enol content in the cyclic ketones studied because the carbonyl harmonic obscured the region of hydroxyl absorption.
4. No definite conclusion could be reached as to enol content in the lactams studied because the carbonyl harmonic obscured the region of hydroxyl absorption.
5. In the spectrum of a lactam, an unsubstituted amide, a monosubstituted amide, a disubstituted amide, or an oxime, a weak absorption will probably appear in the range of 4.05-4.15 μ which is the harmonic of an absorption located at approximately 8.15 μ. This is true of all such compounds investigated here.
6. Finally, the lower wave length absorption of the carbonyl group in ω-butyrolactam shows that there is more C=O double bond character, and therefore less amide resonance. The fact that N-methyl-2-pyrrolidone has a carbonyl more nearly that of the other lactams shows that the inductive effect of the methyl group overcomes this lowered amide resonance of the five membered ring to some degree.

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