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A qualitative study of the "Bohlmann Band"

John Alfred Richman Jr.

A QUALITATIVE STUDY

OF THE

"BOHLMANN BAND"

BY

JOHN ALFRED RICHMAN, JR.

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APPROVED:

W. Allan Powell
J. Gordon Pierce
Wm E. Trout, Jr
Richard A. Mateer
W M Scanlon

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DEDICATION

This Thesis is dedicated to my wife, Susan, and son, Christopher, whose company was an encouragement in the completion of this study.

ACKNOWLEDGMENT

I wish to express my gratitude to Dr. W. Allan Powell for his enthusiasm and guidance during this study.

I appreciate the aid and helpful criticism offered by the chemical research staff of the A. H. Robins Company.

I also wish to express my gratitude to the A. H. Robins Company for permitting the use of their instruments and laboratory facilities to implement this study.

Thanks are offered to Miss Barbara Allen for the drafting of Figure III.

Finally, I wish to express my sincere thanks to Mrs. Anne H. Carnefix who so kindly offered to type this thesis.

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INTRODUCTION

This thesis is concerned with a qualitative study of the "Bohlmann Band", a result of C-H stretching frequencies, which is often observed in the 3.57 to 3.70 μ region in the infrared absorption spectra of amines. The appearance of this band is characteristic of tertiary amines although a few exceptions have been encountered.

The criteria for this band are that there be at least two protons on carbon atoms adjacent to a nitrogen so oriented that they are <u>trans</u> and <u>co-planar</u> to the unshared electron pair of the nitrogen. This requires an environment in which the lone pair of electrons on the nitrogen not be delocalized.

Primary and secondary amines are conveniently recognized by the characteristic N-H stretching frequencies; however, little effort has been undertaken to facilitate

the identification of tertiary amines through a convenient and reliable characteristic absorption band in the infrared spectrum.

The object of this study was to illustrate the occurrence of the "Bohlmann Band" in the infrared spectra of tertiary amines in comparison with primary and secondary amines, and to evaluate and discuss the criteria believed necessary for its appearance, the exceptions and limitations encountered, and the significant features of applying this information to the qualitative aspects of synthetic organic chemistry.

It was the intent of the author to show that the "Bohlmann Band" may serve as a simple, reliable, and readily available source of information pertinent to the progress of reactions, identification of products, illucidation of structure and conformation in the chemistry of tertiary amines.

As a matter of convenience the absorption band positions throughout this study will be expressed in terms of wavelength in microns.

HISTORICAL

I. Advent and Development of Infrared Spectroscopy

The design and application of the first single beam infrared spectrophotometer employing a sodium chloride prism was credited to Coblentz in 1908 (13). Two years later Wood and Trowbridge (23) introduced the echelette grating which spurred the design of a high resolution grating spectrophotometer by Randall and Sleator (23). The successive improvements of the optical system, employment of an a.c. detecting network, and development of the sensitive thermocouple resulted in the first double beam spectrophotometer in 1945.

Ten years later Grubb Parsons (23) introduced the first wide range prism / grating spectrophotometer which was modified to a wide range filter / grating double beam spectrophotometer and introduced by Perkin-Elmer in 1961.

Through innumerable improvements and modifications, infrared spectrophotometers have been placed within reach of most organic chemists and it is anticipated that further improvements, coupled with the widespread use of modern computers, will aid in the advances of spectroscopy.

II. Concept of Characteristic Group Frequencies

The organic chemist often relies upon the very limited portion of infrared radiation between 2.5 μ and 15 μ for much of the information pertinent to the structural characteristics of organic molecules. This is the region in which infrared radiant energy is absorbed by the organic molecule and converted into molecular vibrational and rotational energy giving rise to absorption bands when plotting the intensities versus frequency or wavelength.

As long ago as the 1880's it was known to chemists (2) that the presence of a certain grouping of atoms in a molecule was accompanied by the presence of an absorption band at a particular wavelength in the infrared spectrum of the molecule. Through the efforts of Coblentz (13) in 1928, this concept of characteristic group frequencies was established. The present popularity of the use of

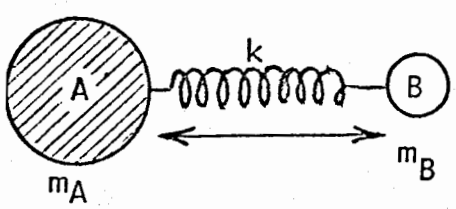
infrared spectroscopy is attributed to this concept of applying empirical relationships which provide information related to certain functional groups simply by a rapid observation or reference to available charts.

III. A Brief Elementary Theory of Infrared Spectroscopy

Infrared radiation promotes rotational and vibrational energy transitions in a molecule between levels of the ground electronic energy state as differentiated from the transitions of different electronic levels found with ultra-violet radiation.

Considering only the vibrational energy, the simplest set of conditions occurs when the group consists of a pair of atoms AB, as shown in Figure I ., one of which A, is chemically bound only to B. Under this set of conditions the molecule AB will exhibit the so-called AB stretching vibration in which B will vibrate along the AB axis and A will move very little.

Figure I.



Assuming that the remainder of the molecule exerts little influence on the bond motion under consideration, application of Hooke's law, Equation 1, to this simple diatom gives the frequency, ν, in CM^{-1} of the vibration (approximately within 5%). Conversion of the frequency in CM^{-1} to wavelength in microns is made by applying the relationship, $\lambda_{microns} = \frac{1}{CM^{-1} \times 10^{-4}}$.

Hydrogen stretching vibrations serve as a good example of this model.

$$\nu = (k/4\pi^2 c^2 m_r)^{\frac{1}{2}} \qquad (1)$$

ν is the frequency of vibration in cm^{-1}

k is the force constant of the AB bond in dynes/cm

c is the velocity of light in cm./sec.

m_r is the reduced mass in grams where $m_r = m_A m_B / m_A + m_B$

Substitution in equation (1) of the accepted numerical values of $c = 3 \times 10^{10}$ cm./sec., $k = 5 \times 10^5$ dynes/cm., $m_C = 19.8 \times 10^{-24}$ g., and $m_H = 1.64 \times 10^{-24}$ g. for the C-H bond, gives a frequency of 3040 cm^{-1} or 3.30 μ which is in acceptable agreement with the experimentally observed wavelength of 3.36 to 3.39 μ and 3.47 to 3.50 μ for the C-H stretching vibrations of the methyl group.

Calculations of this type approach the greater

accuracy when the atoms joined by the bond are of significant mass differences and influences by the remainder of the molecule are insignificant.

From the example shown it is evident why the A-H stretching vibrations are among the most thoroughly studied and valuable bands for qualitative applications.

IV. Carbon-hydrogen Stretching Vibrations

A. C-H Stretching Vibrations in Normal Hydrocarbons

The infrared spectra of normal hydrocarbons is a result of four types of bond vibrations, namely, the stretching and bending modes of C-H and C-C bonds. This study is concerned only with the stretching modes of vibration exhibited by C-H bonds. The C-H bending vibrations are not pertinent to the region of the infrared spectrum considered in this study; however, they may be relied upon as an additional aid in structural assignments.

The C-H stretching vibrations are considered to be the most stable in the infrared spectrum even though they are subject to structural, environmental, and conformational influences. Reference is made here to the illustrations in Table 1 .

Table 1

CARBON-HYDROGEN STRETCHING VIBRATIONS*

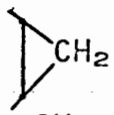
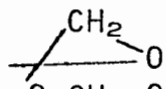
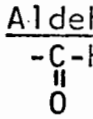
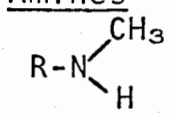
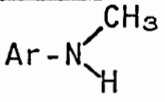
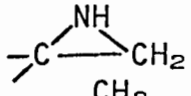
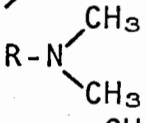
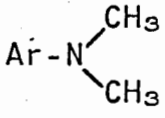
Group	Range μ	Intensity	Assignment
Alkanes			
$-CH_3$	3.36-3.39	m	CH_3 asym.
	3.47-3.50	m	CH_3 sym.
$-CH_2-$	3.40-3.45	m	CH_2 asym.
	3.49-3.52	m	CH_2 sym.
	3.25-3.29	v	CH_2 asym.
-CH-	3.45-3.47	w	CH str.
Alkenes			
$CHR_1=CH_2$	3.23-3.25	m	CH_2 asym.
	3.29-3.32	m	CH_2 sym.
$CHR_1=CHR_2$	3.29-3.32	m	CH str.
$CR_1R_2=CHR_3$	3.29-3.32	m	CH str.
$CR_1R_2=CH_2$	3.23-3.25	m	CH_2 asym.
Alkynes			
R-C≡CH	3.02-3.03	m	CH str.
Ethers			
$-O-CH_3$	3.53-3.55	m	CH_3 sym.
	3.27-3.29	v	CH_2 asym.
$-O-CH_2-O-$ (benzenic)	3.57-3.61	v	CH_2 sym.
-CH=C-O-	3.18-3.28	w	CH str.
Aldehydes			
	3.47-3.77	w-m	CH str.
Amines			
	3.56-3.62	m-s	CH str.

Table 1 (continued)

Group	Range μ	Intensity	Assignment
Amines			
	3.54-3.56	m-s	CH str.
	ca. 3.28	m	CH str.
	3.54-3.56 3.60-3.62	m-s m-s	CH str. CH str.
	ca. 3.57	m-s	CH str.
Pyridines and Quinolines			
=C-H	3.26-3.31	s	CH str.
Pyrimidines and Purines			
=C-H	3.27-3.32	s	CH str.

* Abbreviations: s = strong, m = medium, w = weak, v = variable

The overall range of C-H stretching vibrations for hydrocarbons is from 3.02 to 3.52 μ. This range includes alkynes, alkenes, and alkanes. Although the range is well defined, the exact wavelength at which a particular C-H bond absorbs infrared radiation is dependent upon the environment within the molecule and its physical state.

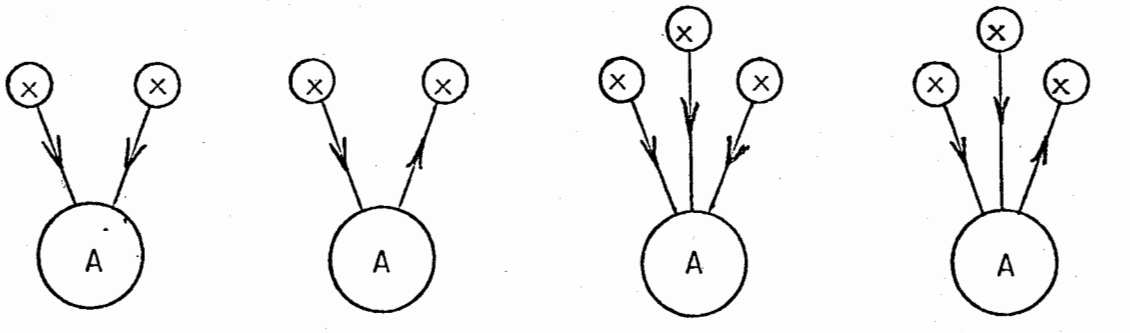
B. Influences on C-H Stretching Vibrations

1. Modes of C-H Stretching Vibrations

The possible stretching vibrational modes for the C-H bonds in hydrocarbons may best be illustrated by referring to Figure II .

Figure II

Stretching Vibration Modes



AX_2 Symmetrical Stretching

AX_2 Asymmetrical Stretching

AX_3 Symmetrical Stretching

AX_3 Asymmetrical Stretching

A stretching vibration is one in which the distance between the two atoms is increased or decreased along the bond axis resulting in a rythmical change in the dipole moment of the molecule which is required in order to be observed in the infrared spectrum. Thus the absorption of energy in the infrared spectrum is a result of the net change in charge distribution within the molecule and the impressed oscillating radiation field.

The bending or deformation modes of vibration were not considered in this study since more energy is required to stretch a bond than to change its angle, and we find these stretching vibrations occurring at longer wavelengths than the region concerned in this investigation.

To illustrate the stretching vibrational modes shown in FigureII, we may note that an examination of a large number of saturated hydrocarbons containing methyl groups showed two distinct bands occurring at 3.38 μ and 3.48 μ in all cases. The band at 3.38 μ has been assigned as the AX_3 asymmetric stretching mode in which two C-H bonds of the methyl group are stretching while the third is contracting. The second band appearing at 3.48 μ arises from an AX_3 symmetrical stretching mode in which all three C-H

bonds expand and contract in phase.

A methylene group gives rise to an AX_2 asymmetrical stretching mode at 3.43 μ and an AX_2 symmetrical stretching mode appearing at 3.51 μ.

It is also of interest to note that the positions of these stretching bonds do not vary more than $\pm$ 0.01 μ in aliphatic hydrocarbons and non-strained cyclic hydrocarbons reflecting the value of these bonds for qualitative information on molecular structure. The carbon-hydrogen stretching vibrations in alkanes are illustrated in Table 1.

2. Environmental Effects on C-H Stretching Vibrations

Thus far the C-H stretching vibrations of alkanes free from strain have been considered. There are other factors, both internal and external with respect to the molecule, which may exert influence on the absorption bands; such as, electrical effects, steric effects, the nature, size and electronegativity of neighboring atoms. Phase changes and hydrogen bonding may also cause shifts in the characteristic absorption bands.

Multiple bond and C-H bond stretching absorption bands are least affected by internal structural changes, thus

they become valuable for correlation; however, under certain conditions a shift is noted. As an example the C-H stretching bond is shifted to a shorter wavelength (higher frequency) when the methylene group is part of a strained ring system.

The presence of a double bond adjacent to a methyl or methylene group produces splitting of the longer wavelength into a pair of bands whose mean wavelength is approximately the same as the non-split band.

It is of interest to note that the C-H stretching vibrations associated with a strained C=C bond vary regularly with the amount of strain.

Some interesting shifts in the C-H stretching vibrations are observed when an oxygen atom is adjacent to a methyl or methylene group. In a methoxy group the CH_3 symmetrical stretching vibration shifts from a range of 3.47 - 3.50 μ to a longer wavelength range of 3.53 - 3.55 μ.

For aldehydes the C-H stretching vibration shifts from a range of 3.45 - 3.47 μ to a range of 3.47 - 3.77 μ which is once again a shift to a longer wavelength. The apparent stability of the asymmetric CH_2 vibration in a cyclic three membered oxirane may possibly be due to a partial

cancellation of the effect of the oxygen by the strain of the ring. At any rate we now have evidence to confirm the effect of a change in the environment of the C-H bond brought about by an atom which differs from carbon in electronegativity.

Reference to Table 1 will aid in demonstrating some of the effects resulting in shifts of the C-H stretching vibrations and the observed magnitudes may be compared.

If oxygen can exert such an influence on the C-H stretching vibration, one should anticipate a similar effect if the atom adjacent to the C-H bond were nitrogen. This is clearly obvious from the examination of the amines in Table 1.

With the exceptions of the aziridine and unsaturated amines, the secondary and tertiary N-methylated amines exhibit an absorption band of wavelength greater than 3.53 μ. Obviously a unique phenomenon arises which warrants attention.

C. C-H Stretching Vibrations in Amines

For obvious reasons all C-H stretching vibrations in a complex molecule would lead to confusion by voluminous

impertinent material; therefore, only those C-H stretching vibrations associated with the carbons bonded adjacently to the nitrogen atom are being considered in this study except in instances where effects exerted by other functionalities are pertinent.

As of this writing there appears to have been no available description of the general trend of variation of the adjacent C-H symmetrical vibrations encountered in the infrared spectra of primary, secondary, and tertiary amines; however, reference to the information derived from this study indicates that, in general, the wavelength of the adjacent C-H stretching vibrations increases as one goes from primary to tertiary amines.

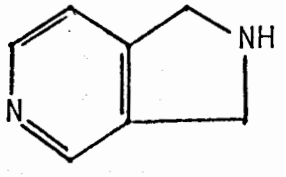
Absorption bands characteristic of the C-H stretching vibrations in amines have attracted attention only during the past few years although the first reported observation was a brief and erroneous conclusion by Colthup (14) in 1950. He concluded that the symmetric C-H stretching vibration of the methyl group, in the spectra of monomethyl and dimethylamines, shifted to a shorter wavelength.

Eight years later Hill and Meakins (18) reported on the spectra of a series of amines having monomethyl and

dimethylamino groups in aliphatic, aromatic, and heterocyclic systems and noted that bands appeared in the 3.54 to 3.62 μ range which weredependent upon the nature of the hydrocarbon to which the group was attached.

During the same year Braunholtz (11) found that many organic bases containing the monomethyl and dimethylamino functions exhibited an absorption band of medium to strong intensity between 3.53 and 3.55 μ. He mentioned that structural modifications which involve the lone pair of nitrogen electrons, such as salt formation, or co-ordination of the nitrogen atom to a metal, cause a disappearance of the absorption band. It was proposed that the band found could be attributed to Fermi-resonance and this phenomenon is concisely described by King (21).

A study by Wright (28) in 1959 on the spectra of a series of derivatives of merimines supported the findings of Hill and Braunholtz.

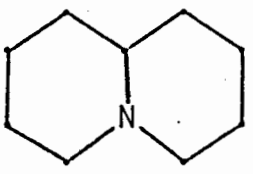


Merimine

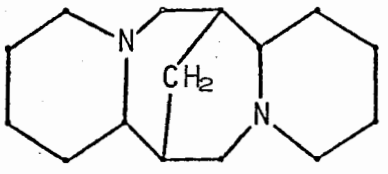
During this same period, an independent study was being made by Bohlmann (6) which applied the methoxyl shift principle of Henbest(17) to the tertiary amine function in an exhaustive work on the conformation of Quinolizidines.

D. Conformational Implications of the "Bohlmann Band"

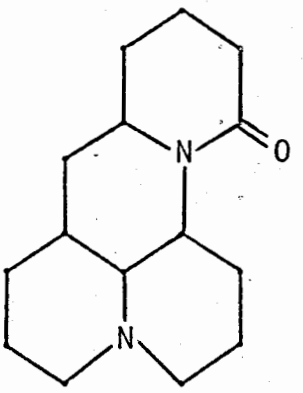
In 1958 Bohlmann (6,7,8) described a characteristic absorption band in the infrared spectrum, occurring in the approximate range of 3.57 to 3.70 μ, which was observed in the spectra of quinolizidines, sparteines, and matrines.



Quinolizidine

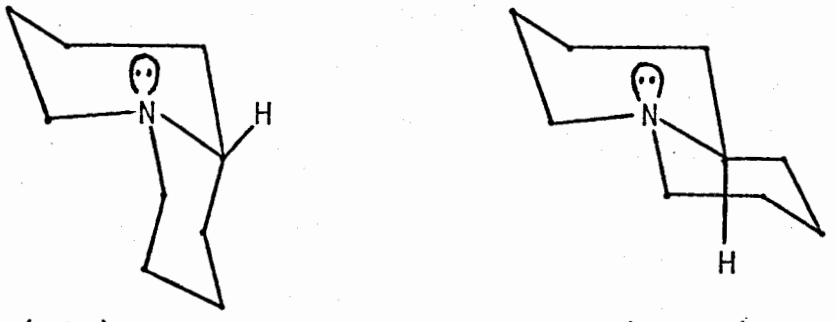


Sparteine



Matrine

Using the separated isomers of quinolizidine, it was demonstrated that the characteristic band appeared in trans-quinolizidines but not in the cis conformations.



(cis) (trans)

Quinolizidine Isomers

This finding served as a model for the explanation of the conformations of the matrines (8). From studies of of this nature Bohlmann described the criteria necessary for the observance of this characteristic absorption band, namely, when at least two C-H bonds adjacent to the nitrogen atom are co-axial and trans to the unshared electron pair.

The criteria for the "Bohlmann Band" were further supported by Battersby (5) in a study of the thermodynamically most stable form for the benzoquinolizidine system.

Application of the "Bohlmann Band" to oxazolidines and tetrahydro-1,3-oxazines by Leonard (22) in 1960 permitted the stereochemical assignments of bicyclic oxazolidines.

Moynehan (24) continued the illucidation of the stereochemistry of monomethylquinolizidines with a study

reported in 1962; but Zinnes (29), in 1965, attempted to utilize the "Bohlmann Band" in a study of Yohimbane with inconclusive results.

Several studies were made which may be of interest although basically they followed the same pattern of applying the "Bohlmann Band" to conformational studies. Some of these were Smith (6) on the constitution of Aspidospermine, Aroney (4) and Booth (9) on the conformations of morphine and morpholines, House (19) on azabicyclic systems, Trager (27) on Corynantheidine alkaloids, and England (16) on hydroxyquinolizidines.

The arguments concerning the preferred conformation of the unshared electron pair of nitrogen in specific environments have been offered by Aroney (4), Allinger (3), Chen (12), Booth (10), and Aaron (1). For a general survey of conformational studies in basic structures, one should examine the work of Elliel (15). Reference will be made to specific conformations during the discussion of results and applications involved in this study.

This thesis will show the practicality of applying the information, derived from the presence or absence of

the "Bohlmann Band", to the study of organic reactions, identification of products and illucidation of structures in the chemistry of tertiary amines.

EXPERIMENTAL

I. Reagents

Carbon tetrachloride, Infrared Spectral Grade, Matheson, Coleman and Bell, Division of Matheson Company, Inc.

Chloroform, Infrared Spectral Grade, Matheson, Coleman and Bell, Division of Matheson Company, Inc.

Most of the amines examined in this study were obtained from the Aldrich Chemical Company.

Amines, otherwise unavailable, were synthesized in the research laboratories of the A.H.Robins Company, Inc.

All other reagents used in this study were common laboratory reagents of C.P. or equivalent grade.

II. Apparatus

Infrared Recording Spectrophotometer, Model IR-8, Beckman Instruments, Inc.

The IR-8 may be used as a single or double beam instrument covering a linear wavelength range from 2.5 to 16 microns. Resolution comparable to research-grade spectrophotometers is attained through the use of diffraction gratings and interference filters. For this study a grating of 300 lines per millimeter was used for the 2.5 to 5.0 micron range. The relationship of the optical, mechanical, and electronic systems of the IR-8 is illustrated in Figure III .

Accessories for the spectrophotometer included a demountable film cell and two liquid cells fabricated with NaCl windows.

Readout of the wavelengths from the recorded spectra was facilitated by the employment of an illuminated magnifier and a millimeter scale.

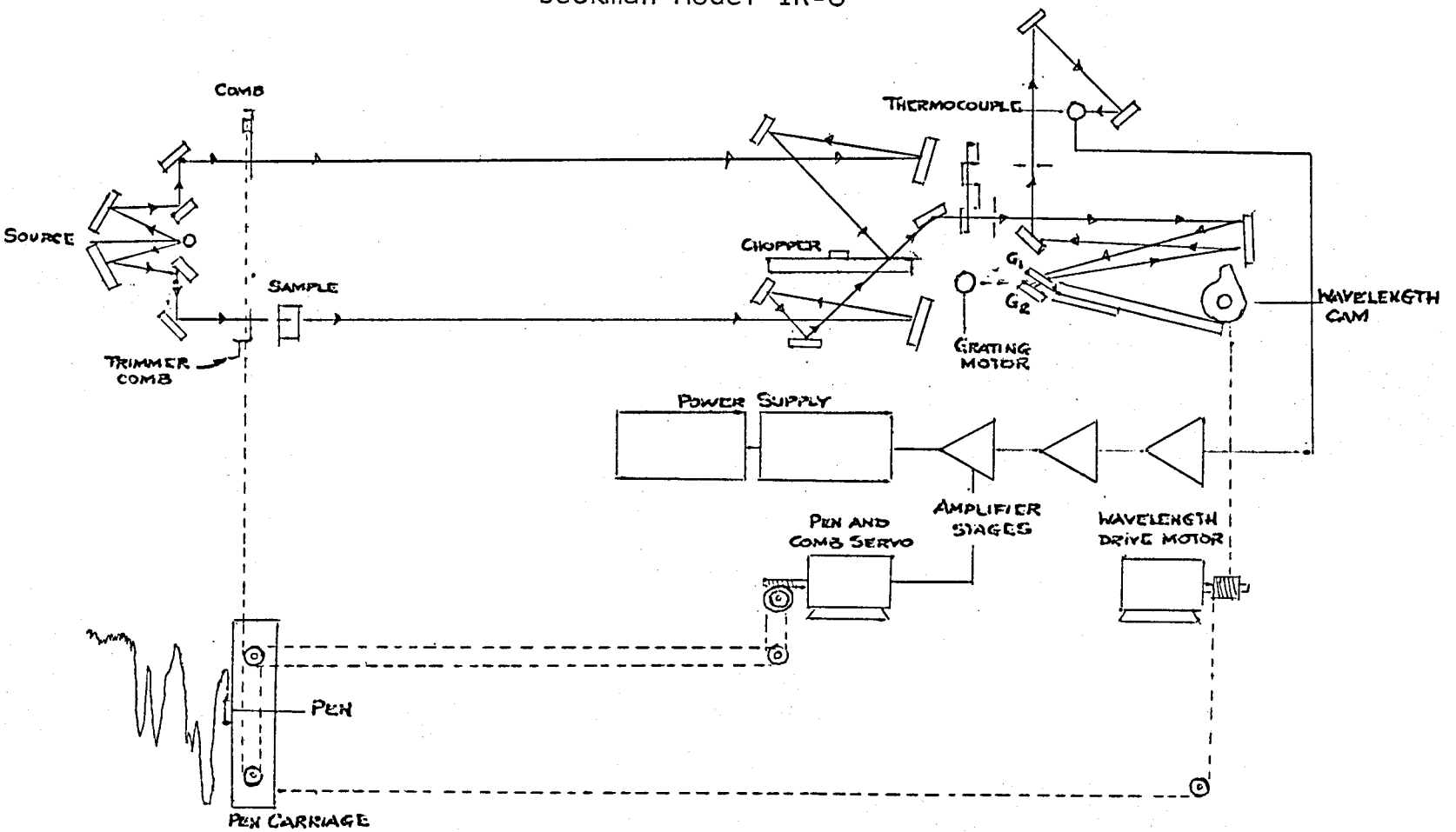
Calibrated standard - Polystyrene film , Dow Chemical Company, available from Beckman Instruments, Inc.

The remainder of the apparatus used was composed of common laboratory equipment.

Figure III

Block Diagram of Infrared Spectrophotometer

Beckman Model IR-8



Relationship of Optical, Mechanical and Electronic Systems

III. Method of Analysis

The amines selected for this study represent a sampling of all types from primary to tertiary in an effort to illustrate the unique character of the "Bohlmann Band" which normally occurs in the 3.57 to 3.70 μ region in the infrared spectra of tertiary amines.

The representative amines studied were first checked by thin layer chromatography for purity. Samples of questionable purity were either redistilled or recrystallized until a trial by TLC indicated acceptable purity.

Some amines required special syntheses and are included in this study under "Syntheses".

Where applicable the amines were examined as thin films between sodium chloride plates and the spectra recorded on a slow scanning speed of 25 minutes per scan at a gain of 6 using the double beam mode of operation. Those samples which were either too volatile or viscous to be examined as thin films were dissolved in spectral grade carbon tetrachloride or chloroform and the spectra studied in matched liquid cells of sodium chloride windows using the double

beam mode of operation with a slow scanning speed of 25 minutes per scan at a gain of 8.

A polystyrene film was employed as a standard for calibration using the sharp band occurring at 3.507 μ to insure accurate calibration of the instrument and correct positioning of the recorder chart.

Since the wavelength scale was linear, the absorption bands were easily read using an illuminated magnifier and a millimeter scale. Using recorder chart paper No. 7611, available from Beckman Instruments, Inc., the relationship is 0.1 μ = 50 mm.

The region of the spectrum with which this study is concerned is that located between 3.0 and 4.0 microns.

IV. Syntheses

In order to examine amines which were not available commercially or included in the laboratory stock of intermediates, several syntheses were required either to prepare a specific amine or to demonstrate some of the examples presented in the discussion and application of the information derived from the "Bohlmann Band".

It is intended that the syntheses which follow will be given in the order in which they are encountered throughout this study.

These syntheses are offered as typical examples for comparison with compounds of similar structural features.

The numbering system, I-A, II-A, and III-A, refers to primary, secondary, and tertiary amines respectively. Miscellaneous compounds are denoted by MS. This system of numbering coincides with that used in the appropriate figures, tables, and spectra throughout this study.

I. 4-Benzyl-2,3,4,5-tetrahydro-1,4-benzoxazepine * (III-A-30)

To a stirring suspension of 20.0 g. K_2CO_3 in 400 ml. of dry toluene, was added 25.0 g. (0.17 mole) of 2,3,4,5-Tetrahydro-1,4-benzoxazepine. With moderate stirring at a temperature of 60° C., 29.1 g.(0.17 mole) of benzyl bromide dissolved in 100 ml. dry toluene was added dropwise. The temperature was maintained at 60° C. for 24 hours. During the reaction time samples were removed and checked by TLC to follow the reaction. The reaction was cooled, filtered, and the filtrate evaporated on a rotary steam evaporator. The concentrate was partitioned between water and ether and the ether extracts were washed with water and dried over $MgSO_4$. Evaporation of the filtered ether extracts, gave an oil which was vacuum distilled, B.R. 97 - 102°C./0.003 mm.Hg., to yield 28.5 g.(o.12 mole) of colorless oil representing a 70% yield. The structure of the product was supported by IR and NMR spectral data. A sample of the free base was converted to the HCL salt in dry ether with ethereal HCL. Repeated recrystallization from isopropanol/isopropyl ether yielded a white crystaline salt which melted at 203-204°C.

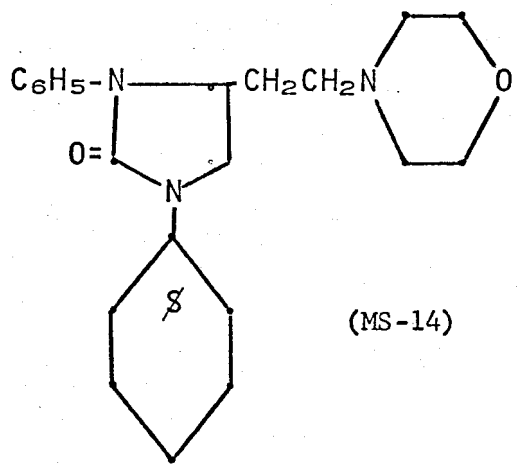
Analysis by Microtech Laboratories:

Calc'd. for $C_{16}H_{17}NO.HCL$: C, 69.68; H, 6.58; N, 5.08; Cl, 12.86

Found : C, 69.73; H, 6.62; N, 5.09; Cl, 12.83

* Related structure is shown on page 33.

II. 1-Cyclohexyl-4-(2-morpholinylethyl)-3-phenyl-2-imidazolidinone



(MS-14)

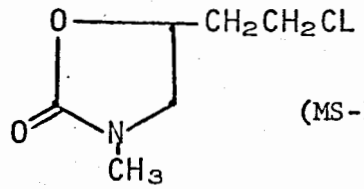
To an excess (200 ml.) of morpholine was added 50 g. (0.16 mole) of 4-(2-Chloroethyl)-1-cyclohexyl-3-phenyl-2-imidazolidinone and refluxed for 48 hours. The reaction was cooled and the crystalline morpholine hydrochloride removed. The filtrate was concentrated on a rotary steam evaporator at reduced pressure. The concentrate was made acidic with cold 6 N. HCl and extracted several times with ether. The aqueous acid solution was made basic with 6 N. NaOH and extracted with ether. The ether extracts from the basified solution were dried and evaporated to an oil which was converted to the maleate salt in isopropanol and recrystallized from a mixture of isopropanol and isopropyl ether as a white crystalline salt , M.P. 141-142° C. Yield: 32.3 g.

Analysis by Microtech:

Calc'd. for $C_{25}H_{35}N_3O_6$: C,63.41; H,7.45; N,8.87

Found : C,63.64; H,7.45; N,8.93

III. 5-(2-Chloroethyl)-3-methyl-2-oxazolidinone



(MS-16)

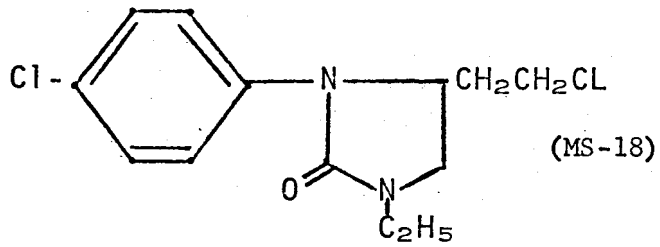
To 198 g. (2 moles) of phosgene, dissolved in 800 ml.of cold $CHCL_3$ contained in a 3 liter, 3 necked, round bottom flask equipped with a mechanical stirrer, dropping funnel, pot thermometer and condenser, was added 204 g. (2 moles) of 1-Methyl-3-pyrrolidinol in 450 ml. $CHCL_3$. The reaction temperature was maintained at 10° C. during the addition then slowly raised to a gentle reflux and maintained for 3 hours. The $CHCL_3$ solution was cooled and extracted in order with dilute HCL, dilute NaOH and water. The $CHCL_3$ layer was dried over Na_2SO_4, filtered and evaporated. The remaining oil was vacuum distilled and the product was collected at B.R. 120-125°C. and 0.2 mm.Hg. to yield 169 g. (52% yield) of colorless oil.

Analysis by Microtech:

Calc'd for $C_6H_{10}NO_2CL$: C, 44.04; H,6.16; N, 8.56

Found : C, 44.59; H,6.31; N, 8.41

IV. 4-(2-Chloroethyl)-3-(p-chlorophenyl)-1-ethyl-imidazolidinone



(MS-18)

To a 3 liter, 3 neck round bottom flask containing a solution of 111.6 g. (0.5 mole) of 3-(p-Chloroanilino)-1-ethylpyrrolidine in 1500 ml. $CHCL_3$ at 0° C. was added dropwise a cold solution of 150 g. (1.5 moles) of phosgene in 500 ml. $CHCL_3$. During this addition the temperature was maintained at 10 - 15° C. The reaction was slowly brought to reflux with heat and stirring and continued for 48 hours. The reaction was then cooled and extracted with water. The $CHCL_3$ layer was dried over Na_2SO_4 , treated with activated carbon and filtered. Upon evaporation a clear yellow oil was obtained. Crude yield : 129 g.,90 %.

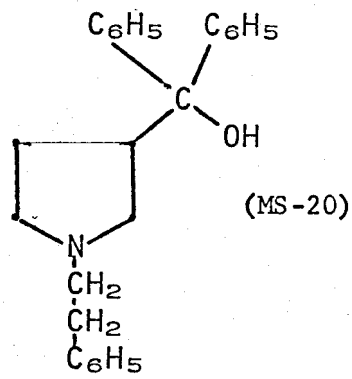
Vacuum distillation gave the product as a pale yellow oil which was collected at B.R. 176-180°C./0.05 mm. Hg.

Analysis by Microtech:

Calc'd. for $C_{13}H_{16}CL_2N_2O$: C,54.37; H,5.62; N,9.75; Cl,24.69

Found : C,54.52; H,5.42; N,9.47; Cl,24.37

V. [1-(2-Phenylethyl)-3-pyrrolidinyl]-diphenylmethanol



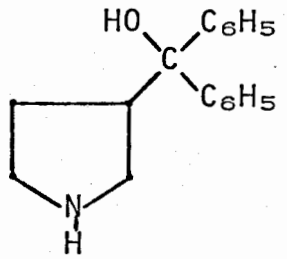
(MS-20)

To a suspension of 5.7 g.(o.15 mole) of $LiAlH_4$ in 350 ml. of tetrahydrofuran was added slowly a THF solution of 50 g. (0.135 mole) of 3-[1-(2-Phenylethyl)-2-oxo]-pyrrolidinyldiphenyl methanol. The reaction was stirred at reflux for 1 hour, cooled, and the excess $LiAlH_4$ was destroyed with 50 ml. each of H_2O and 50 % NaOH. The reaction was filtered and evaporated to an oil which crystallized on cooling to room temperature . The product was recrystallized from isopropyl ether and vacuum dried to yield 42.4 g. (87.9 %) of the white crystalline product which melted at M.P. 118-119° C.

Analysis by Microtech:

Calc'd. for $C_{25}H_{27}NO$	:	C,83.99; H,7.61; N,3.92
Found	:	C,83.46; H,7.66; N,3.88

VI. 3-Pyrrolidinyldiphenylmethanol



(MS-22)

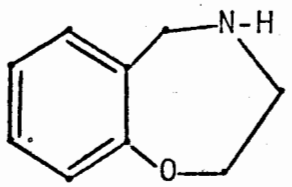
To a 500 ml. round bottom flask was added 34.3 g.(0.1 mole) of (1-Benzyl-3-pyrrolidinyl)-diphenylmethanol , 250 ml. of glacial acetic acid and ca. 2 g. of Raney Ni catalyst . After shaking the mixture overnight at room temperature, it was filtered and transfered to a Paar bomb and reduced with hydrogen over a Pd/C catalyst at 70°C. overnight. The reaction was filtered and diluted with water, made basic in the cold with 50% NaOH causing the product to precipitate from solution. Recrystallization of the product from an aqueous methanolic medium gave 11.8 g. (47 % yield) of white crystals., M.P. 156-157°C.

Analysis by Microtech:

Calc'd. for $C_{17}H_{19}NO$: C,80.59; H,7.56; N,5.53

Found : C,80.58; H,7.56; N,5.62

VII. 2,3,4,5-Tetrahydro-1,4-benzoxazepine (Refer to compound I of page 27)



(II-A-13)

Debenzylation of 173 g. (0.72 mole) of 4-Benzyl-2,3,4,5-tetrahydro-1,4-benzoxazepine in absolute ethanol with hydrogen over a Pd/C (5%) catalyst was carried out in three equal portions using a Paar apparatus. The filtrates were combined, evaporated, and fractionally distilled under vacuum . The product was collected at B.R. 90-95°C./0.06 mm.Hg. as a pale yellow oil.

The structure of the debenzylated free base was verified by IR and NMR spectral data. Thin layer chromatography indicated that the product was free of impurities.

A small sample was converted to the hydrochloride salt in isopropanol with ethereal HCL and recrystallized from a combination of isopropanol and isopropyl ether as white crystals , M.P. 179-180°C.

Analysis by Microtech:

Calc'd. for $C_9H_{11}NO.HCl$:	C,58.22; H,6.52; N,7.55; Cl,19.10
Found :	C,58.00; H,6.79; N,7.39; Cl,19.32

V. EXPERIMENTAL RESULTS

In order to establish a basis for reference to the C-H stretching vibrations, a progressive examination of the infrared spectra of normal and cyclic hydrocarbons was made. The effects attributed to the presence of oxygen or nitrogen on these stretching vibrations were studied. The results of this reference study are shown in Figure IV and Table 2.

In an effort to present a comprehensive representation of the 3.0 to 4.0 μ region of the infrared spectra of the amines examined, a selection was made from each class to illustrate this study. These are shown in Figure V and Table 3. To further clarify the presentation of the experimental results, only the prominent absorption bands occurring in the range from 3.20 to 3.70 μ were recorded in the figures and tables.

The characteristic "Bohlmann Band" is emphasized by a solid dark block where it appears in the appropriate figure, and the corresponding tabulated wavelength value of this absorption band is underscored in the table.

An additional presentation of the prominent absorption

bands of substituted anilines and toluidines was compiled from the infrared spectral data collected in this study and supplemented with data published in a study by Hill and Meakins (18). These data are presented separately in Figure VI and Table 4 to illustrate possible exceptions to the appearance of the "Bohlmann Band".

The recorded infrared spectra of the amines examined in this study, showing the prominent absorption bands in the 3.20 to 3.70 μ region, are presented in the Appendix followed by tabulated tables of the corresponding wavelength values.

The wavelength accuracy specified by Beckman Instruments, Inc. (25) is $\pm$ 0.008 micron, and the accuracy of the tabulated values of prominent absorption bands is estimated to be within these limits.

FIGURE IV

PROMINENT C-H STRETCHING WAVELENGTHS IN SELECTED ORGANIC COMPOUNDS

[Limited to the Region of 3.20 to 3.70 μ]

Refer to Table 2 for actual values.

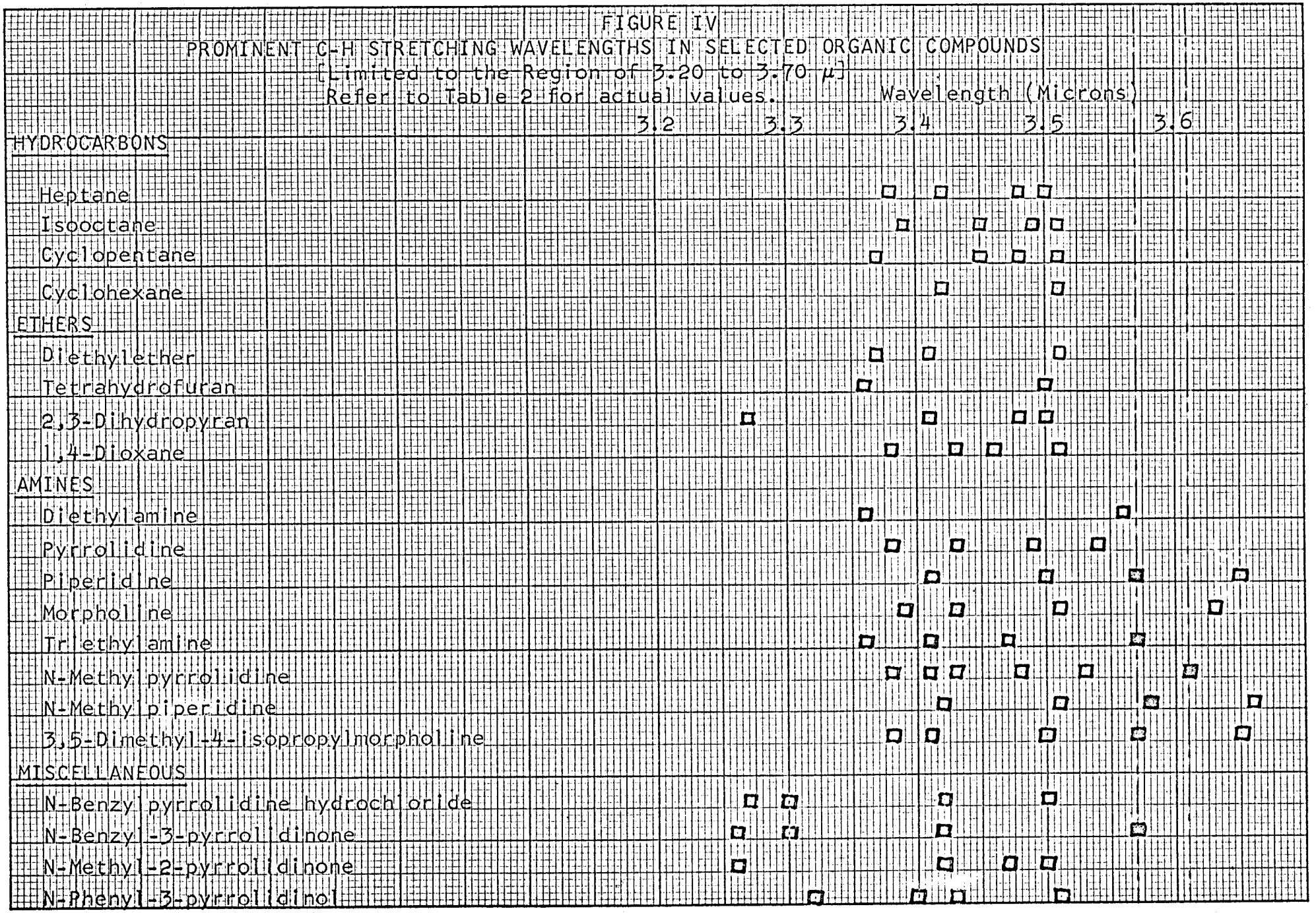


FIGURE V

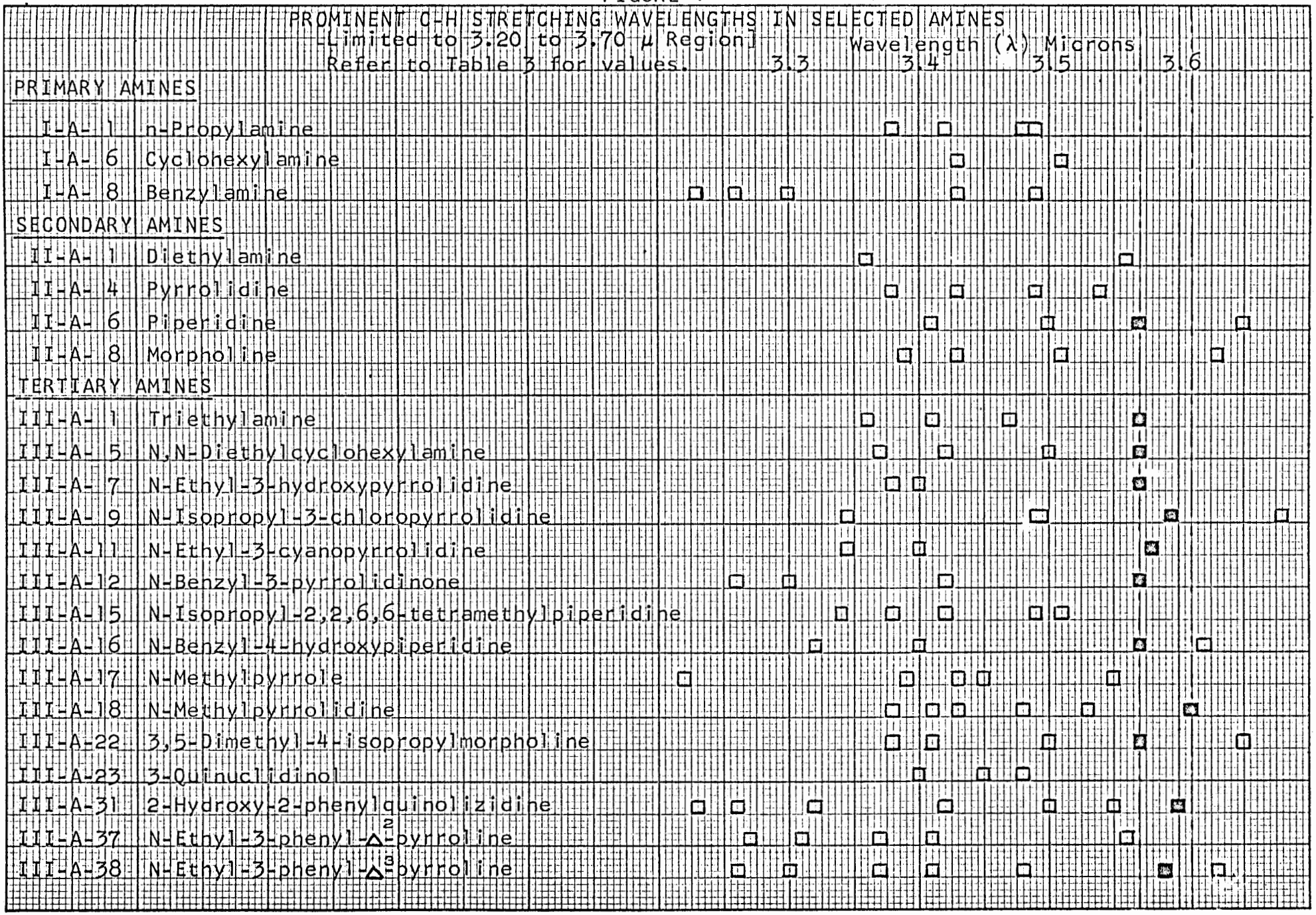

PROMINENT C-H STRETCHING WAVELENGTHS IN SELECTED AMINES
-Limited to 3.20 to 3.70 μ Region-
Refer to Table 3 for values.
Wavelength (λ) Microns
3.3
3.4
3.5
3.6
PRIMARY AMINES
I-A- 1 n-Propylamine
I-A- 6 Cyclohexylamine
I-A- 8 Benzylamine
SECONDARY AMINES
II-A- 1 Diethylamine
II-A- 4 Pyrrolidine
II-A- 6 Piperidine
II-A- 8 Morpholine
TERTIARY AMINES
III-A- 1 Triethylamine
III-A- 5 N,N-Diethylcyclohexylamine
III-A- 7 N-Ethyl-3-hydroxypyrrolidine
III-A- 9 N-Isopropyl-3-chloropyrrolidine
III-A-11 N-Ethyl-3-cyanopyrrolidine
III-A-12 N-Benzyl-3-pyrrolidinone
III-A-15 N-Isopropyl-2,2,6,6-tetramethylpiperidine
III-A-16 N-Benzyl-4-hydroxypiperidine
III-A-17 N-Methylpyrrole
III-A-18 N-Methylpyrrolidine
III-A-22 3,5-Dimethyl-4-isopropylmorpholine
III-A-23 3-Quinuclidinol
III-A-31 2-Hydroxy-2-phenylquinolizidine
III-A-37 N-Ethyl-3-phenyl-Δ2-pyrroline
III-A-38 N-Ethyl-3-phenyl-Δ3-pyrroline

FIGURE VI

PROMINENT C-H STRETCHING WAVELENGTHS IN THE INFRARED SPECTRA OF SELECTED ANILINES AND TOLUIDINES

(Limited to the Region of 3.20 to 3.70 μ)

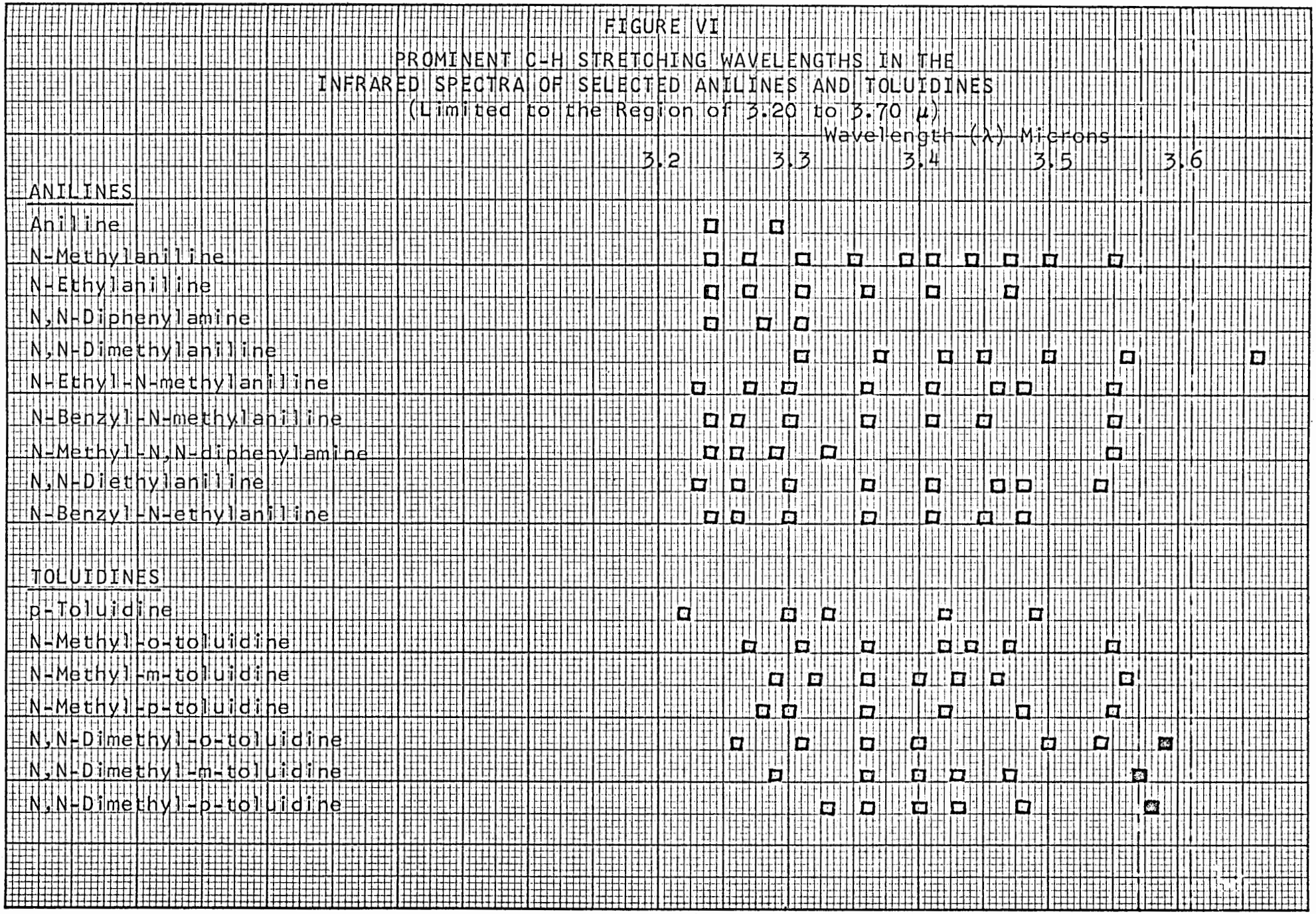


TABLE 2

PROMINENT C-H STRETCHING WAVELENGTHS IN SELECTED ORGANIC COMPOUNDS
[Limited to the Region of 3.20 to 3.70 μ]

	PROMINENT ABSORPTION BANDS (Microns)
HYDROCARBONS	
Heptane	3.38,3.42,3.48,3.50
Isooctane	3.39,3.45,3.49,3.51
Cyclopentane	3.37,3.45,3.48,3.51
Cyclohexane	3.42,3.51
ETHERS	
Diethylether	3.37,3.41,3.51
Tetrahydrofuran	3.36,3.50
2,3-Dihydropyran	3.27,3.41,3.48,3.50
1,4-Dioxane	3.38,3.43,3.46,3.51
AMINES	
Diethylamine	3.36,3.56
Pyrrolidine	3.38,3.43,3.49,3.54
Piperidine	3.41,3.50,3.57,3.65
Morpholine	3.39,3.43,3.51,3.63
Triethylamine	3.36,3.41,3.47,3.57

TABLE 2 (Continued)

AMINES	PROMINENT ABSORPTION BANDS (Microns)
N-Methylpyrrolidine	3.38,3.41,3.43,3.48,3.53,3.61
N-Methylpiperidine	3.42,3.51,3.58,3.66
3,5-Dimethyl-4-isopropylmorpholine	3.38,3.41,3.50,3.57,3.65
MISCELLANEOUS	
N-Benzylpyrrolidine hydrochloride	3.27,3.30,3.42,3.50
N-Benzyl-3-pyrrolidinone	3.26,3.30,3.42,3.57
N-Methyl-2-pyrrolidinone	3.26,3.42,3.47,3.50
N-Methylpyrrole	3.22,3.39,3.43,3.45,3.55
N-Phenyl-3-pyrrolidinol	3.32,3.40,3.43,3.51

TABLE 3

PROMINENT C-H STRETCHING WAVELENGTHS IN THE INFRARED SPECTRA OF SELECTED AMINES
[Limited to the Region of 3.20 to 3.70 μ]

		PROMINENT ABSORPTION BANDS (Microns)
PRIMARY AMINES		
I-A- 1	n-Propylamine	3.38,3.42,3.48,3.49
I-A- 6	Cyclohexylamine	3.43,3.51
I-A- 8	Benzylamine	3.23,3.26,3.30,3.43,3.49
SECONDARY AMINES		
II-A- 1	Diethylamine	3.36,3.56
II-A- 4	Pyrrolidine	3.38,3.43,3.49,3.54
II-A- 6	Piperidine	3.41,3.50,3.57,3.65
II-A- 8	Morpholine	3.39,3.43,3.51,3.63
TERTIARY AMINES		
III-A- 1	Triethylamine	3.36,3.41,3.47,3.57
III-A- 5	N,N-Diethylcyclohexylamine	3.37,3.42,3.50,3.57
III-A- 7	N-Ethyl-3-hydroxypyrrolidine	3.38,3.40,3.57
III-A- 9	N-Isopropyl-3-chloropyrrolidine	3.37,3.49,3.59,3.68
III-A-11	N-Ethyl-3-cyanopyrrolidine	3.37,3.40,3.58

TABLE 3 (Continued)

TERTIARY AMINES		PROMINENT ABSORPTION BANDS (Microns)
III-A-12	N-Benzyl-3-pyrrolidinone	3.26,3.30,3.42,3.57
III-A-15	N-Isopropyl-2,2,6,6-tetramethylpiperidine	3.34,3.38,3.42,3.49,3.51
III-A-16	N-Benzyl-4-hydroxypiperidine	3.32,3.40,3.57,3.62
III-A-17	N-Methylpyrrole	3.22,3.39,3.43,3.45,3.55
III-A-18	N-Methylpyrrolidine	3.38,3.41,3.43,3.48,3.53,3.61
III-A-22	3,5-Dimethyl-4-isopropylmorpholine	3.38,3.41,3.50,3.57,3.65
III-A-23	3-Quinuclidinol	3.40,3.45,3.48
III-A-31	2-Hydroxy-2-phenylquinolizidine	3.23,3.26,3.32,3.42,3.50,3.55,3.60
III-A-37	N-Ethyl-3-phenyl-Δ^2pyrroline	3.27,3.31,3.37,3.41,3.56
III-A-38	N-Ethyl-3-phenyl-Δ^3-pyrroline	3.26,3.30,3.37,3.41,3.48,3.59,3.63

TABLE 4

PROMINENT C-H STRETCHING WAVELENGTHS IN THE INFRARED SPECTRA OF SELECTED ANILINES AND TOLUIDINES
(Limited to the Region of 3.20 to 3.70)

ANILINES	PROMINENT ABSORPTION BANDS (Microns)
Aniline	3.24,3.29
N-Methylaniline	3.24,3.27,3.31,3.35,3.39,3.41,3.44,3.47,3.50,3.55
N-Ethylaniline	3.24,3.27,3.31,3.36,3.41,3.47
N,N-Diphenylamine	3.24,3.28,3.31
N,N-Dimethylaniline	3.31,3.37,3.42,3.45,3.50,3.56,3.66
N-Ethyl-N-methylaniline	3.23,3.27,3.30,3.36,3.41,3.46,3.48,3.55
N-Benzyl-N-methylaniline	3.24,3.26,3.30,3.36,3.41,3.45,3.55
N-Methyl-N,N-diphenylamine	3.24,3.26,3.29,3.33,3.55
N,N-Diethylaniline	3.23,3.26,3.30,3.36,3.41,3.46,3.48,3.54
N-Benzyl-N-ethylaniline	3.24,3.26,3.30,3.36,3.41,3.45,3.48
TOLUIDINES	
p-Toluidine	3.22,3.30,3.33,3.42,3.49
N-Methyl-o-toluidine	3.27,3.31,3.36,3.42,3.44,3.46,3.47,3.55
N-Methyl-m-toluidine	3.29,3.32,3.36,3.40,3.43,3.46,3.56

TABLE 4 (Continued)

TOLUIDINES	PROMINENT ABSORPTION BANDS (Microns)
N-Methyl-p-toluidine	3.28,3.30,3.36,3.42,3.48,3.55
N,N-Dimethyl-o-toluidine	3.26,3.31,3.36,3.40,3.50,3.54,3.59
N,N-Dimethyl-m-toluidine	3.29,3.36,3.40,3.43,3.47,3.57
N,N-Dimethyl-p-toluidine	3.33;3.36,3.40,3.43,3.48,3.58

VI. Discussion of Results

A. Characteristics of the "Bohlmann Band"

1. Origin and Location of the "Bohlmann Band"

Examination of the wavelength values of the prominent C-H stretching absorption bands shown in Figure IV and Table 2 reveals that an infrared absorption band occurring at a wavelength value greater than 3.51 μ is not observed for non-cyclic or cyclic hydrocarbons nor is there any appreciable change in the absorption band positions as a result of cyclization.

Insertion of an oxygen atom into the molecule to form an open-chain or cyclic ether, also results in no apparent shift of the carbon-hydrogen stretching wavelengths when compared with those of the hydrocarbon series of this study. Thus far no absorption band of wavelength greater than 3.51 μ has been observed. It should be noted that these symmetrical ethers do not contain a methoxyl group. However, when a nitrogen atom is inserted into the hydrocarbon molecule to form a primary or secondary open-chain or cyclic amine, absorption bands of wavelength values greater than 3.51 μ appear for the secondary amines but not

for primary amines. Further substitution of an alkyl group on the nitrogen atom of the secondary amine to form a tertiary amine results in the appearance of absorption bands at an even greater wavelength value. In considering the amines, one appears justified in differentiating primary from secondary and tertiary amines by observing the infrared absorption band wavelengths occurring at values greater than 3.51 μ,

A comparison of the infrared absorption spectra of non-cyclic or cyclic secondary and tertiary amines reveals that a unique absorption band, in the 3.57 to 3.61 μ region, appears with dramatic regularity for tertiary amines and is rarely observed in secondary amines.

Amines which exhibit this characteristic "Bohlmann Band" are recognized by a relatively strong, sharp absorption band appearing in the 3.57 to 3.61 μ region of the infrared spectrum. The appearance of this unique absorption band for tertiary amines provides a possible qualitative method of differentiating between primary, secondary, and tertiary amines from an examination of the C-H stretching wavelengths in the infrared spectrum. There are exceptions involved which will be discussed

later and mention is made of this utility in the "Applications" section of this study. Hereinafter, λ_β shall refer to the wavelength of the "Bohlmann Band" expressed in microns and λ_{max} shall refer to the band of maximum wavelength observed which is less than the lower limit, i.e., $\lambda_{max}<3.57\ \mu$, of the "Bohlmann Band" and will be used when the "Bohlmann Band" is absent in the spectral examples.

2. Relative Intensity of the "Bohlmann Band"

Since most of the tertiary amines were examined as thin films, an attempt to avoid or minimize concentration variation resulted in a choice of the C-H asymmetric stretching absorption band located in 3.38-3.42 μ region of the spectra as an internal reference. Since this band appeared in almost all of the amines examined and generally appears as the strongest, most stable absorption band in this region, the ratio of the intensity of this band to that of the "Bohlmann Band" was noted. Although this may not be a truly valid comparison, it serves to allow a rough comparison of the relative intensity of the "Bohlmann Band" as the group attached to the nitrogen is varied from methyl

to benzyl. A rough comparison gave the following order of magnitude for the relative intensity of the "Bohlmann Band" in non-cyclic and cyclic systems. The values shown were derived from the average ratios of the intensity of the reference to that of the "Bohlmann Band".

$$C_6H_5CH_2- > CH_3- > C_2H_5- > (CH_3)_2CH-$$

Examples of the spectra are presented in the Appendix.

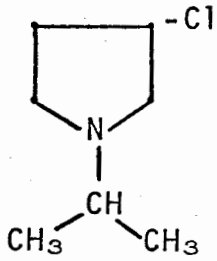
B. Criteria Necessary for Occurrence of the "Bohlmann Band"

1. C-H Vibrations Involved in the "Bohlmann Band"

In changing from a non-cyclic to a cyclic tertiary amine, restrictions are imposed upon the C-H bonds of the ring which prevent free rotation and cause these cyclic systems to take on a preferred conformation. This offers an opportunity to study the C-H bonds under restricted conditions and determine which C-H bonds are responsible for the appearance of the "Bohlmann Band".

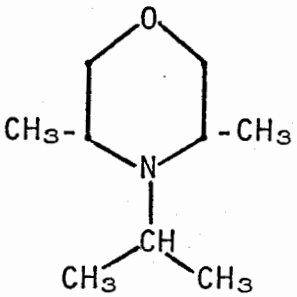
Reference to Figure V and Table 3 reveals that the "Bohlmann Band" occurs in the infrared absorption spectra of tertiary amines only when certain requirements are satisfied. A comparison of the spectra of 1-Isopropyl-3-chloropyrrolidine (III-A-9), 4-Isopropyl-3,5-dimethyl-

morpholine (III-A-22), N-Isopropyl-2,2,6,6-tetramethyl-piperidine (III-A-15), and N-Ethyl-2,2,5,5-tetramethyl-pyrrolidine (III-A-34)



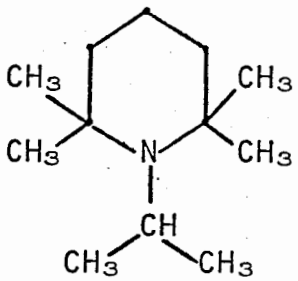
(III-A-9)

$\lambda_\beta = 3.59\mu$



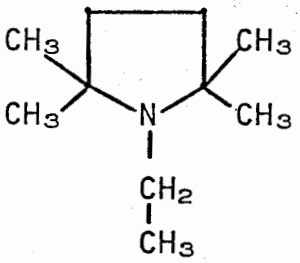
(III-A-22)

$\lambda_\beta = 3.57\mu$



(III-A-15)

$\lambda_{max} \cong 3.51\mu$



(III-A-34)

$\lambda_{max} \cong 3.51\mu$

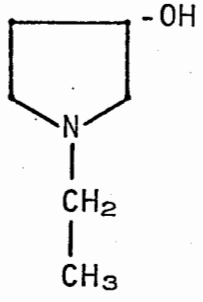
indicate that the unique absorption bands occurring at wavelength values of 3.59 μ and 3.57 μ for (III-A-9) and (III-A-22) respectively while being absent in the spectra of (III-A-15) and (III-A-34) must be dependent on the protons of the carbon atoms adjacent to the nitrogen atom since the spectra of (III-A-15) and (III-A-34) do not exhibit absorption bands of wavelength values greater than 3.51 μ. It logically follows that the occurrence of this unique absorption band, in the infrared spectra of tertiary amines, is attributed to a function of the C-H stretching vibrational mode of the C-H bonds adjacent to the

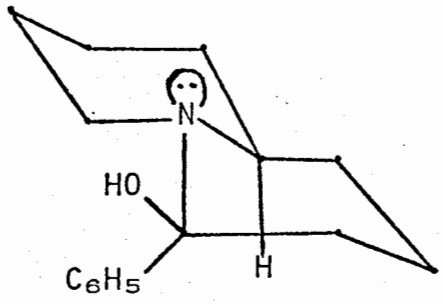
nitrogen atom.

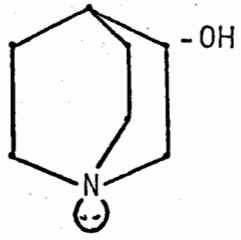
Bohlmann (6) has in part specified that there must be at least two protons adjacent to the nitrogen atom for the appearance of this band. This condition is satisfied by (III-A-9), (III-A-22) and (III-A-34) but not by (III-A-15); however, the spectrum of (III-A-34) does not exhibit a "Bohlmann Band". It then is apparent that the C-H bonds adjacent to the nitrogen atom must exist as separate C-H bonds adjacent to the nitrogen atom. Thus, the first criterion has been established for the appearance of the "Bohlmann Band".

2. Restricted Orientation of the Unshared Pair of Electrons on the Nitrogen Atom

A further restriction is placed upon the molecular configuration of a tertiary amine if it is to exhibit the "Bohlmann Band". Consider a comparison of the spectra of N-Ethyl-3-hydroxypyrrolidine (III-A-7) and 3-Quinuclidinol (III-A-23) of Figure V and Table 3 with the trans-Quinolizidine (III-A-31) of the Appendix.







(III-A-7) (III-A-31) (III-A-23)

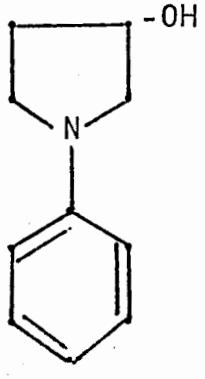
$\lambda_\beta = 3.57\mu$ $\lambda_\beta = 3.60\mu$ $\lambda_{max} < 3.48\mu$

In this comparison (III-A-7) and (III-A-31) exhibit the unique "Bohlmann Band" while 3-Quinuclidinol (III-A-23) does not. At first this might appear contradictory; however, it serves to establish the second criterion for the appearance of the "Bohlmann Band" in that the unshared pair of electrons on the tertiary nitrogen must be so oriented that they are co-planar and trans to at least two protons each of which is bonded to different carbon atoms adjacent to the nitrogen atom of the tertiary amine. Application of this criterion explains the absence of the "Bohlmann Band" in the infrared spectrum of 3-Quinuclidinol (III-A-23) because a trans, co-planar relationship between the nitrogen unshared electron pair and the adjacent protons is structurally prohibited.

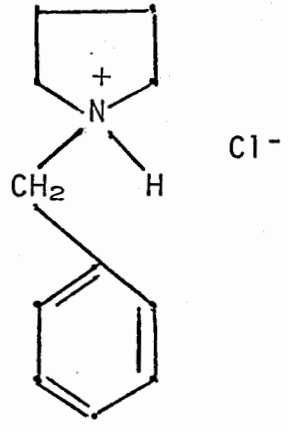
C. Environmental Effects on the "Bohlmann Band"

1. Electron Pair Delocalization

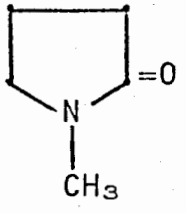
The infrared spectra of tertiary amines, in which the unshared pair of electrons on the nitrogen atom are delocalized, do not exhibit a characteristic "Bohlmann Band". To illustrate the effects of electron delocalization, reference is made to the 3.00 to 4.00 μ regions in the spectra of the examples given. These spectra are shown in Section II, Miscellaneous Spectra, of the Appendix.



(MS-11)



(MS-9)



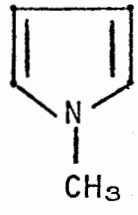
(MS-10)

The nitrogen electron pair of N-Phenyl-3-pyrrolidinol (MS-11) is subjected to delocalization by the π orbitals of the phenyl group. It is of interest that this occurs in most anilines and toluidines except in the N,N-Dimethylated-toluidines, all of which exhibit a "Bohlmann Band",

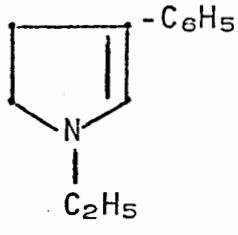
apparently due to the presence of a methyl group on the benzene ring. The employment of the electron pair in salt formation, as in N-Benzyl-pyrrolidinium hydrochloride (MS-9), obviously precludes the appearance of this characteristic band. The effect of electron pair delocalization by an electron withdrawing group, such as carbonyl, is represented by the butyrolactam, N-Methyl-2-pyrrolidinone (MS-10).

2. Effect of Other Functionalities

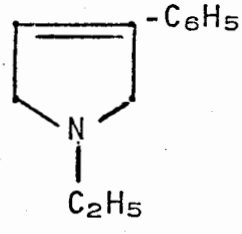
The delocalizing effect is limited to the carbon atoms adjacent to the nitrogen; and little or no influence is exerted by groups on the β carbon atoms. The reader is referred to the spectral data shown in Figure V and Table 3. Of the various degrees of unsaturation exemplified by the amines shown below, only the 3,4-dehydro-derivative (III-A-38) exhibits a strong, sharp absorption band at 3.59 μ.



(III-A-17)



(III-A-37)

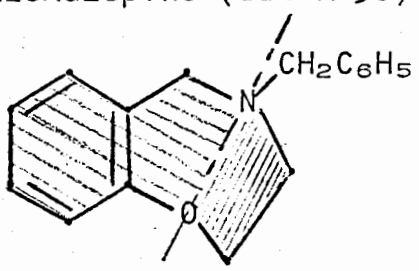


(III-A-38)

This factor further supports the requirement for a non-delocalized electron pair on the nitrogen atom as a criterion for the appearance of the characteristic band. It should be noted that in the examples shown, unsaturation adjacent to the nitrogen atom, as in enamines, also precludes the appearance of a "Bohlmann Band" in the infrared spectrum.

3. Effect of Conformational Ring Strain

In the event of ring strain, it is logical that the molecule will assume a conformation resulting in the most comfortable energy status. This principle is explained in detail by Eliel (15) and reference is made to his efforts. The author intends to avoid lengthy discussions which are already adequately documented. Attention is directed to the conformation of 4-Benzyl-2,3,4,5-tetrahydro-1,4-benzoxazepine (III-A-30) shown below.



(III-A-30)

Construction and examination of a "Dreiding molecular model" of the molecular structure corresponding to (III-A-30), reveals that the benzene ring may be co-planar with the nitrogen and oxygen moieties, yet the ethylenic bridge between nitrogen and oxygen is forced into another angular relationship. In such crowded conditions, it is understandable that trans and co-planar relationships are strained. Possibly this explains the weakness of the characteristic band in example (III-A-30). Such instances give cause for a precautionary warning in attempting to apply the "Bohlmann Band" criteria to strained ring systems.

D. Exceptions to the Rules

The exceptions encountered in simple tertiary amines are few; however, it should be emphasized that even the unexpected can be rationalized. In systems such as Piperidine (II-A-6) the absorption band occurring in the "Bohlmann Band" region is easily explained by reference to Eliel (15) who has confirmed that, at least 20% of the time, the piperidine molecule exists in a conformation which satisfies the requirements specified by Bohlmann

for the appearance of the characteristic band. Perhaps there may be exceptions other than those mentioned; in such event, the author offers an apology for the oversight.

VII. Application of Results

A. Differentiation of Amines

The C-H stretching wavelengths, occurring in the 3.2 to 3.7 μ region of the infrared spectrum, provide a means of differentiating between primary, secondary, and tertiary amines. Close examination of the infrared spectrum of an isolated, purified amine reveals that the wavelength value of 3.51 μ may be used as a reference point. From the results of Section VI-A-1, it was concluded that primary amines do not exhibit a prominent absorption band at a wavelength value in excess of 3.51 μ while tertiary amines exhibit a characteristic "Bohlmann Band" in the 3.57 to 3.61 μ region, and secondary amines show prominent absorption bands between these regions. One must consider the effects of unsaturation, environment of the unshared pair of electrons on the nitrogen atom, ring strain and conformational attitude in the interpretation of the infrared spectral data. Experience and familiarity in the interpretation of infrared spectral data are prerequisites to an accurate conclusion; however, if the amine examined is free from the environmental effects

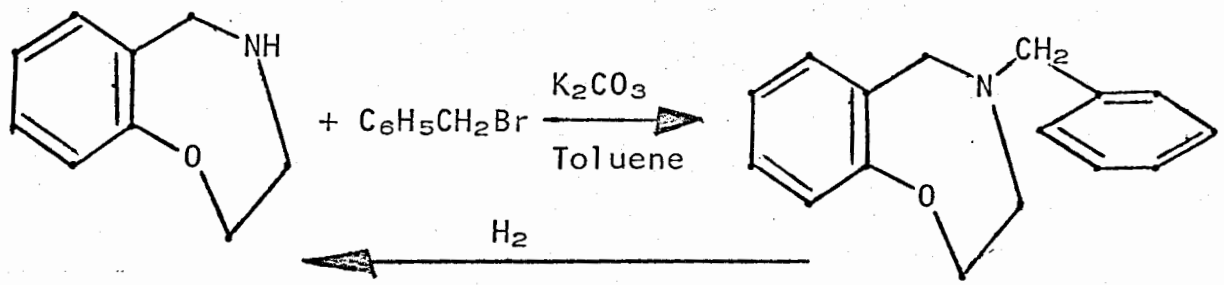
mentioned, the following relationships may be applied.

Primary Amines	Secondary Amines	Tertiary Amines
$\lambda_{max} \leq 3.51\ \mu$	$3.51\mu < \lambda_{max} < 3.57\ \mu$	$\lambda_{max} > 3.56\ \mu$

B. Utility in Organic Syntheses

In the reactions of amines, the presence or absence of a characteristic "Bohlmann Band" in the infrared spectrum affords a facile and useful method of monitoring the progress of the reaction, aids in the identification of the reaction products and provides information on the molecular conformation. To illustrate the utility of this band in synthetic organic reactions, several examples are given. During each reaction a small sample may be withdrawn, purified as the free base, and the infrared spectrum examined. The detailed procedures for these reactions have been described in the experimental sub-section, IV "Syntheses", and the infrared spectra for the 3.0 to 4.0 μ region of the compounds which follow are given in the Appendix. These are referred to for the examples shown on the following pages.

1. Alkylations

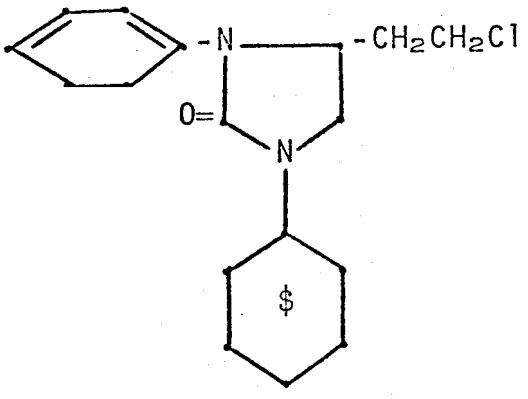


(II-A-13)

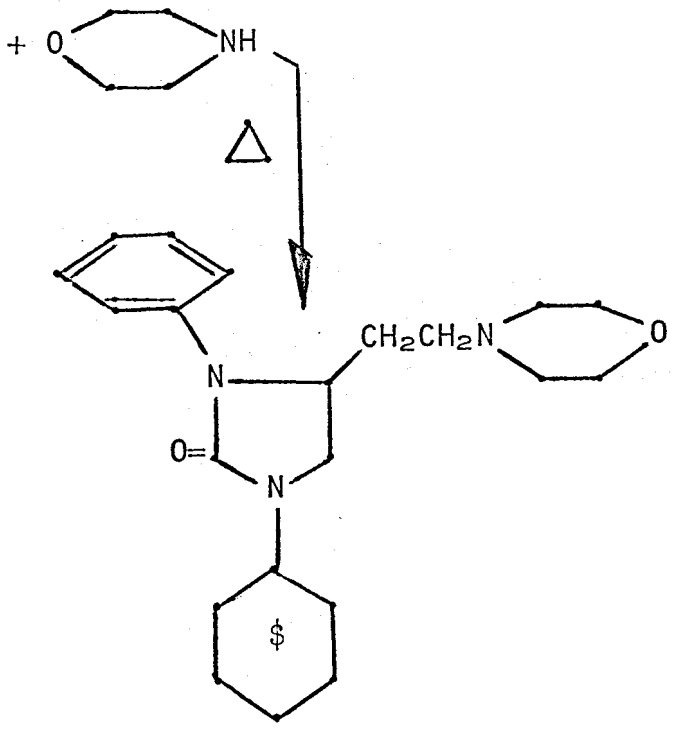
(III-A-30), $\lambda_\beta = 3.59\mu$

Compound (II-A-13) does not exhibit a characteristic "Bohlmann Band" in the infrared spectrum; however, on alkylation of (II-A-13) with benzylbromide to give (III-A-30), a tertiary amine results which exhibits a band at 3.59 μ. The band is relatively weak in this case due to ring distortion.

Debenzylation of (III-A-30) with hydrogen over a Pd catalyst, gives (II-A-13), a secondary amine, which does not result in the appearance of a "Bohlmann Band" in the infrared spectrum. This example is offered to illustrate a condition in which the "Bohlmann Band" is relatively weak. In the remainder of the examples, the characteristic band will be more intense.



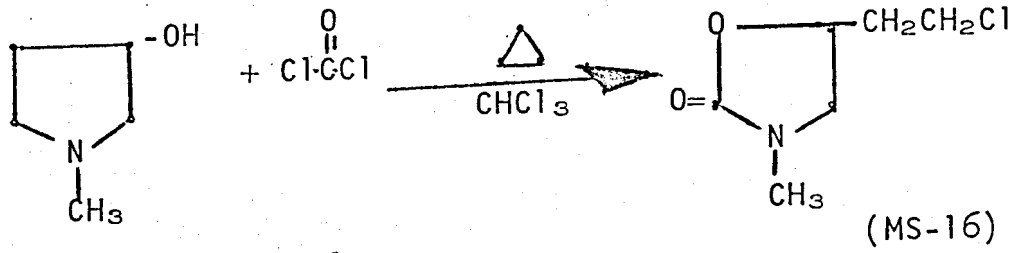
(MS-13)



(MS-14), $\lambda_\beta = 3.61\ \mu$

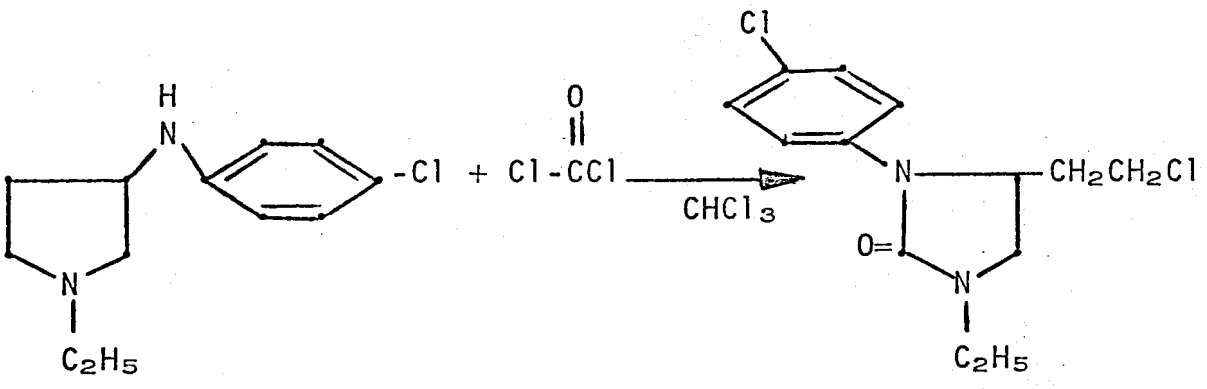
The "Bohlmann Band" is absent in the spectrum of (MS-13) and appears sharp and strong at 3.61 μ in (MS-14) arising from the presence of the tertiary nitrogen of the morpholinoethyl group.

2. Rearrangements



(MS-15), $\lambda_\beta = 3.61\ \mu$

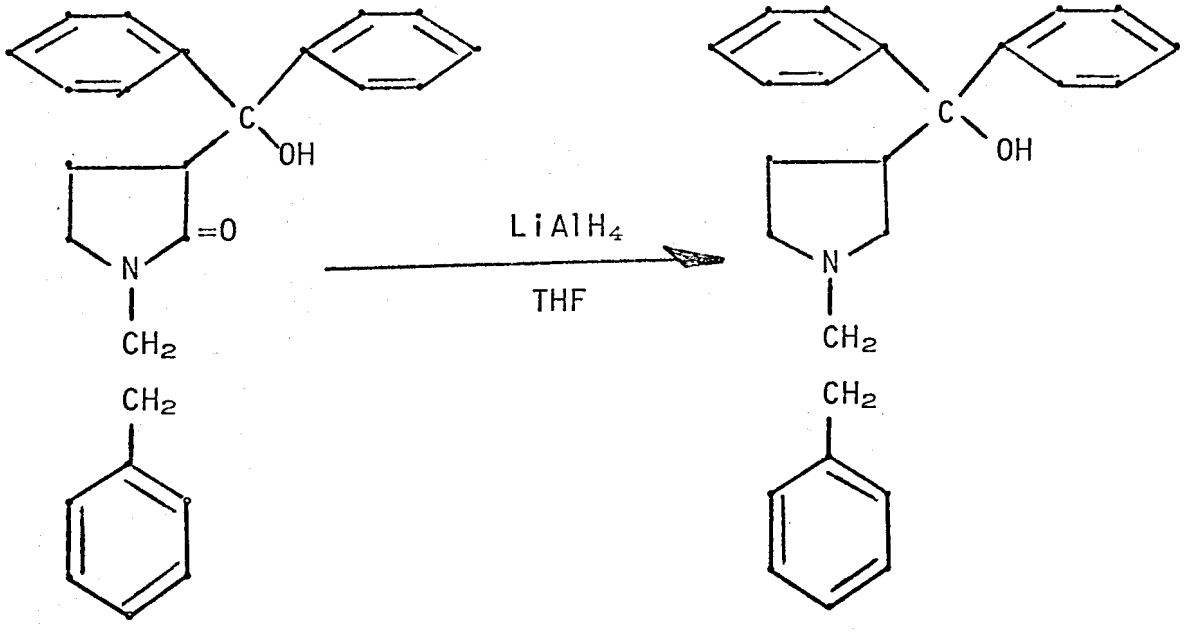
(MS-16)



(MS-17), λ_β = 3.60 μ (MS-18)

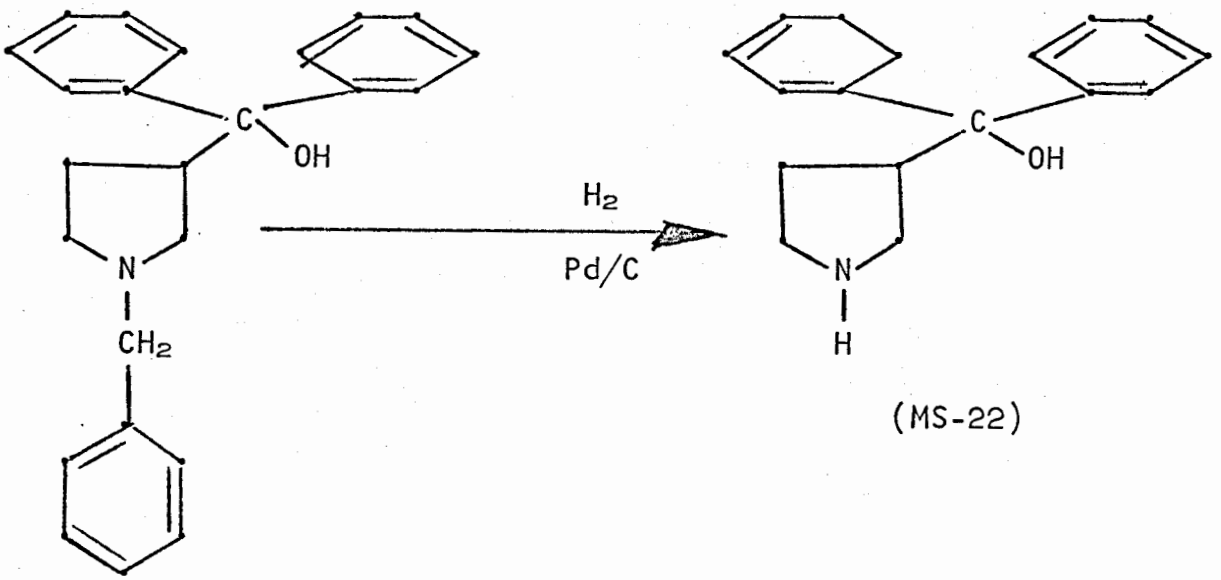
Compounds (MS-15) and (MS-17) exhibit the characteristic "Bohlmann Band" while (MS-16) and (MS-18) do not.

3. Reductions



(MS-19) (MS-20), λ_β = 3.57 μ

Reduction of the carbonyl group of (MS-19), which does not give rise to a "Bohlmann Band", with $LiAlH_4$ yields (MS-20) which gives a strong band at 3.57 μ characteristic of the tertiary amine.



(MS-22)

(MS-21), $\lambda_{\beta} = 3.59\ \mu$

Debenzylation of (MS-21) results in the absence of a "Bohlmann Band" in the spectrum of (MS-22).

There are obviously more reactions which may be studied by observing the presence or absence of a characteristic "Bohlmann Band" in the infrared spectra and the author hopes the few examples described will suffice to demonstrate the utility of this study.

C. Quantitative Possibilities

A comparison of the "Bohlmann Band" intensities for various concentrations of N-methyl-3-pyrrolidinol in carbon tetrachloride revealed that this band may be useful in quantitative applications. This possibility was not investigated further since it was decided to restrict this study to qualitative aspects.

SUMMARY

The "Bohlmann Band" normally appears in the 3.57 to 3.70 μ region of the infrared spectrum and is a result of the C-H stretching vibrations. This unique band is common to most aliphatic tertiary amines and provides a simple means of identifying and differentiating these amines from primary and secondary amines. Data obtained in this study shows that the wavelength range of this band may be further restricted to values between 3.57 μ and 3.62 μ. On occasion, there appear two bands in this region; however, both are peculiar to aliphatic tertiary amines.

Bohlmann (6) investigated the presence of this characteristic band in Quinolizidine systems. This study extended the application of this band to less complex tertiary amine systems. The criteria which Bohlmann established for the occurrence of this band were that there must be at least two protons on carbon atoms adjacent to a nitrogen and oriented co-planar and trans to the unshared electron pair.

The study of a large number of tertiary amines revealed that the criteria established for the appearance of

the "Bohlmann Band" in the infrared spectra of Quinolizidines may be extended to apply to other aliphatic tertiary amines. The unexpected appearance or absence of this characteristic band was rare and explanations of the exceptions were offered on the bases of electron pair delocalization or molecular conformation.

Substituent groups in positions on carbon atoms other than those adjacent to the nitrogen exert little or no effect on the "Bohlmann Band".

Several examples demonstrating the application of the results of this study were illustrated.

The characteristic "Bohlmann Band", which is in essence a simple and useful qualitative aid, will provide organic chemists with additional information for a more detailed interpretation of the infrared spectra of amines.

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AUTOBIOGRAPHY

I, John Alfred Richman, Jr., was born in Richmond, Virginia, on the fifteenth day of January in the year 1930. I was graduated from John Marshall High School of Richmond in 1947 and in the same year enrolled in the University of Richmond. During my senior year at the University of Richmond, the "Korean War" began and I served as an electronics technician with the United States Navy, having been graduated from the Electronics Technician School, Class A, of Great Lakes, Illinois. Upon completion of four years of active duty, I enrolled at the University of Virginia in the School of Engineering where I concentrated in electronics.

I returned to the University of Richmond in 1955 and was graduated with a B. S. degree in Chemistry in June of 1956. I then accepted a position as a chemical research engineer with the Hercules Powder Company of Hopewell, Virginia. The following year I accepted a position as a research chemist with the A. H. Robins Company of Richmond, Virginia, having been employed there since 1957.

APPENDIX I

Infrared Spectra of Amines

(3.0 to 4.0 μ)

FIGURE VII

PROMINENT C-H STRETCHING WAVELENGTHS IN PRIMARY AMINES

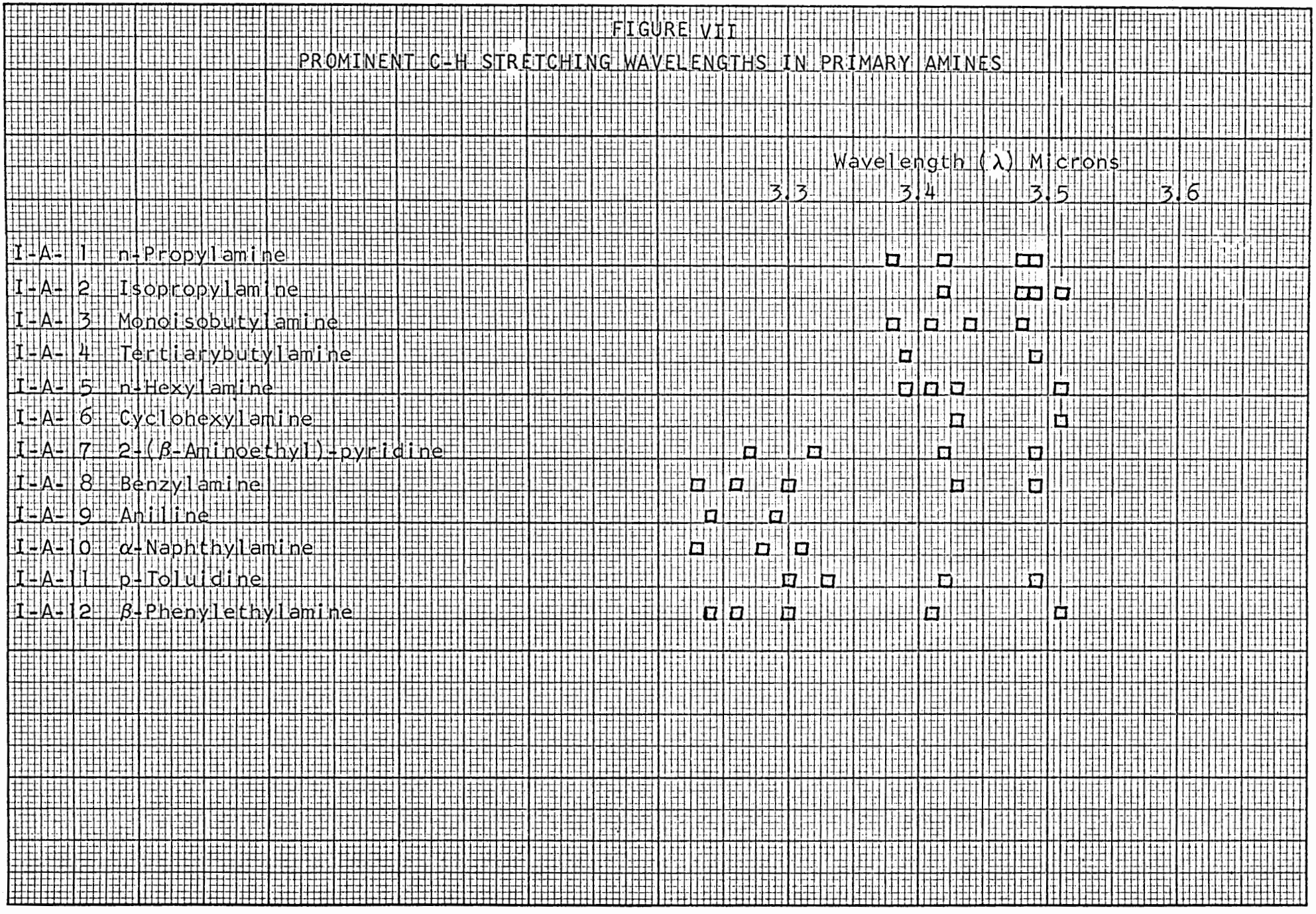


FIGURE VIII

PROMINENT C-H STRETCHING WAVELENGTHS IN SECONDARY AMINES

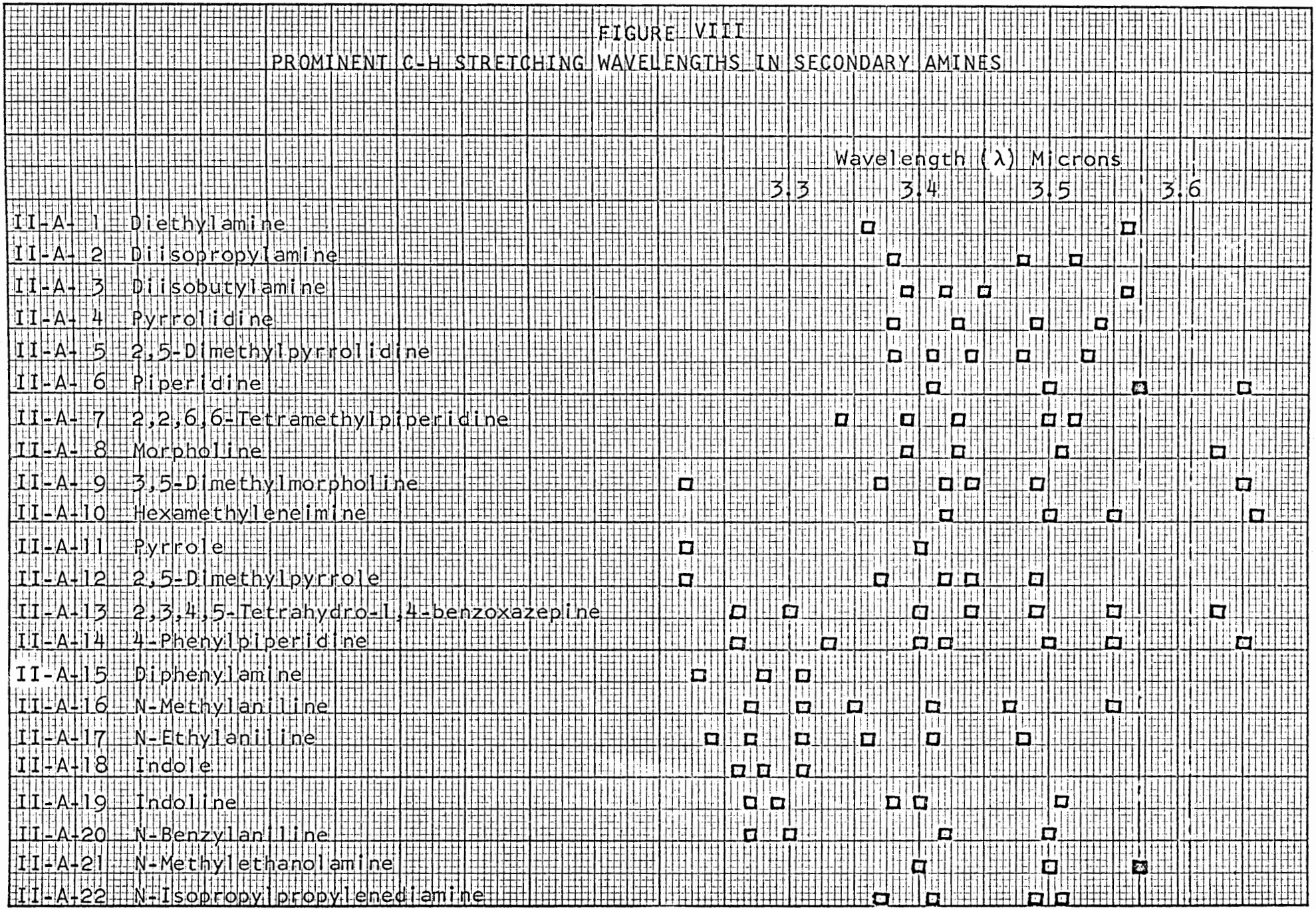


FIGURE VIII (Continued)

PROMINENT C-H STRETCHING WAVELENGTHS IN SECONDARY AMINES

continued

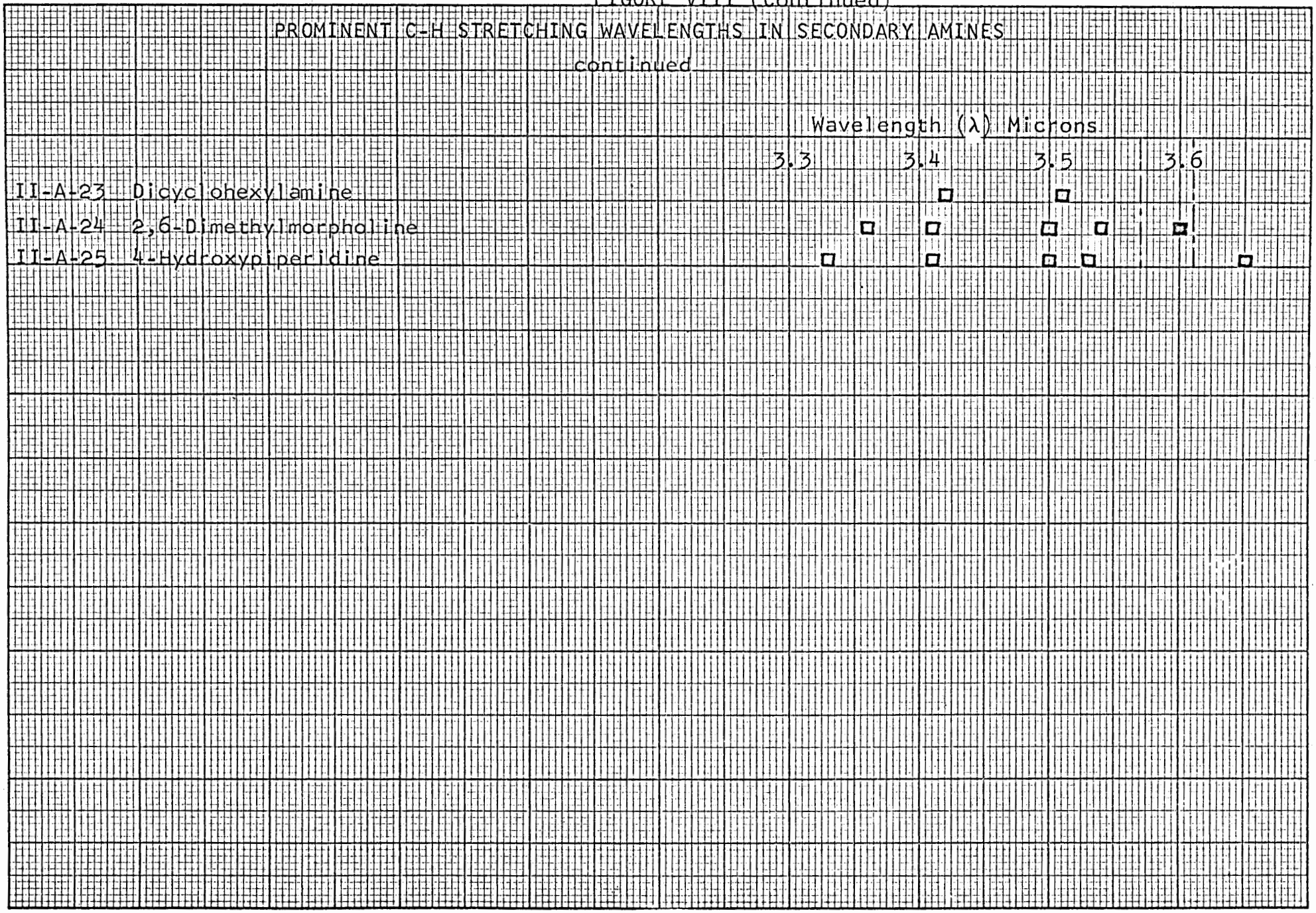


FIGURE IX

PROMINENT C-H STRETCHING WAVELENGTHS IN TERTIARY AMINES

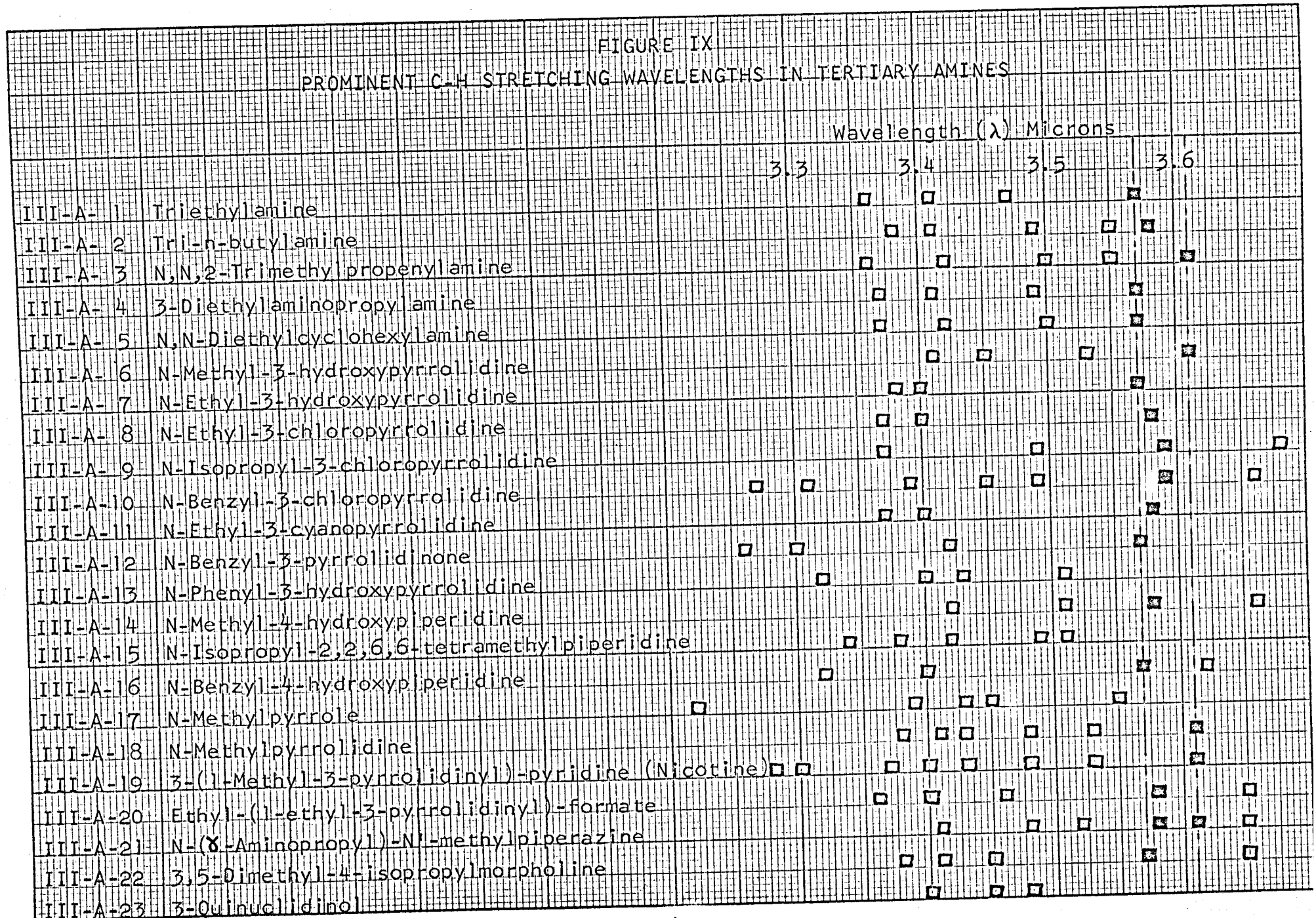


FIGURE IX (Continued)

PROMINENT C-H STRETCHING WAVELENGTHS IN TERTIARY AMINES

(continued)

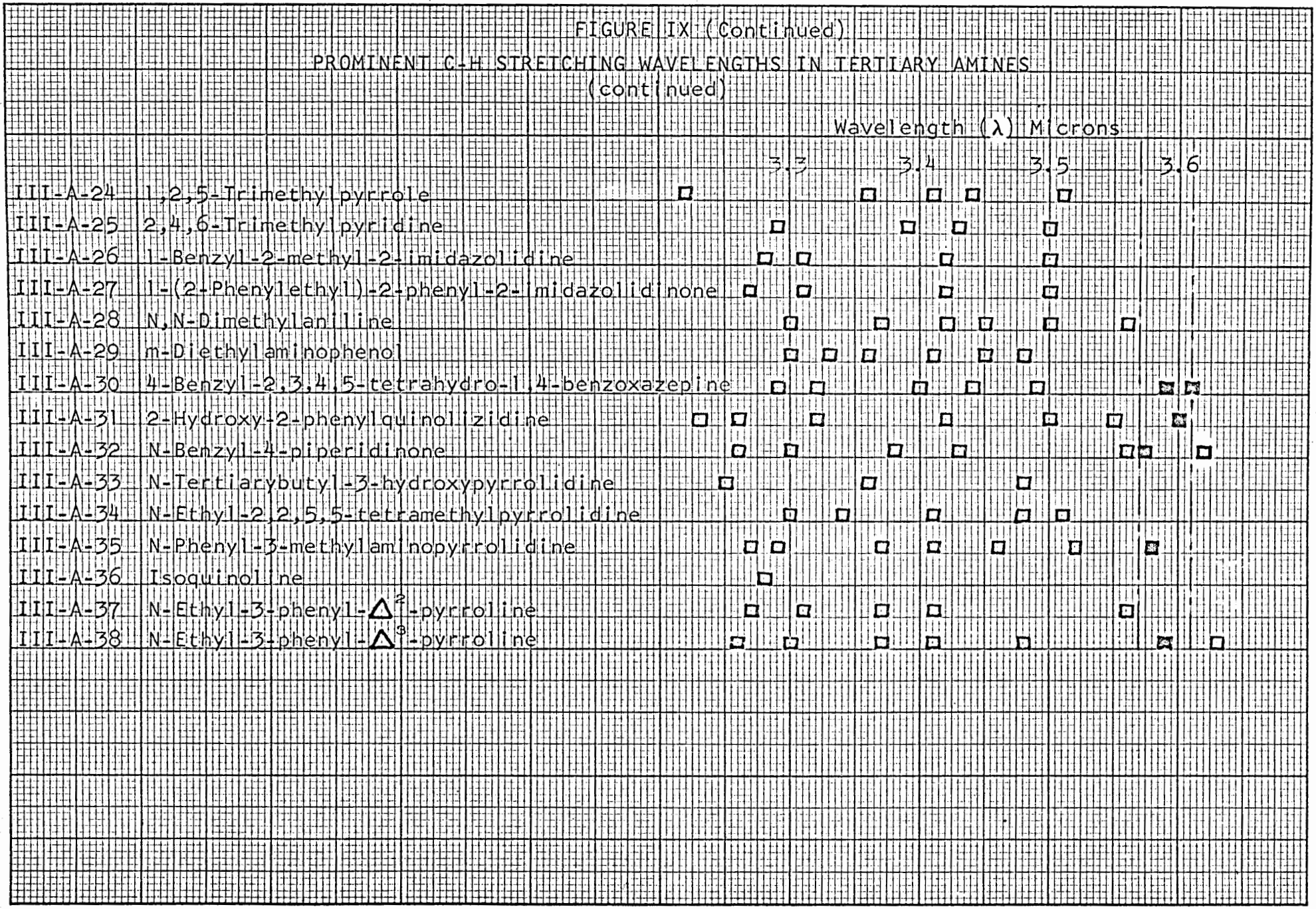


TABLE 5

PROMINENT C-H STRETCHING WAVELENGTHS
IN THE INFRARED SPECTRA OF PRIMARY AMINES

[Limited to the Region of 3.20 to 3.70 μ]

PRIMARY AMINES		PROMINENT ABSORPTION BANDS (MICRONS)
I-A- 1	n-Propylamine	3.38,3.42,3.48,3.49
I-A- 2	Isopropylamine	3.42,3.48,3.49,3.51
I-A- 3	Monoisobutylamine	3.38,3.41,3.44,3.48
I-A- 4	Tertiarybutylamine	3.39,3.49
I-A- 5	n-Hexylamine	3.39,3.41,3.43,3.51
I-A- 6	Cyclohexylamine	3.43,3.51
I-A- 7	2-(β-Aminoethyl)-pyridine	3.27,3.32,3.42,3.49
I-A- 8	Benzylamine	3.23,3.26,3.30,3.43,3.49
I-A- 9	Aniline	3.24,3.29
I-A-10	α-Naphthylamine	3.26,3.28,3.31
I-A-11	p-Toluidine	3.30,3.33,3.42,3.49
I-A-12	β-Phenylethylamine	3.24,3.26,3.30,3.41,3.51

TABLE 6

PROMINENT C-H STRETCHING WAVELENGTHS
IN THE INFRARED SPECTRA OF SECONDARY AMINES

[Limited to the Region of 3.20 to 3.70 μ]

SECONDARY AMINES		PROMINENT ABSORPTION BANDS (MICRONS)
II-A- 1	Diethylamine	3.36,3.56
II-A- 2	Diisopropylamine	3.38,3.48,3.52
II-A- 3	Diisobutylamine	3.39,3.42,3.45,3.56
II-A- 4	Pyrrolidine	3.38,3.43,3.49,3.54
II-A- 5	2,5-Dimethylpyrrolidine	3.38,3.41,3.44,3.48,3.53,3.78
II-A- 6	Piperidine	3.41,3.50,3.57,3.65
II-A- 7	2,2,6,6-Tetramethylpiperidine	3.34,3.39,3.43,3.50,3.52
II-A- 8	Morpholine	3.39,3.43,3.51,3.63
II-A- 9	3,5-Dimethylmorpholine	3.22,3.37,3.42,3.44,3.49,3.65
II-A-10	Hexamethyleneimine	3.42,3.50,3.55,3.66,3.72
II-A-11	Pyrrole	3.22,3.40,3.92
II-A-12	2,5-Dimethylpyrrole	3.22,3.37,3.42,3.44,3.49

TABLE 6 (Continued)

SECONDARY AMINES		PROMINENT ABSORPTION BANDS (MICRONS)
II-A-13	2,3,4,5-Tetrahydro-1,4-benzoxazepine	3.26,3.30,3.40,3.44,3.49,3.55,3.63
II-A-14	4-Phenylpiperidine	3.26,3.33,3.40,3.42,3.50,3.55,3.65
II-A-15	Diphenylamine	3.23,3.28,3.31
II-A-16	N-Methylaniline	3.27,3.31,3.35,3.41,3.47,3.55
II-A-17	N-Ethylaniline	3.24,3.27,3.31,3.36,3.41,3.48
II-A-18	Indole	3.26,3.28,3.31
II-A-19	Indoline	3.27,3.29,3.38,3.40,3.51
II-A-20	N-Benzylaniline	3.27,3.30,3.42,3.50
II-A-21	N-Methylethanolamine	3.40,3.50,3.57
II-A-22	N-Isopropylpropylenediamine	3.37,3.41,3.49,3.51
II-A-23	Dicyclohexylamine	3.42,3.51
II-A-24	2,6-Dimethylmorpholine	3.36,3.41,3.50,3.54,3.60
II-A-25	4-Hydroxypiperidine	3.33,3.41,3.50,3.53,3.65

TABLE 7

PROMINENT C-H STRETCHING WAVELENGTHS
IN THE INFRARED SPECTRA OF TERTIARY AMINES

[Limited to the Region of 3.20 to 3.70 μ]

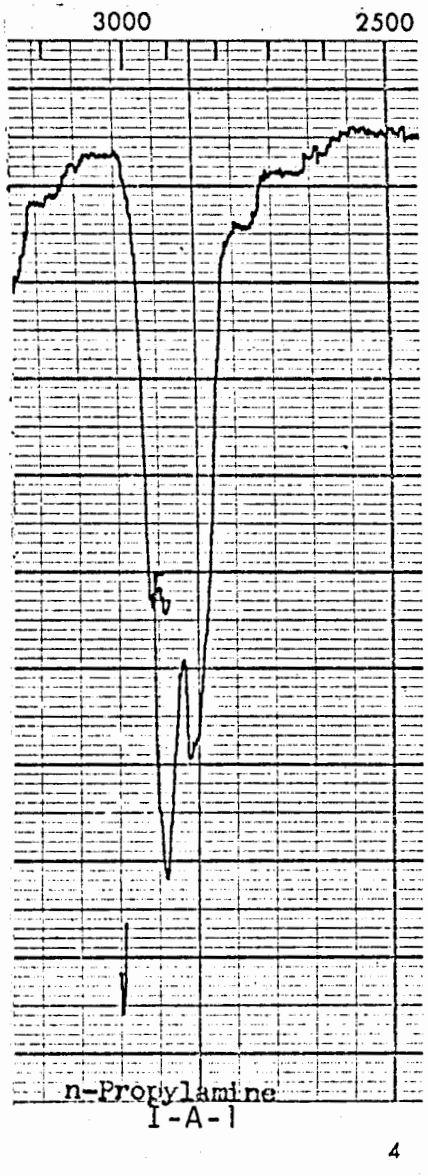
TERTIARY AMINES		PROMINENT ABSORPTION BANDS (MICRONS)
III-A- 1	Triethylamine	3.36,3.41,3.47,3.57
III-A- 2	Tri-n-butylamine	3.38,3.41,3.49,3.55,3.58
III-A- 3	N,N,2-Trimethylpropenylamine	3.36,3.42,3.50,3.55,3.61
III-A- 4	3-Diethylaminopropylamine	3.37,3.41,3.49,3.57
III-A- 5	N,N-Diethylcyclohexylamine	3.37,3.42,3.50,3.57
III-A- 6	N-Methyl-3-hydroxypyrrolidine	3.41,3.45,3.53,3.61
III-A- 7	N-Ethyl-3-hydroxypyrrolidine	3.38,3.40,3.57
III-A- 8	N-Ethyl-3-chloropyrrolidine	3.37,3.40,3.58,3.70
III-A- 9	N-Isopropyl-3-chloropyrrolidine	3.37,3.49,3.59,3.68
III-A-10	N-Benzyl-3-chloropyrrolidine	3.27,3.31,3.39,3.45,3.49,3.59,3.66
III-A-11	N-Ethyl-3-cyanopyrrolidine	3.37,3.40,3.58
III-A-12	N-Benzyl-3-pyrrolidinone	3.26,3.30,3.42,3.57

TABLE 7 (Continued)

TERTIARY AMINES		PROMINENT ABSORPTION BANDS (MICRONS)
III-A-13	N-Phenyl-3-hydroxypyrrolidine	3.32,3.40,3.43,3.51
III-A-14	N-Methyl-4-hydroxypiperidine	3.42,3.51,3.58,3.66
III-A-15	N-Isopropyl-2,2,6,6-tetramethylpiperidine	3.34,3.38,3.42,3.49,3.51
III-A-16	N-Benzyl-4-hydroxypiperidine	3.32,3.40,3.57,3.62
III-A-17	N-Methylpyrrole	3.22,3.39,3.43,3.45,3.55
III-A-18	N-Methylpyrrolidine	3.38,3.41,3.43,3.48,3.53,3.61
III-A-19	3-(1-Methyl-3-pyrrolidinyl)-pyridine (Nicotine)	3.28,3.30,3.37,3.40,3.43,3.48,3.53,3.61
III-A-20	Ethyl-(1-ethyl-3-pyrrolidinyl)-formate	3.36,3.40,3.46,3.58,3.65
III-A-21	N-(γ-Aminopropyl)-N'-methylpiperazine	3.41,3.48,3.52,3.58,3.61,3.65
III-A-22	3,5-Dimethyl-4-isopropylmorpholine	3.38,3.41,3.50,3.57,3.65
III-A-23	3-Quinuclidinol	3.40,3.45,3.48
III-A-24	1,2,5-Trimethylpyrrole	3.22,3.36,3.41,3.44,3.51
III-A-25	2,4,6-Trimethylpyridine	3.29,3.39,3.43,3.50
III-A-26	1-Benzyl-2-methyl-2-imidazolidine	3.28,3.31,3.42,3.50

TABLE 7 (Continued)

TERTIARY AMINES		PROMINENT ABSORPTION BANDS (MICRONS)
III-A-27	1-(2-Phenylethyl)-2-phenyl-2-imidazolidinone	3.27,3.31,3.42,3.50
III-A-28	N,N-Dimethylaniline	3.30,3.37,3.42,3.45,3.50,3.56
III-A-29	m-Diethylaminophenol	3.30,3.33,3.36,3.41,3.45,3.48
III-A-30	4-Benzyl-2,3,4,5-tetrahydro-1,4-benzoxazepine	3.26,3.29,3.32,3.40,3.41,3.44,3.49,3.59 3.61
III-A-31	2-Hydroxy-2-phenylquinolizidine	3.23,3.26,3.32,3.42,3.50,3.55,3.60
III-A-32	N-Benzyl-4-piperidinone	3.26,3.30,3.38,3.43,3.56,3.62
III-A-33	N-Tertiarybutyl-3-hydroxypyrrolidine	3.25,3.36,3.48
III-A-34	N-Ethyl-2,2,5,5-tetramethylpyrrolidine	3.30,3.34,3.41,3.48,3.51
III-A-35	N-Phenyl-3-methylaminopyrrolidine	3.27,3.29,3.37,3.41,3.46,3.52,3.58
III-A-36	Isoquinoline	3.28
III-A-37	N-Ethyl-3-phenyl-Δ^2-pyrroline	3.27,3.31,3.37,3.41,3.56
III-A-38	N-Ethyl-3-phenyl-Δ^3-pyrroline	3.26,3.30,3.37,3.41,3.48,3.59,3.63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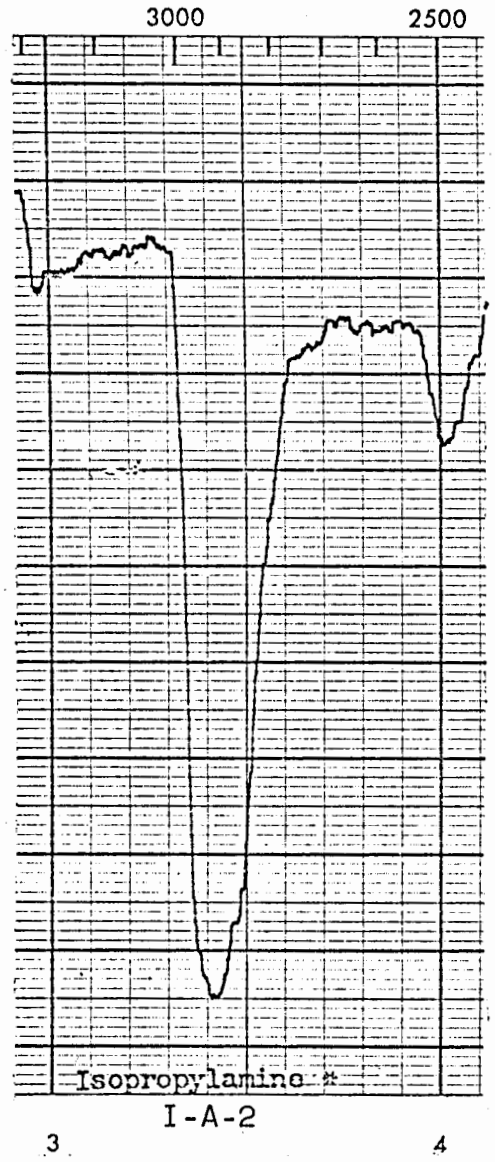
2500
n-Propylamine
I-A-1
4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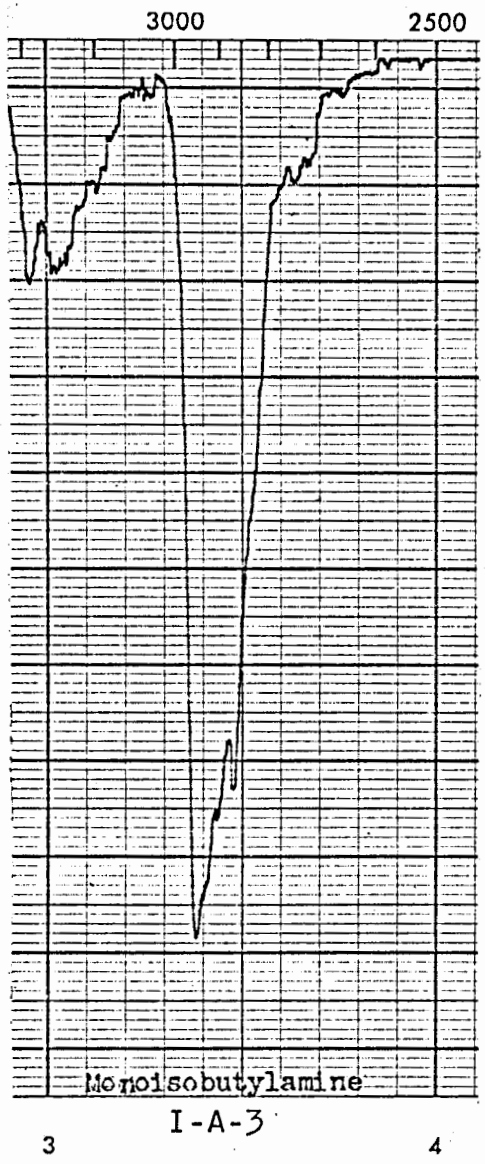
2500
Isopropylamine *
I-A-2
3
4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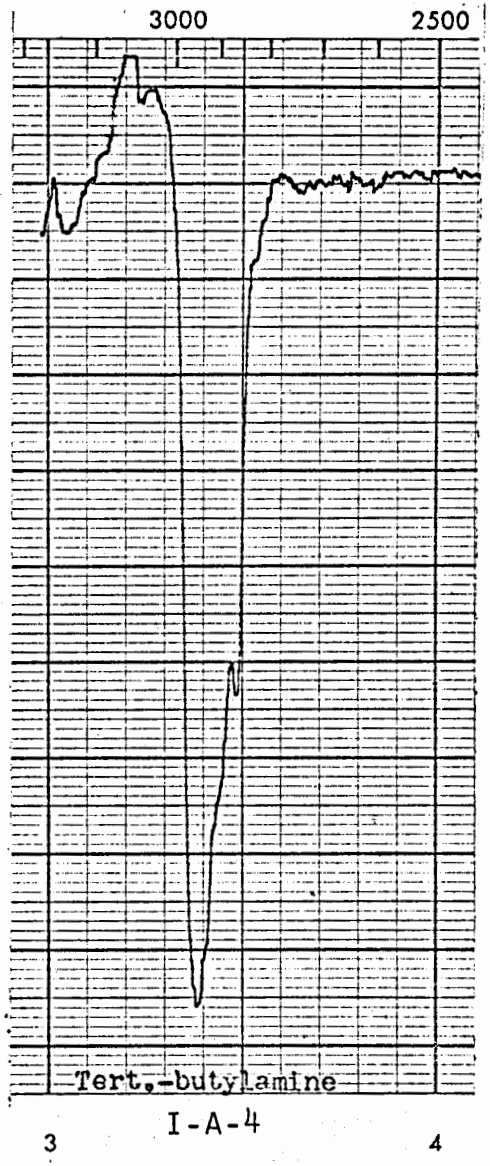
2500
Monoisobutylamine
I-A-3
3
4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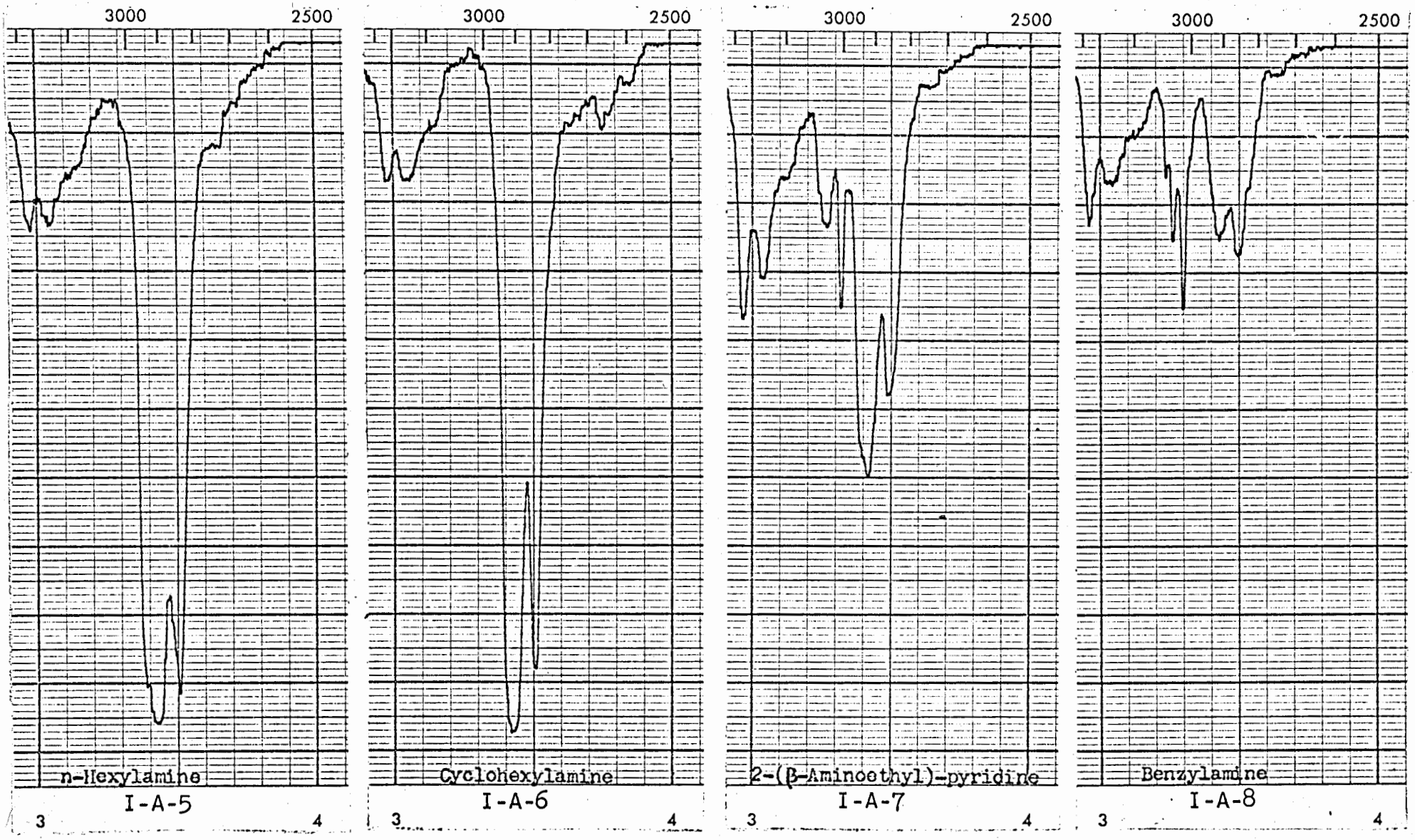
2500
Tert.-butylamine
I-A-4
3
4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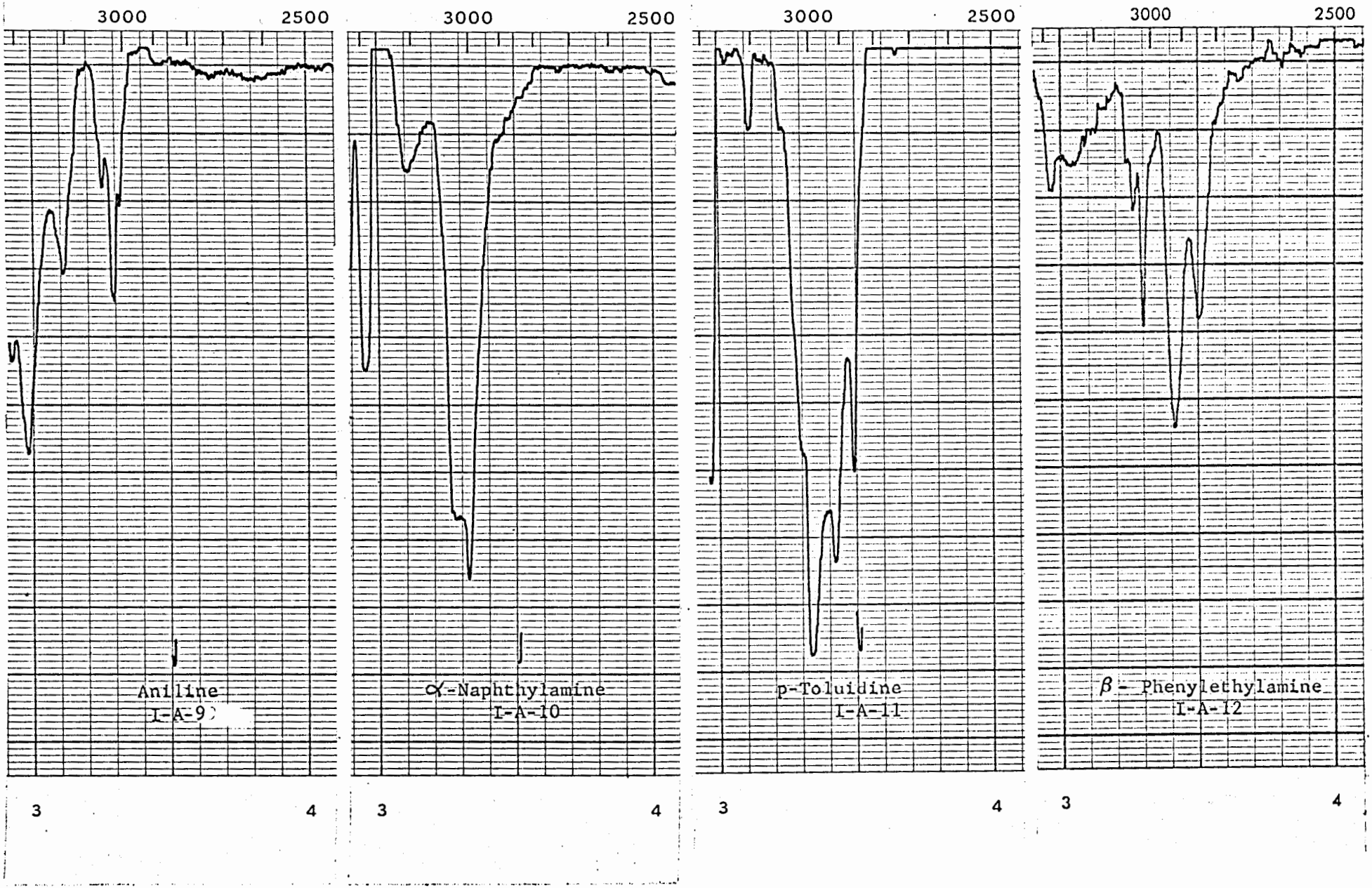
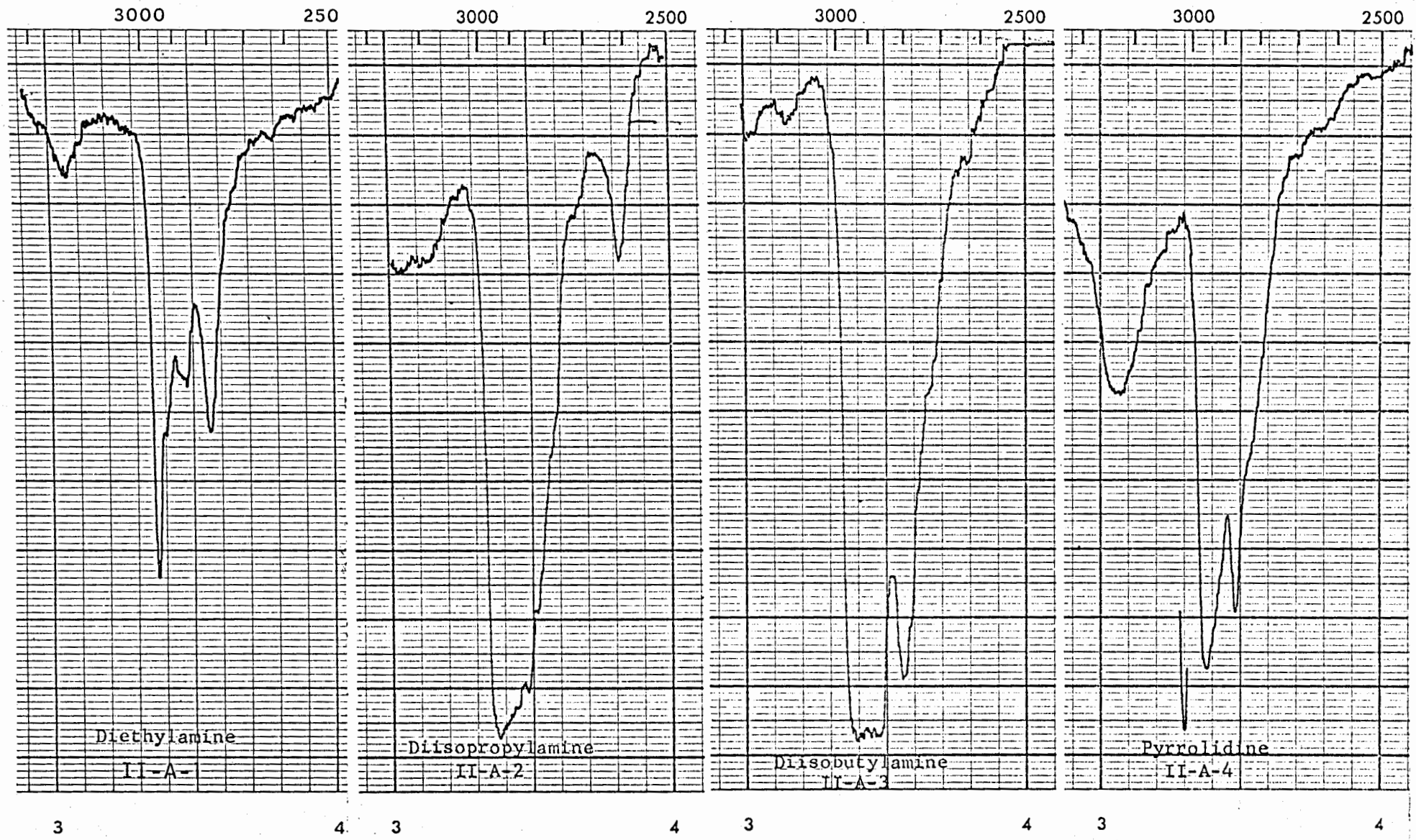
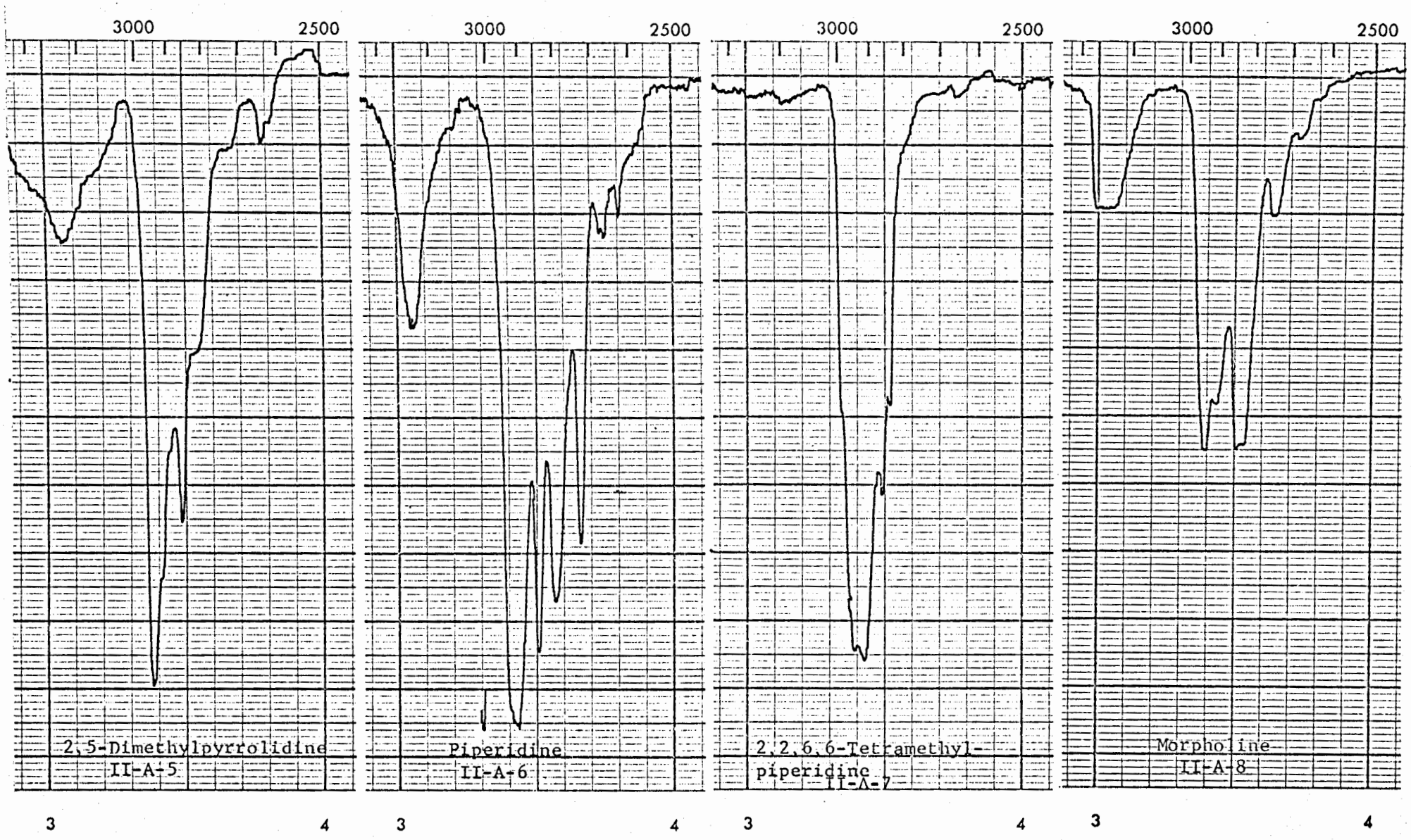
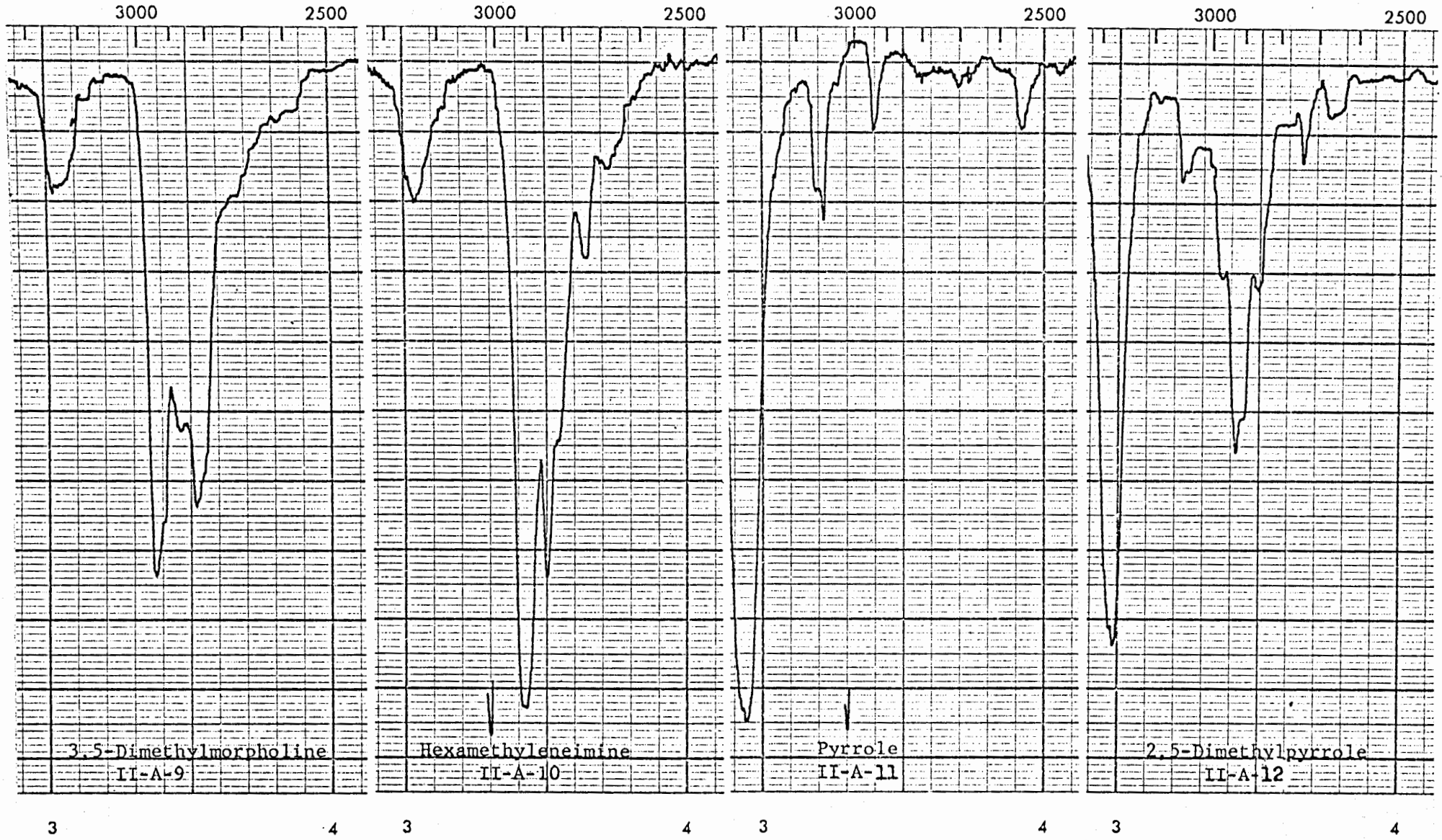
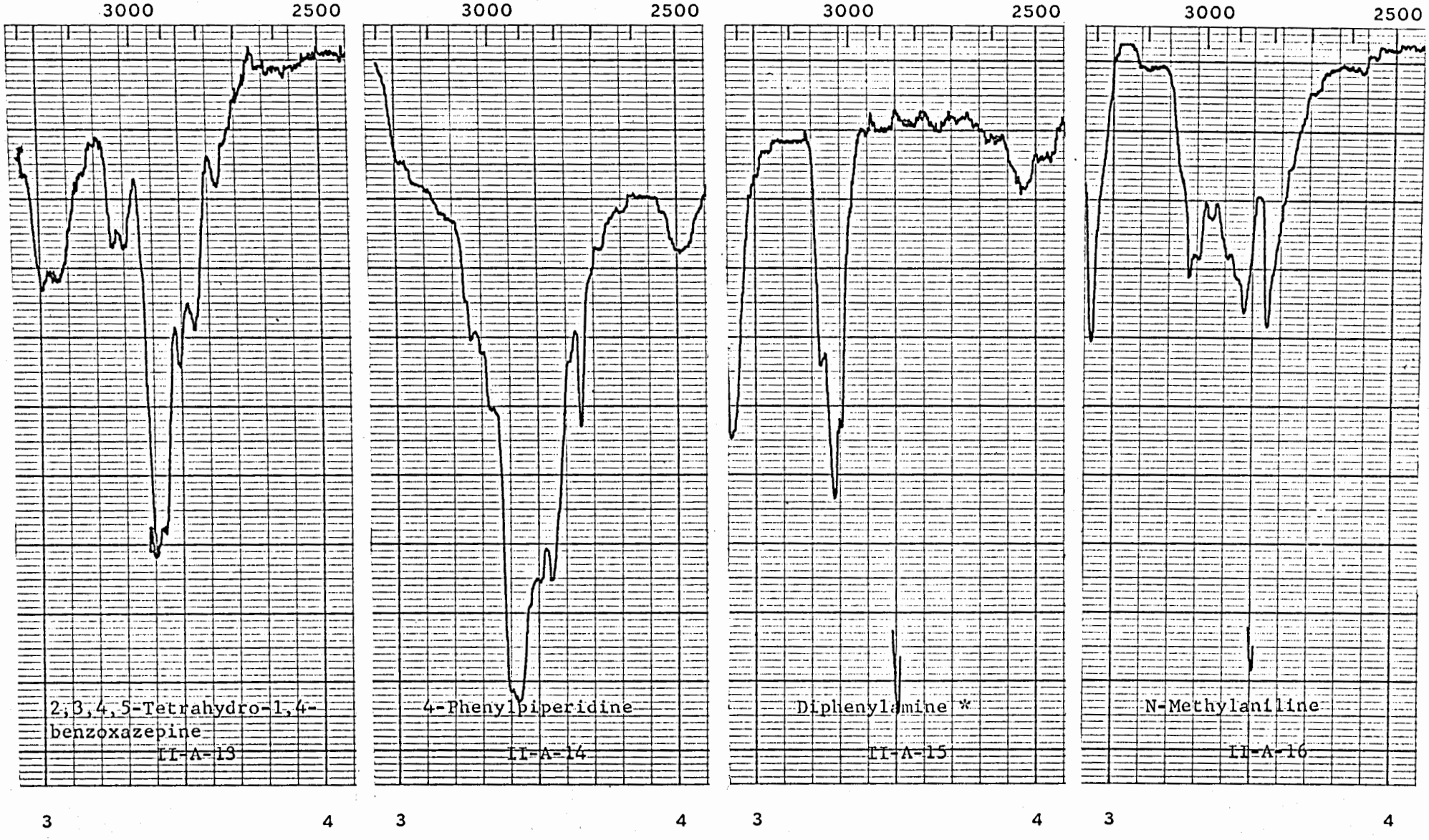
2500
n-Hexylamine
I-A-5
3
4
3000
2500
Cyclohexylamine
I-A-6
3
4
3000
2500
2-(β-Aminoethyl)-pyridine
I-A-7
3
4
3000
2500
Benzylamine
I-A-8
3
4

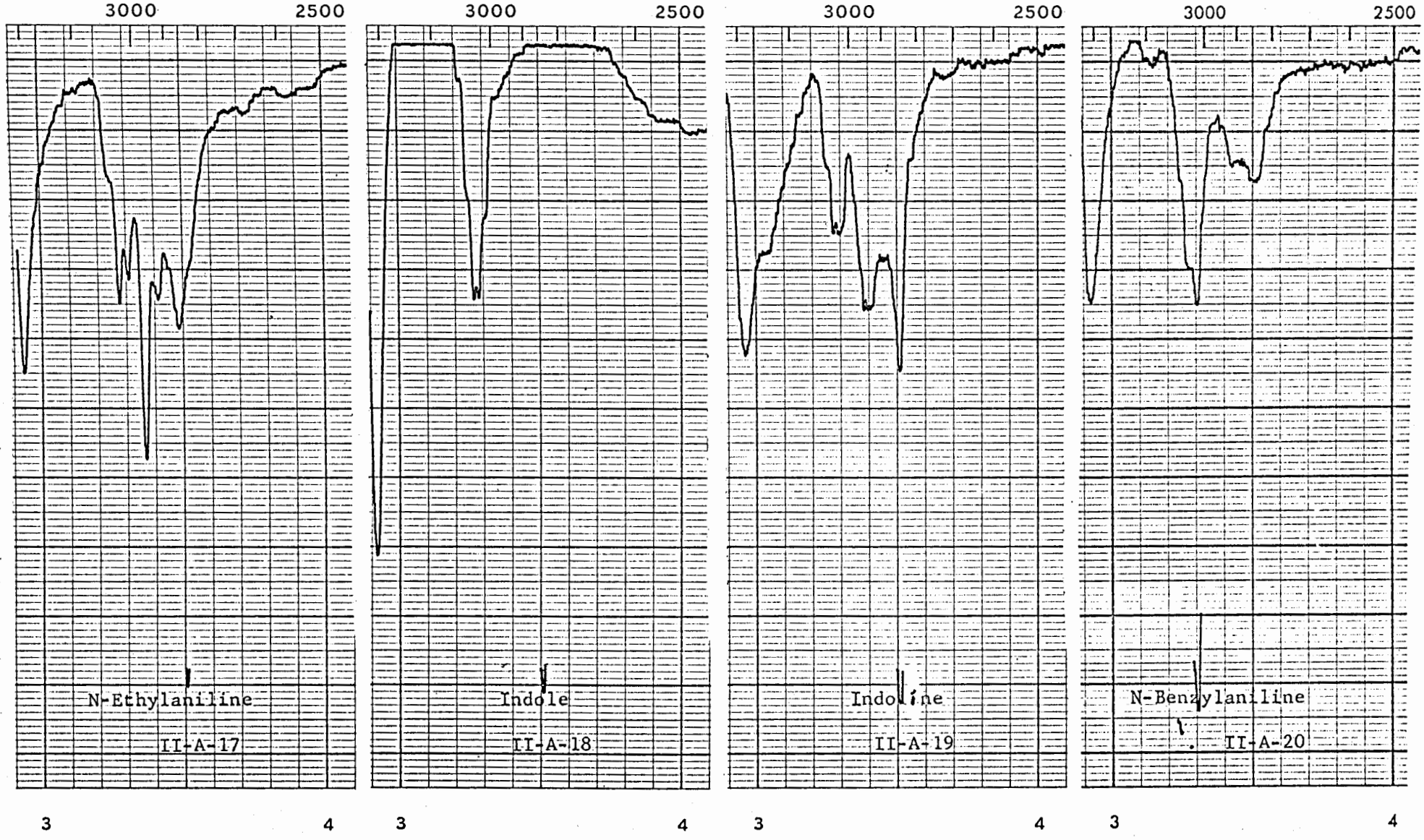

3000
2500
Aniline
I-A-9
3000
2500
α-Naphthylamine
I-A-10
3000
2500
p-Toluidine
I-A-11
3000
2500
β - Phenylethylamine
I-A-12
3
4
3
4
3
4
3
4

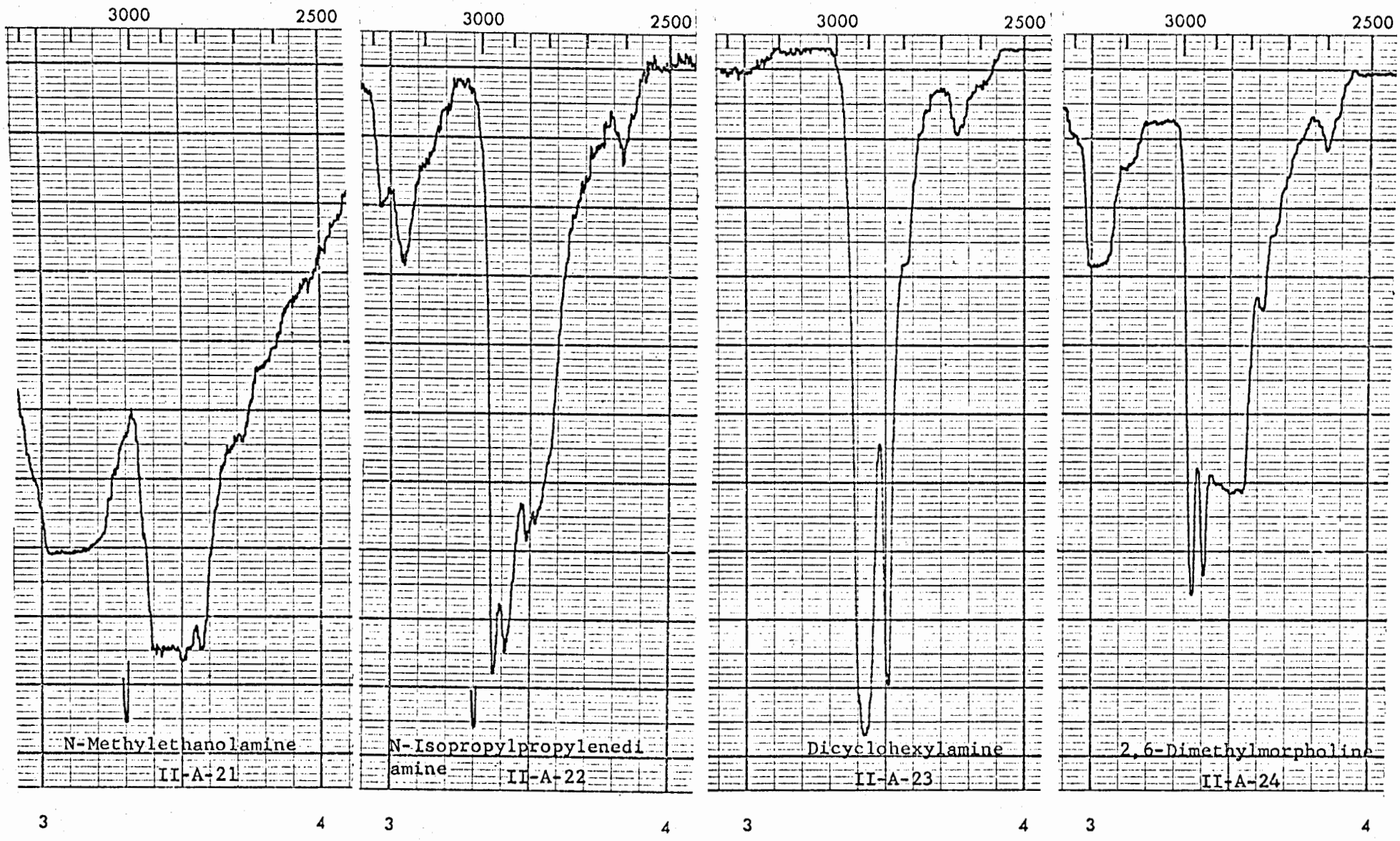

3000
250
Diethylamine
II-A-
3000
2500
Diisopropylamine
II-A-2
3000
2500
Diisobutylamine
II-A-3
3000
2500
Pyrrolidine
II-A-4
3
4
3
4
3
4
3
4

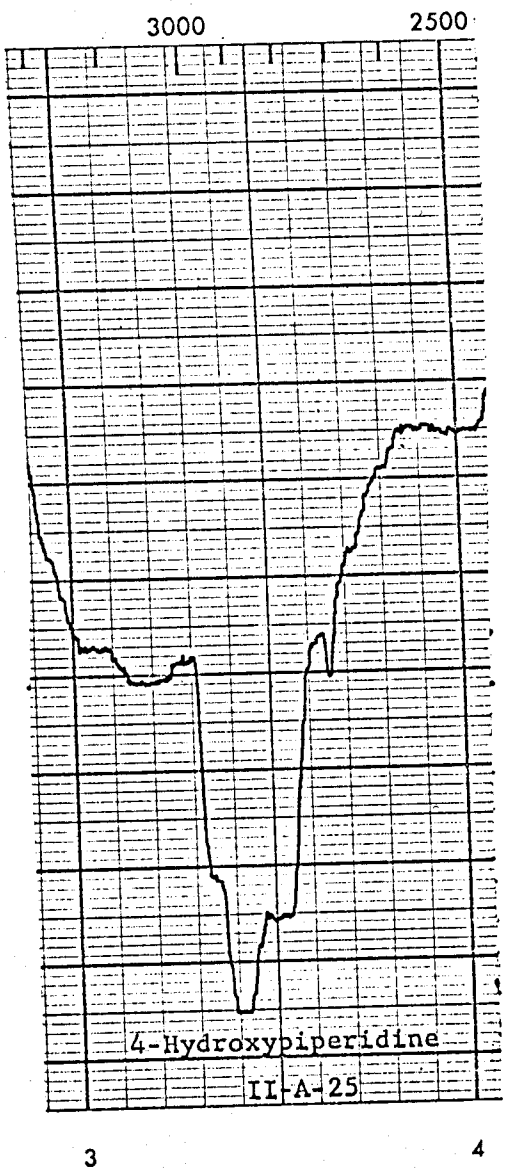

3000
2500
3
4
2,5-Dimethylpyrrolidine
II-A-5
Piperidine
II-A-6
2,2,6,6-Tetramethyl-
piperidine
II-A-7
Morpholine
II-A-8

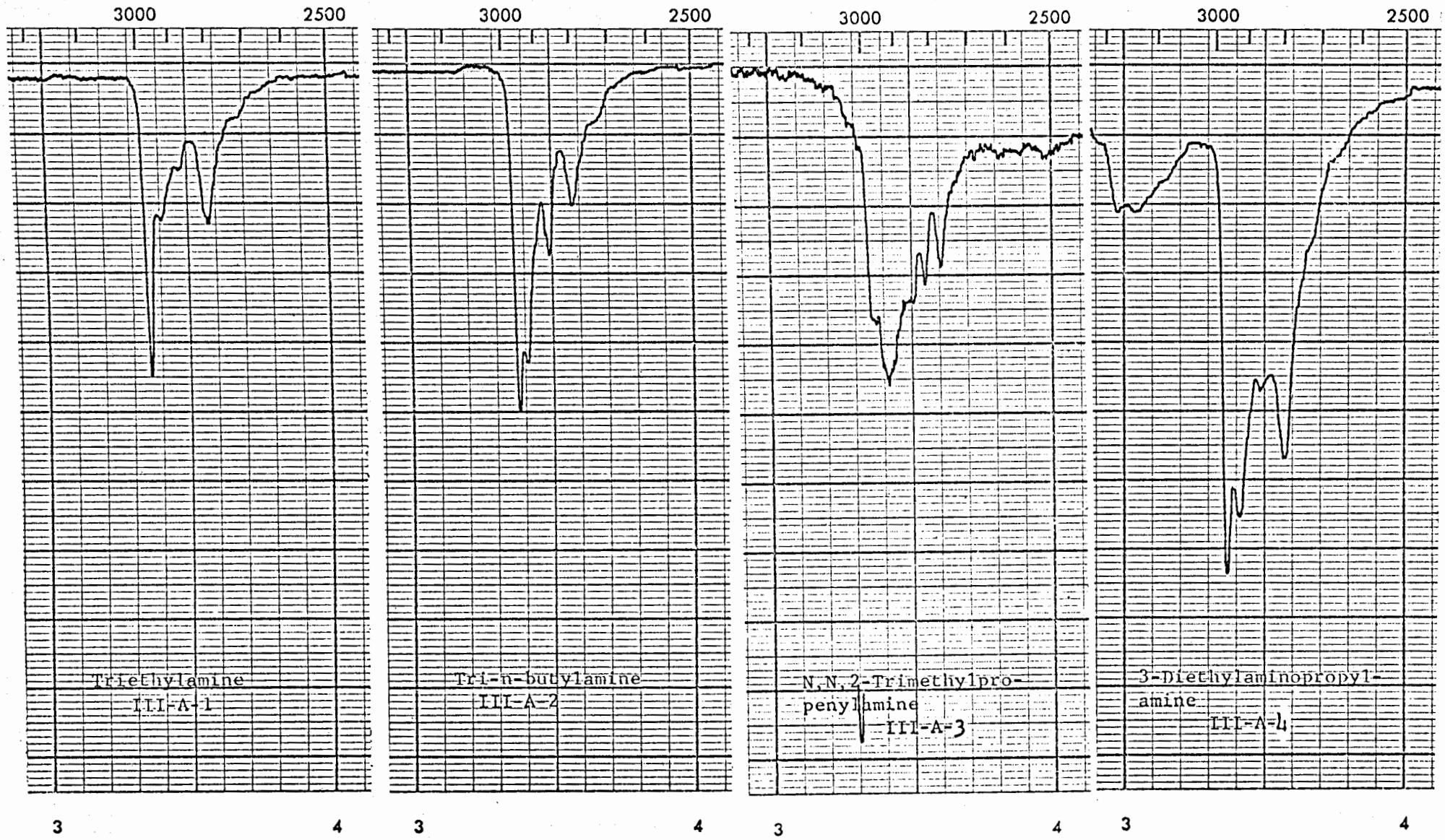

3000
2500
3,5-Dimethylmorpholine
II-A-9
Hexamethyleneimine
II-A-10
Pyrrole
II-A-11
2,5-Dimethylpyrrole
II-A-12
3
4

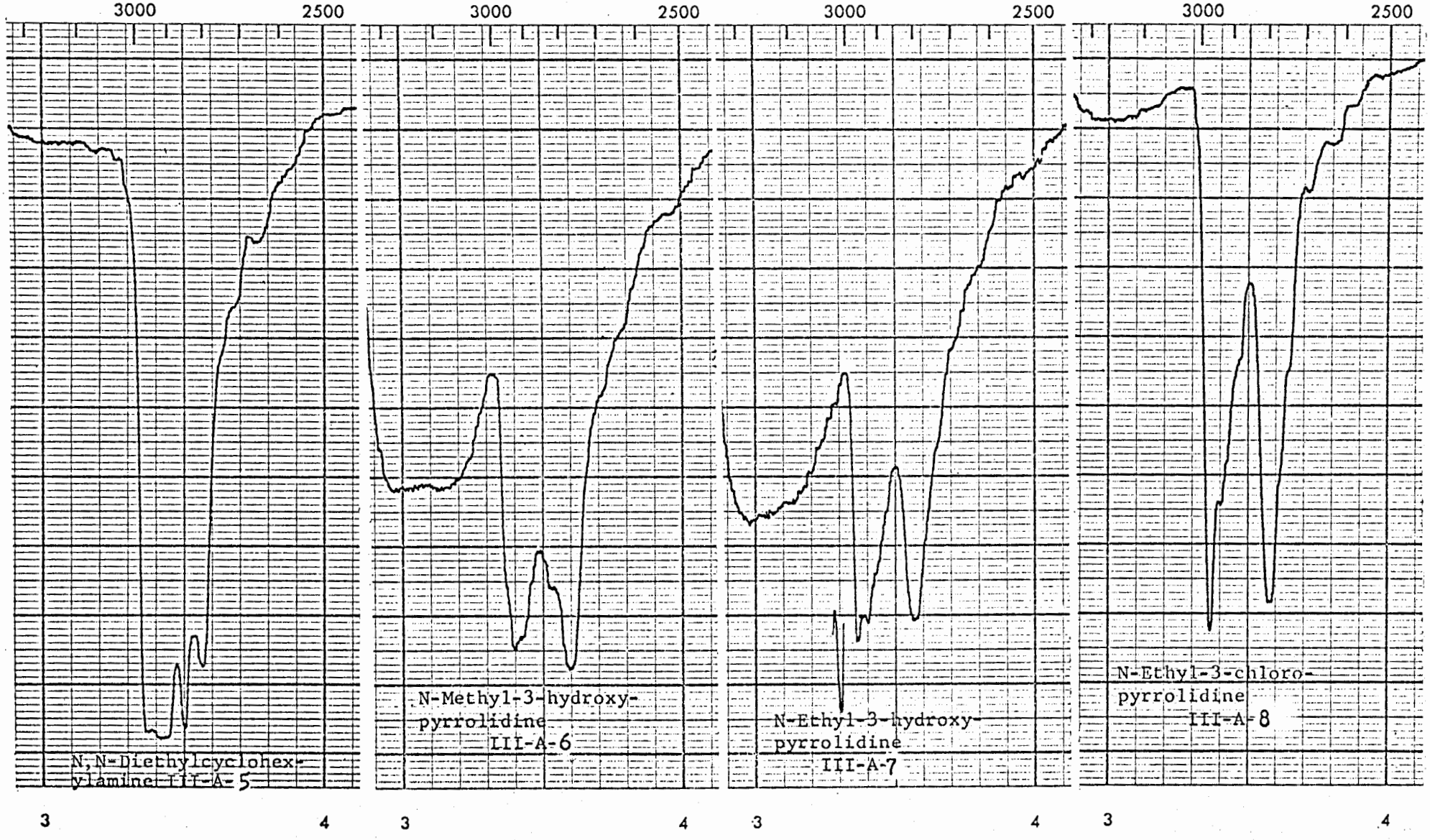

3000
2500
2,3,4,5-Tetrahydro-1,4-benzoxazepine
II-A-13
4-Phenylpiperidine
II-A-14
Diphenylamine *
II-A-15
N-Methylaniline
II-A-16
3
4

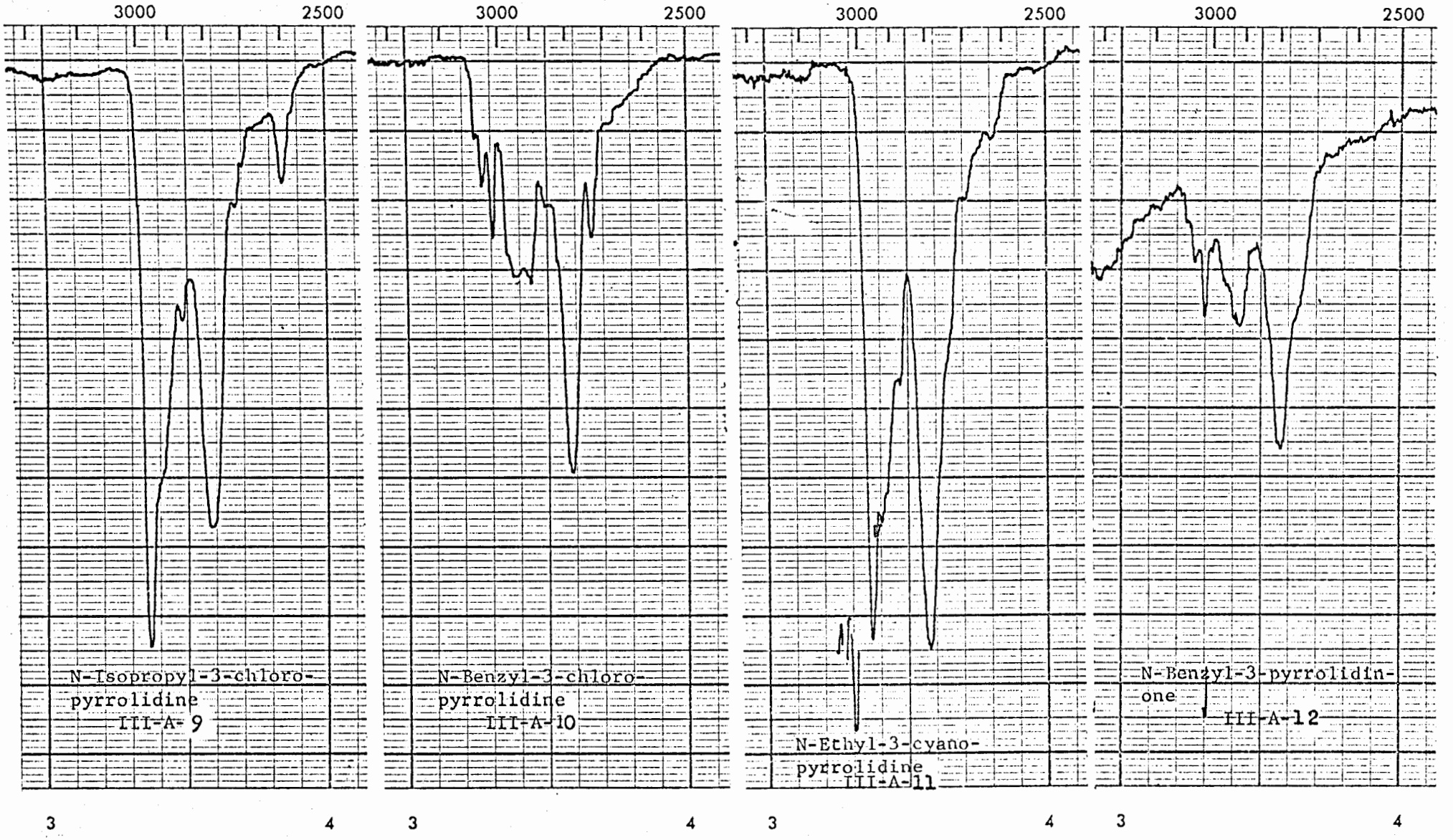

3000
2500
N-Ethylaniline
II-A-17
3000
2500
Indole
II-A-18
3000
2500
Indoline
II-A-19
3000
2500
N-Benzylaniline
II-A-20
3
4
3
4
3
4
3
4

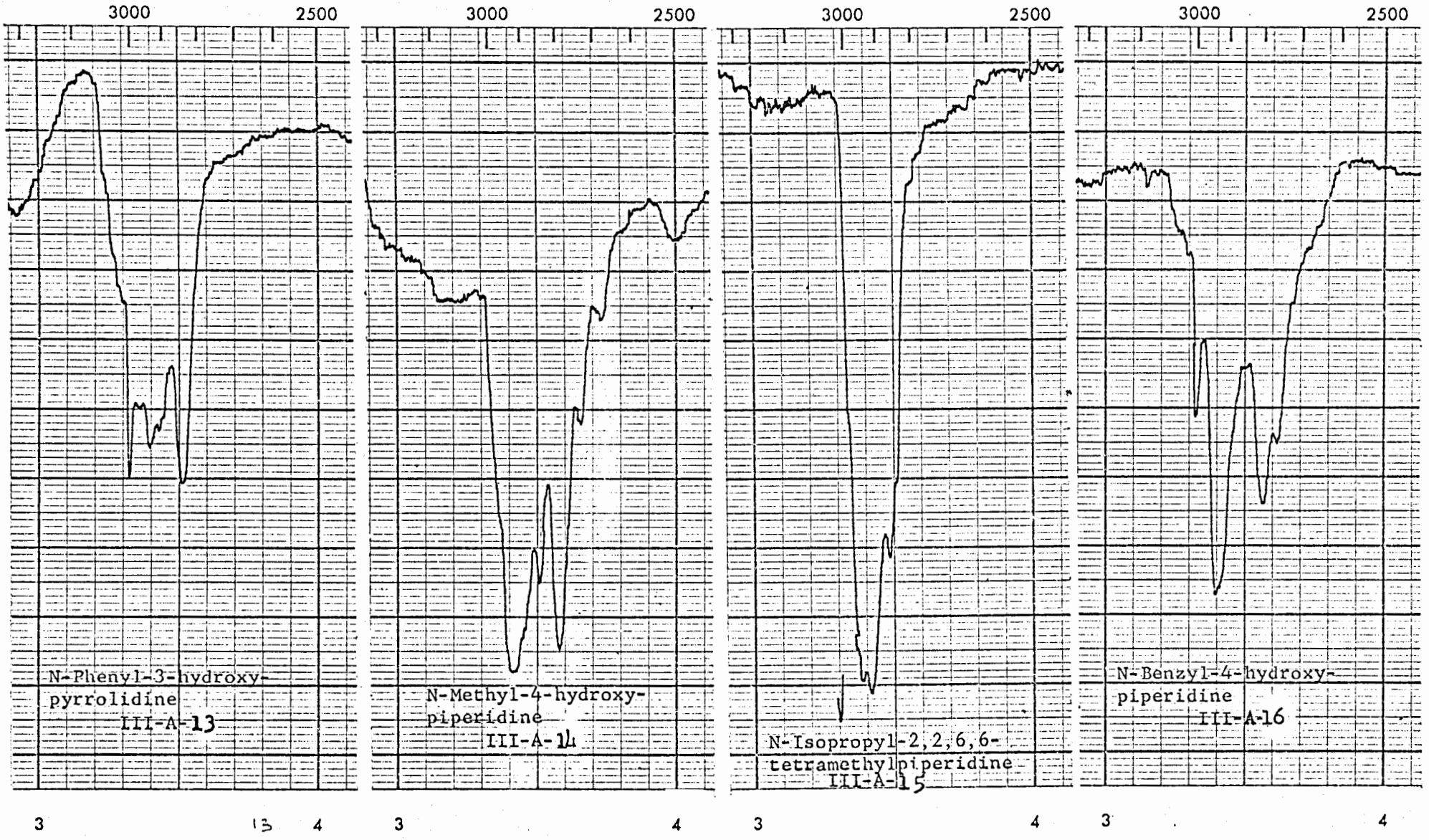

3000
2500
N-Methylethanolamine
II-A-21
3
4
3000
2500
N-Isopropylpropylenedi
amine
II-A-22
3
4
3000
2500
Dicyclohexylamine
II-A-23
3
4
3000
2500
2,6-Dimethylmorpholine
II-A-24
3
4

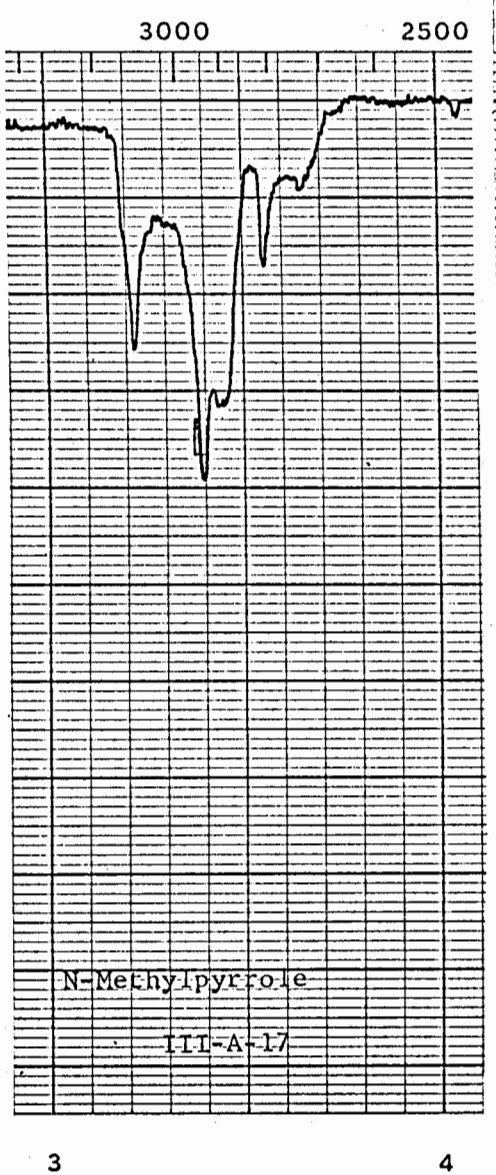

3000
2500
4-Hydroxypiperidine
II-A-25
3
4

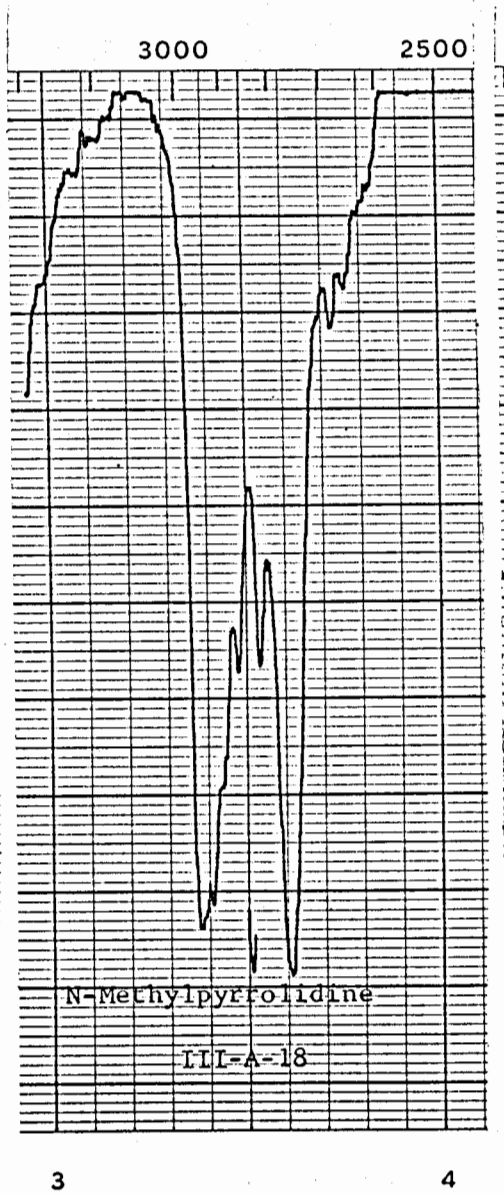

3000
2500
Triethylamine
III-A-1
3
4
3000
2500
Tri-n-butylamine
III-A-2
3
4
3000
2500
N,N,2-Trimethylpro-
penylamine
III-A-3
3
4
3000
2500
3-Diethylaminopropyl-
amine
III-A-4
3
4


3000
2500
N,N-Diethylcyclohex-
ylamine III-A-5
N-Methyl-3-hydroxy-
pyrrolidine
III-A-6
N-Ethyl-3-hydroxy-
pyrrolidine
III-A-7
N-Ethyl-3-chloro-
pyrrolidine
III-A-8
3
4


3000
2500
N-Isopropyl-3-chloro-
pyrrolidine
III-A-9
3000
2500
N-Benzyl-3-chloro-
pyrrolidine
III-A-10
3000
2500
N-Ethyl-3-cyano-
pyrrolidine
III-A-11
3000
2500
N-Benzyl-3-pyrrolidin-
one
III-A-12
3
4
3
4
3
4
3
4


3000
2500
N-Phenyl-3-hydroxy-
pyrrolidine
III-A-13
3
4
3000
2500
N-Methyl-4-hydroxy-
piperidine
III-A-14
3
4
3000
2500
N-Isopropyl-2,2,6,6-
tetramethylpiperidine
III-A-15
3
4
3000
2500
N-Benzyl-4-hydroxy-
piperidine
III-A-16
3
4


3000
2500
N-Methylpyrrole
III-A-17
3
4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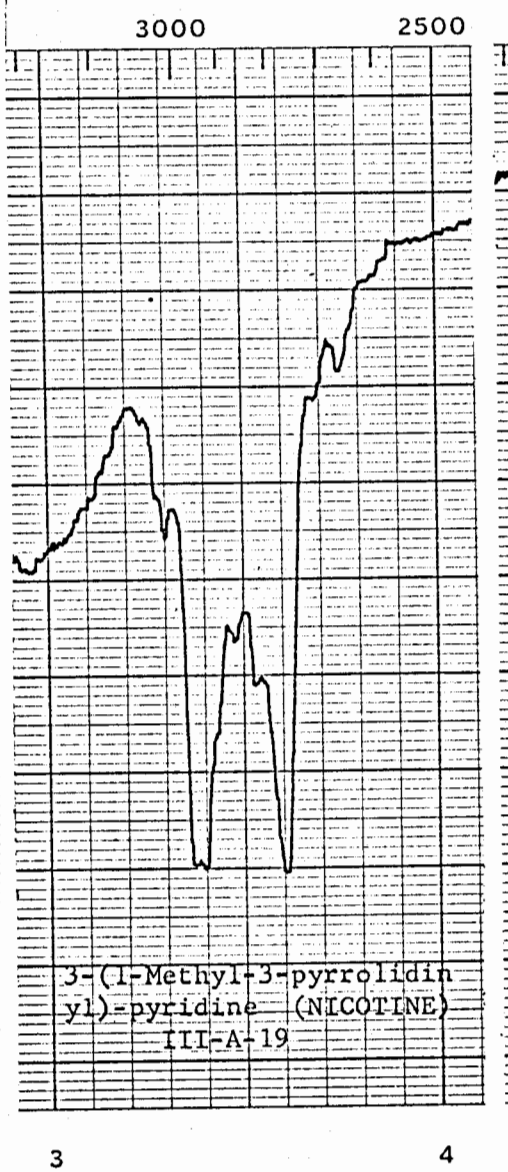
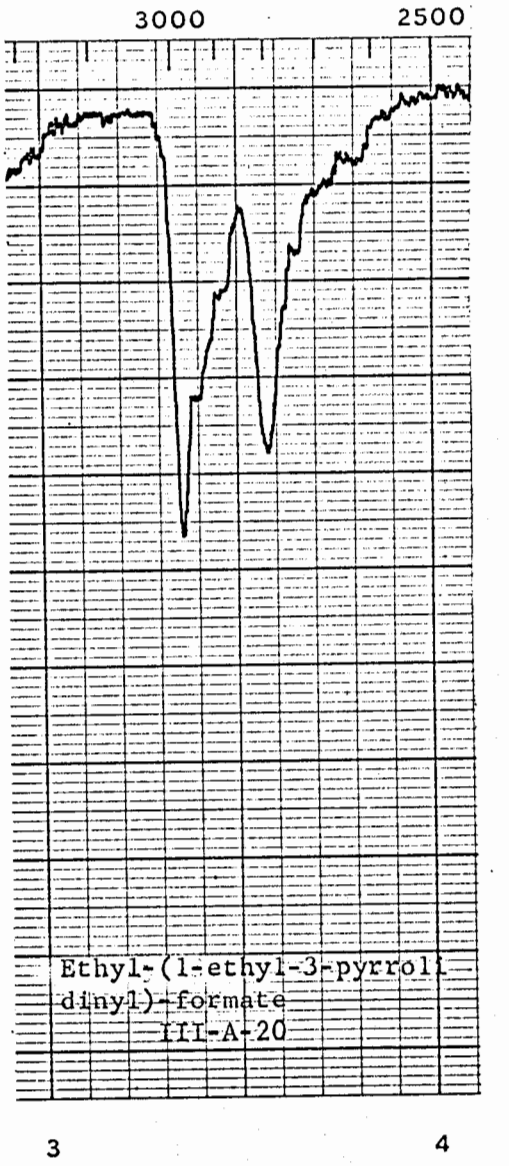
2500
N-Methylpyrrolidine
III-A-18
3
4


3000
2500
3-(1-Methyl-3-pyrrolidin
yl)-pyridine (NICOTINE)
III-A-19
3
4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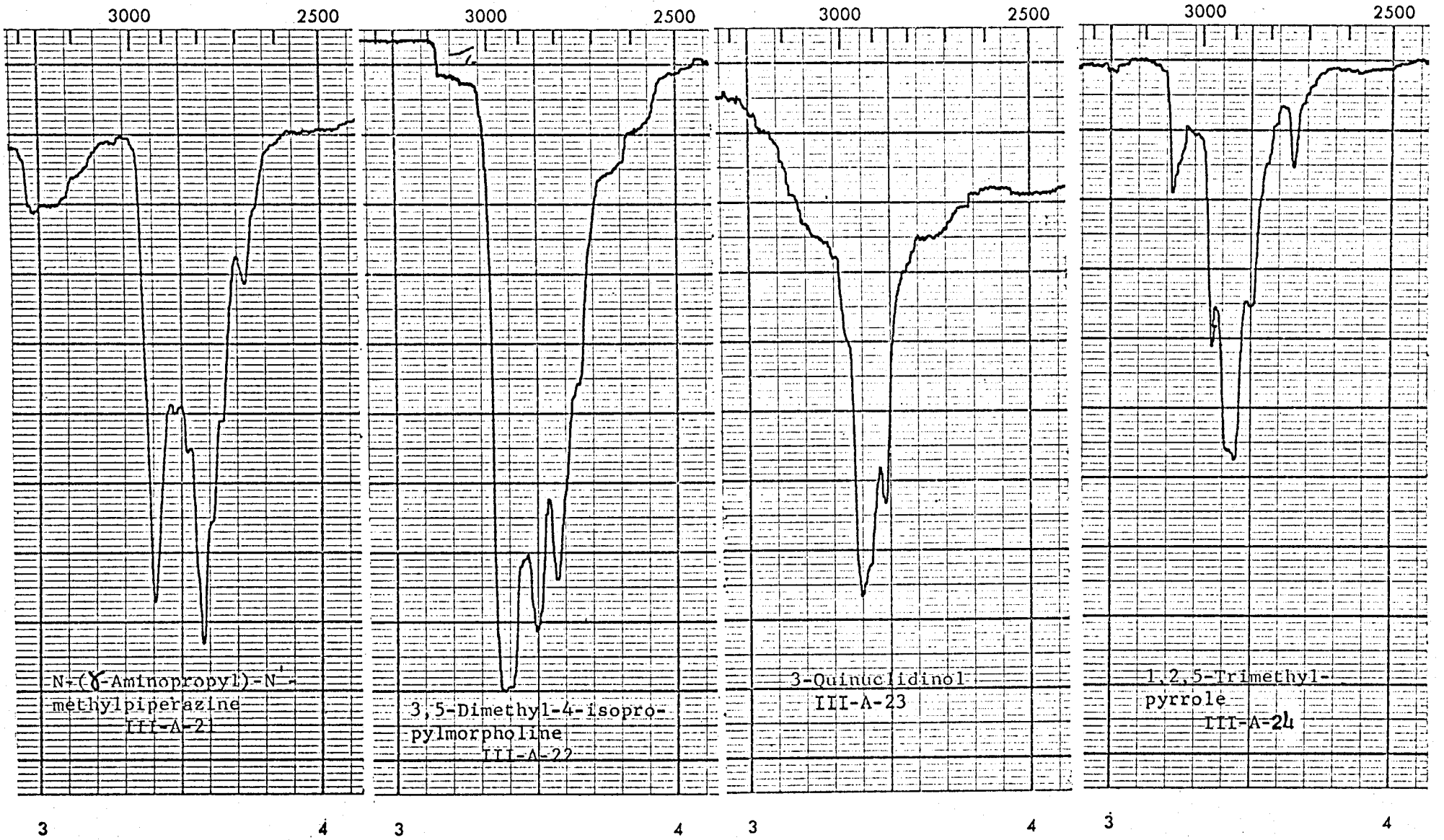
2500
Ethyl-(1-ethyl-3-pyrroli
dinyl)-formate
III-A-20
3
4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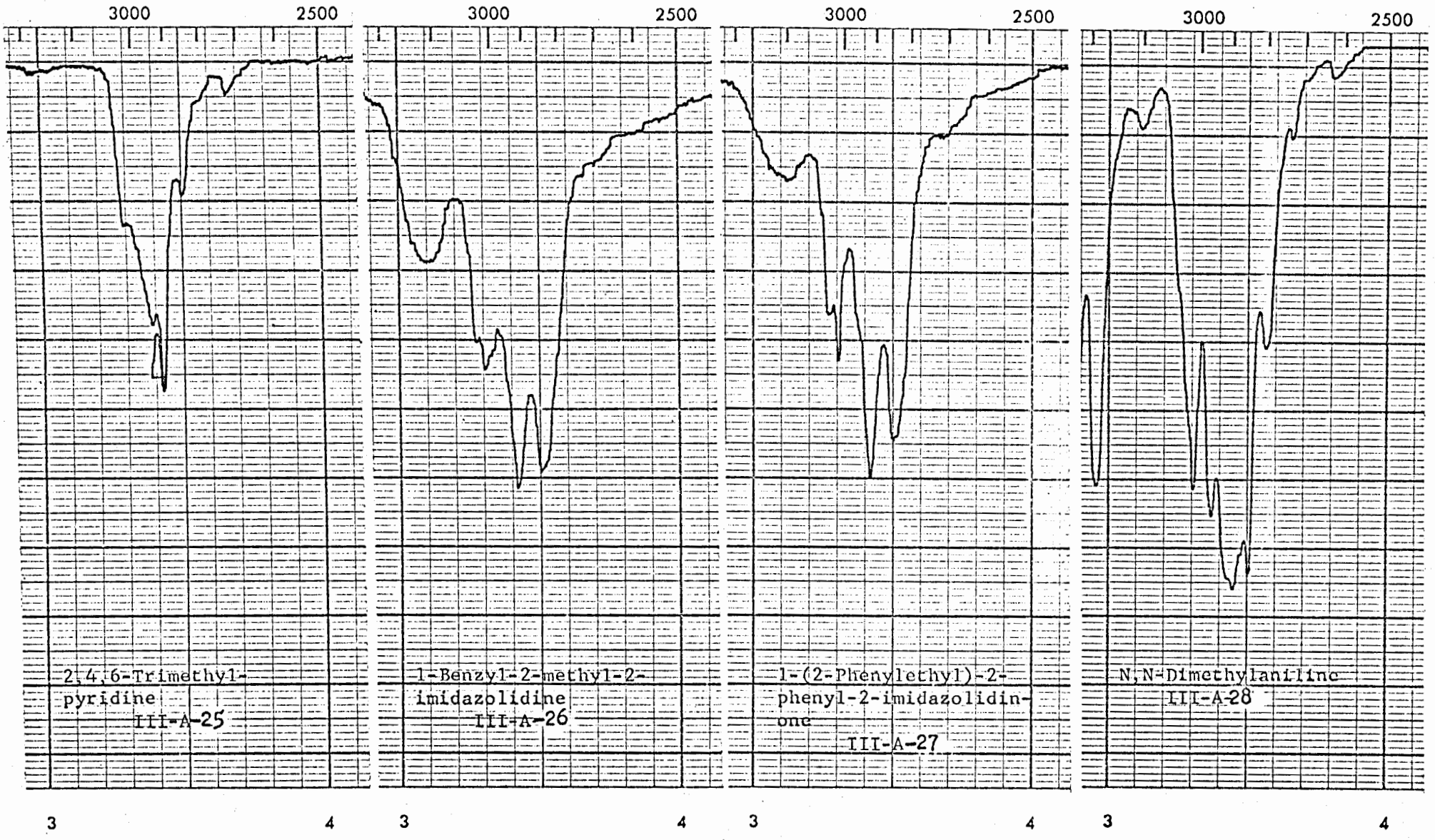
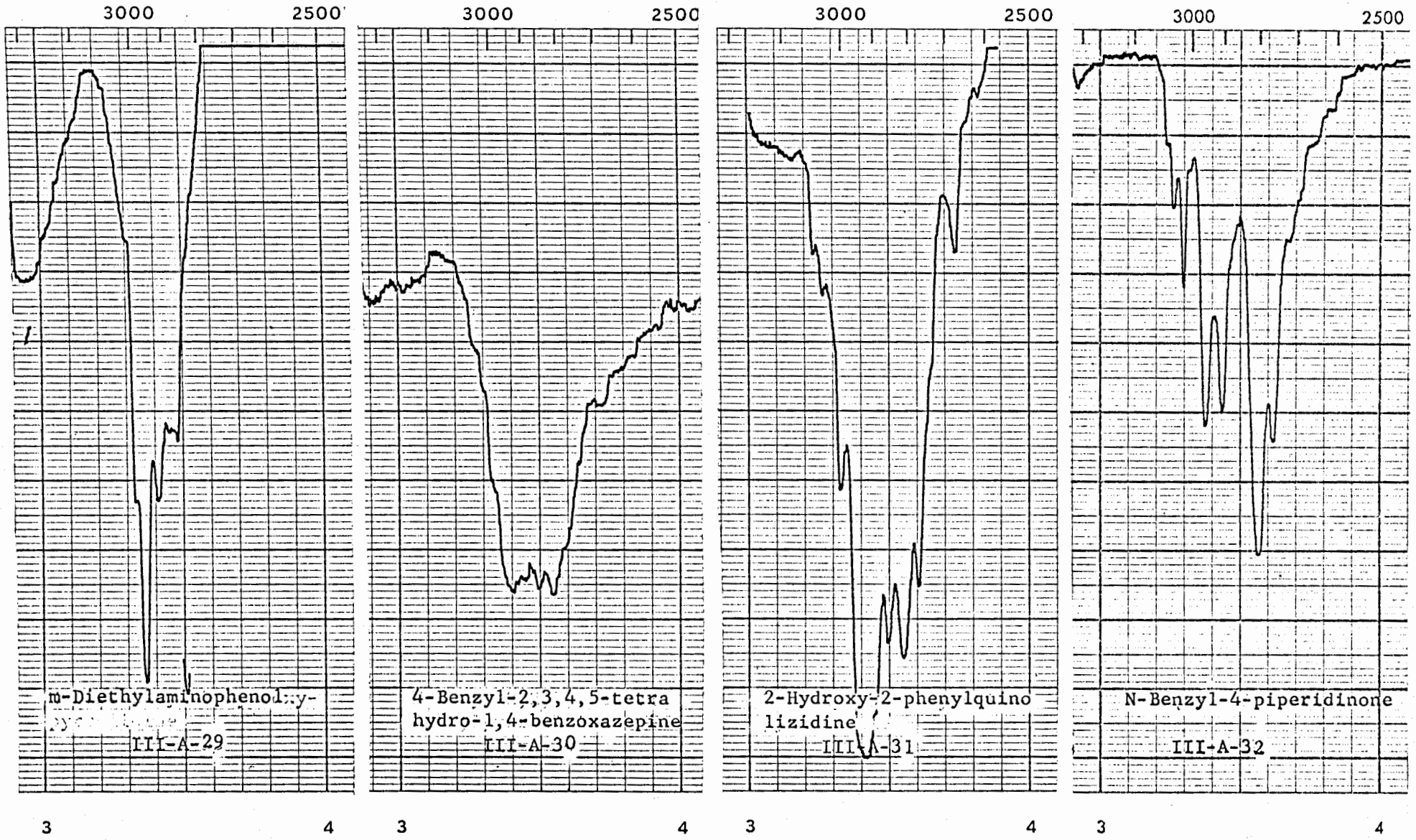
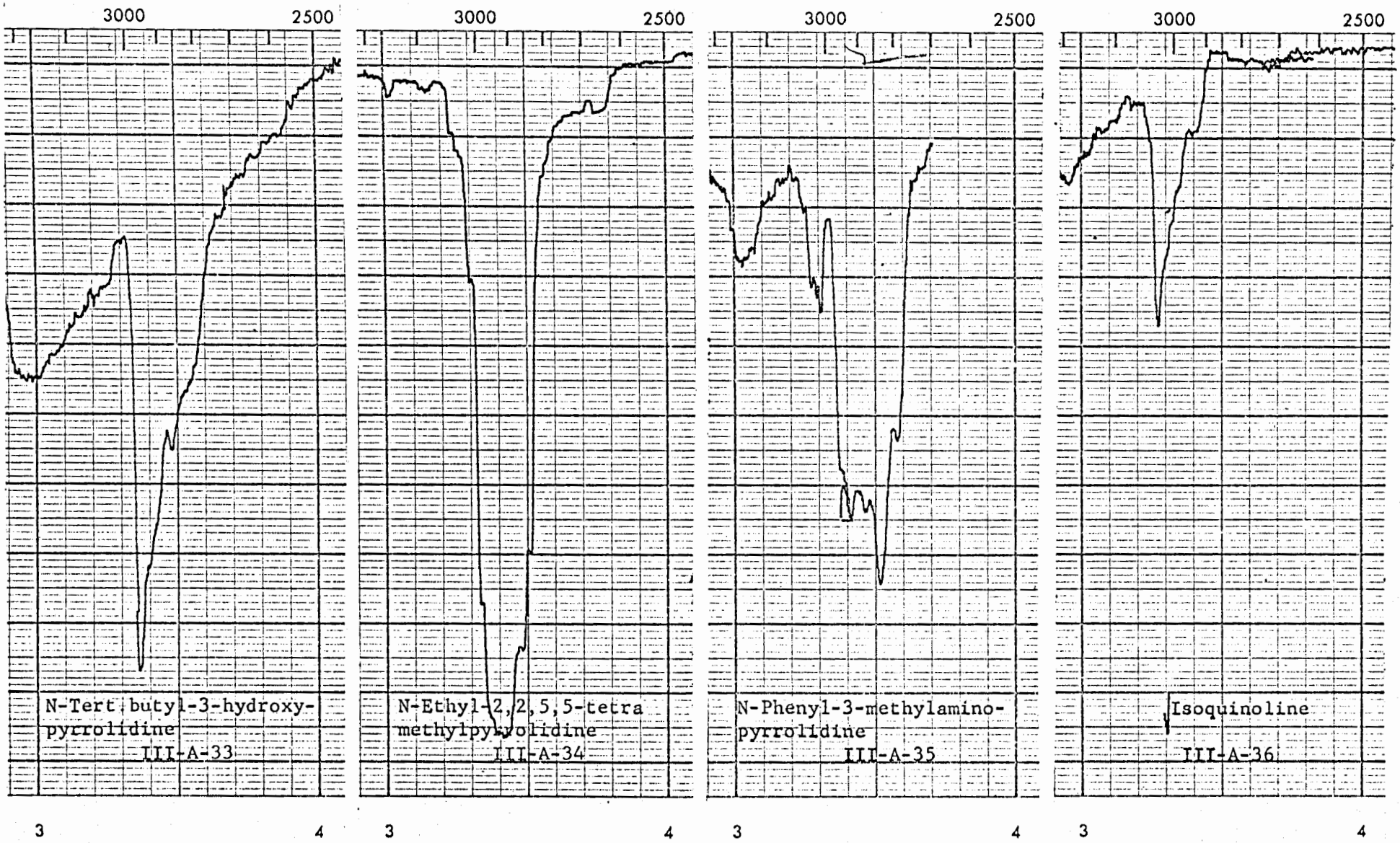
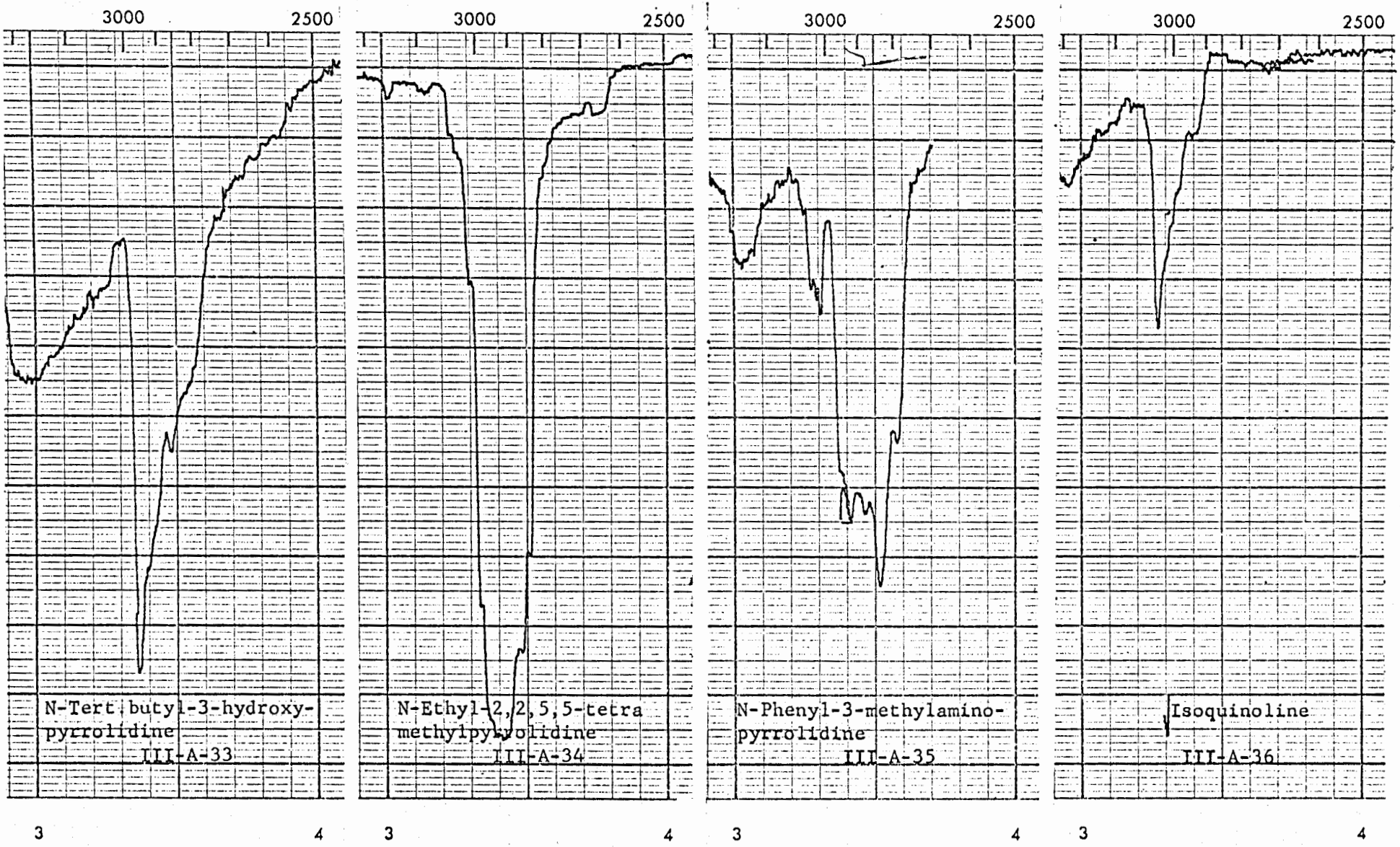
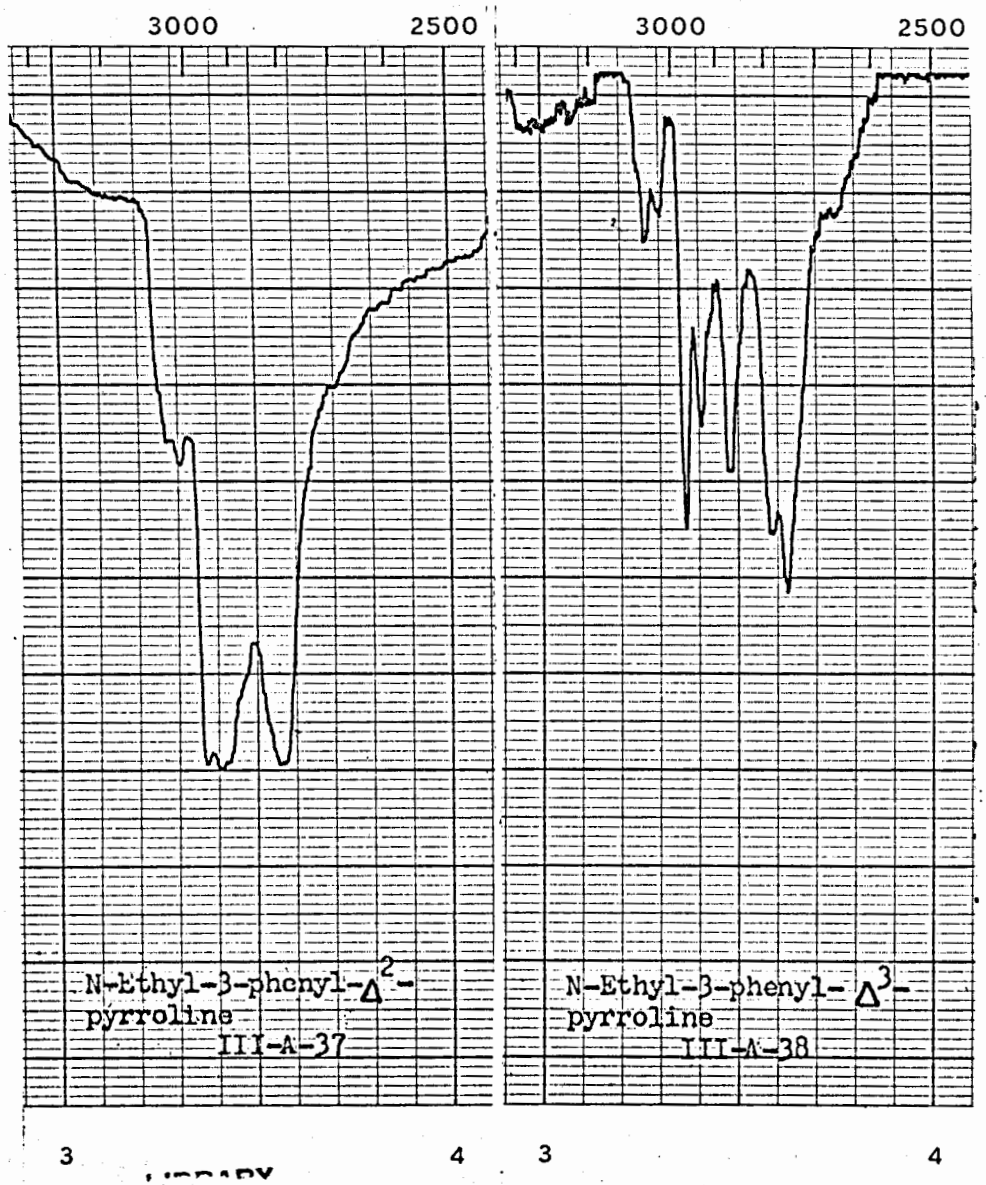
2500
N-(γ-Aminopropyl)-N'-methylpiperazine
III-A-21
3000
2500
3,5-Dimethyl-4-isopropylmorpholine
III-A-22
3000
2500
3-Quinuclidinol
III-A-23
3000
2500
1,2,5-Trimethylpyrrole
III-A-24
3
4
3
4
3
4
3
4


3000
2500
3000
2500
3000
2500
3000
2500
2,4,6-Trimethyl-
pyridine
III-A-25
1-Benzyl-2-methyl-2-
imidazolidine
III-A-26
1-(2-Phenylethyl)-2-
phenyl-2-imidazolidin-
one
III-A-27
N,N-Dimethylaniline
III-A-28
3
4
3
4
3
4
3
4


3000
2500
m-Diethylaminophenol:y-
III-A-29
3
4
3000
2500
4-Benzyl-2,3,4,5-tetra
hydro-1,4-benzoxazepine
III-A-30
3
4
3000
2500
2-Hydroxy-2-phenylquino
lizidine
III-A-31
3
4
3000
2500
N-Benzyl-4-piperidinone
III-A-32
3
4


3000
2500
N-Tert.butyl-3-hydroxy-pyrrolidine
III-A-33
3
4
3000
2500
N-Ethyl-2,2,5,5-tetra methylpyrrolidine
III-A-34
3
4
3000
2500
N-Phenyl-3-methylamino-pyrrolidine
III-A-35
3
4
3000
2500
Isoquinoline
III-A-36
3
4


3000
2500
N-Tert.butyl-3-hydroxy-pyrrolidine
III-A-33
3000
2500
N-Ethyl-2,2,5,5-tetra methylpyrrolidine
III-A-34
3000
2500
N-Phenyl-3-methylamino-pyrrolidine
III-A-35
3000
2500
Isoquinoline
III-A-36
3
4
3
4
3
4
3
4



APPENDIX II

Infrared Spectra of Miscellaneous Organic Compounds

(3.0 to 4.0 μ)

FIGURE X

PROMINENT C-H STRETCHING WAVELENGTHS IN THE INFRARED SPECTRA OF SELECTED MISCELLANEOUS ORGANIC COMPOUNDS

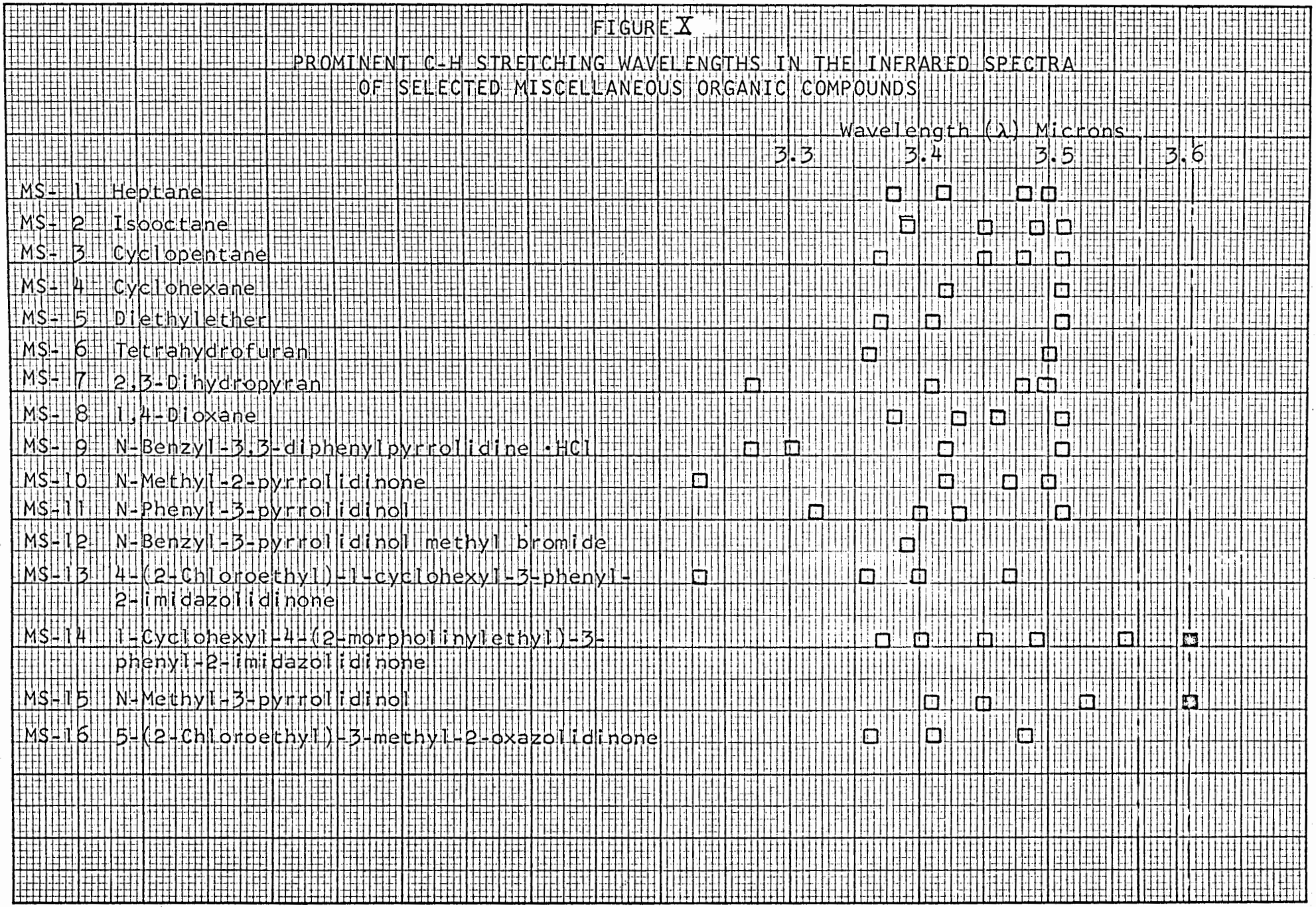


FIGURE X (Continued)
(continued)

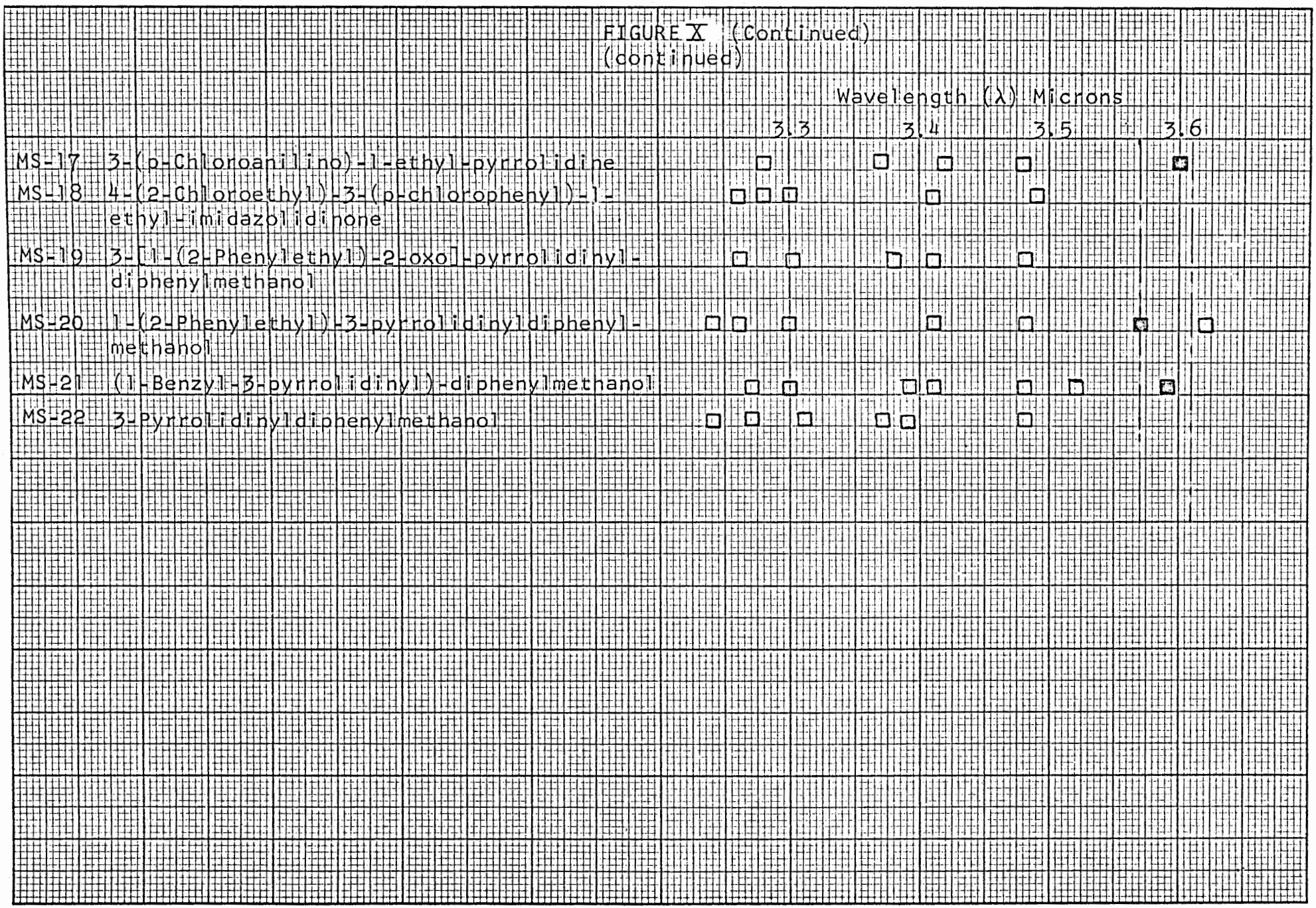


TABLE 8

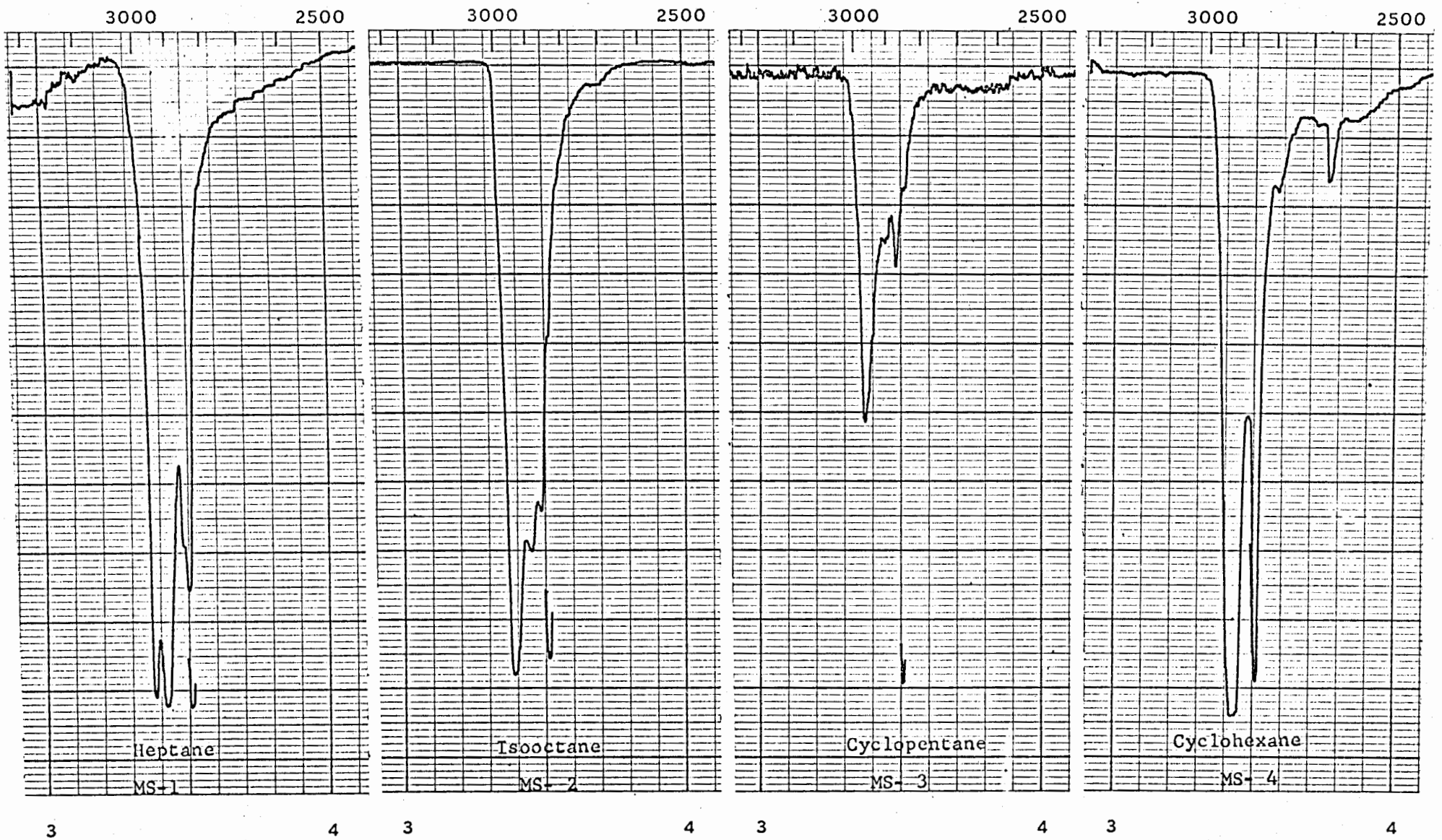
PROMINENT C-H STRETCHING WAVELENGTHS
IN THE INFRARED SPECTRA OF SELECTED MISCELLANEOUS ORGANIC COMPOUNDS

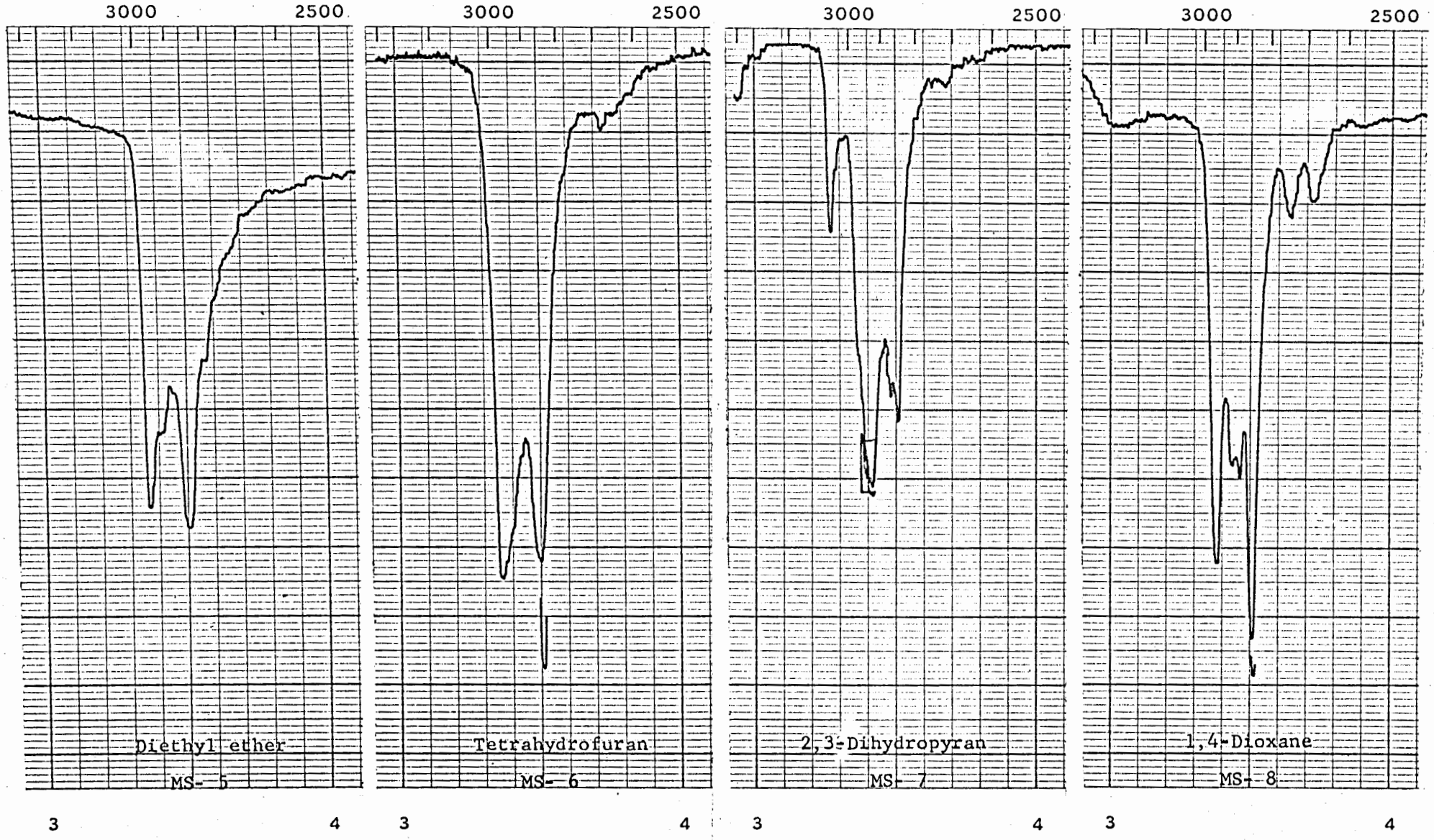
[Limited to the Region of 3.20 to 3.70 μ]

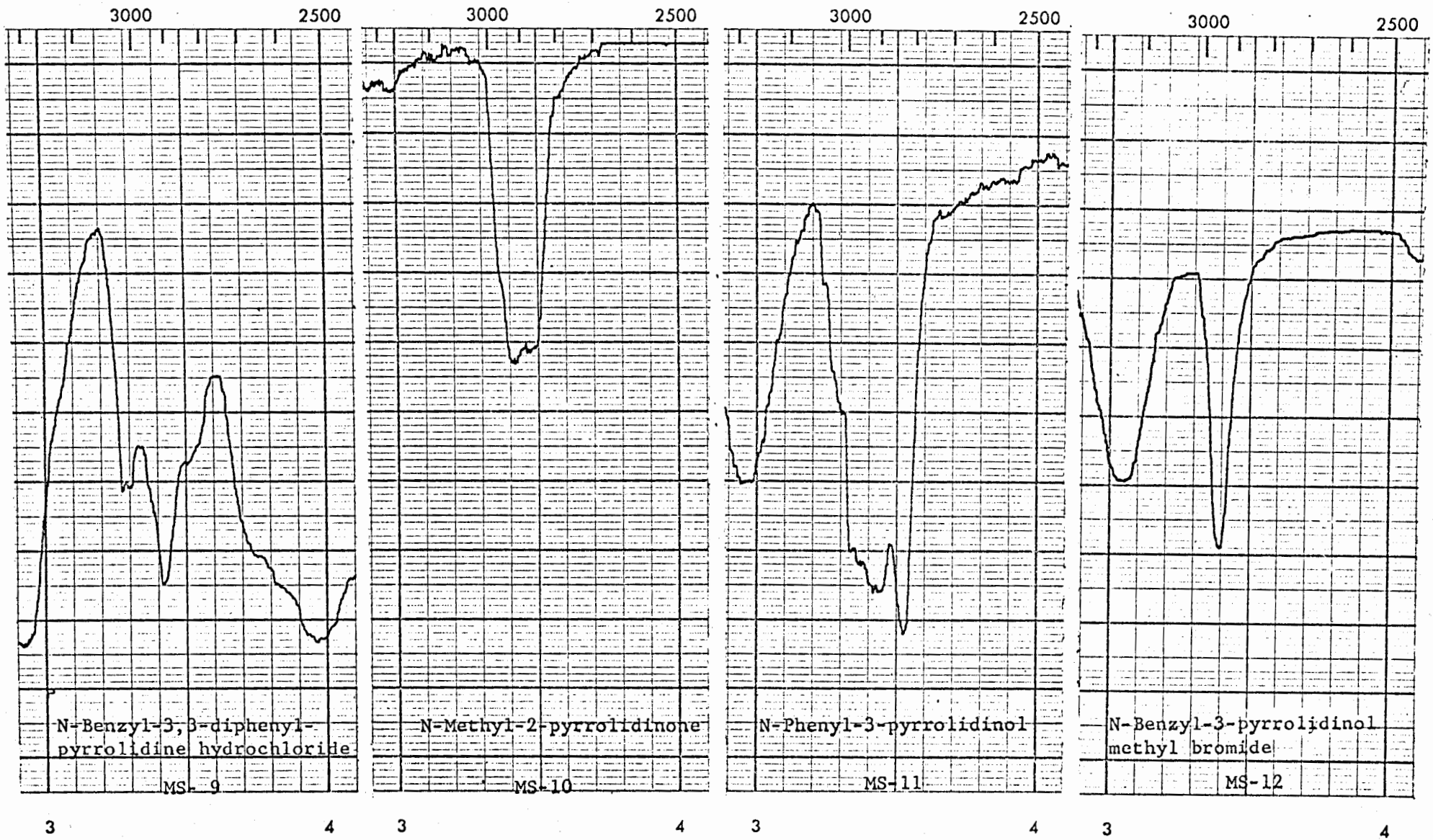
COMPOUND	PROMINENT ABSORPTION BANDS (MICRONS)
MS- 1 Heptane	3.38,3.42,3.48,3.50
MS- 2 Isooctane	3.39,3.45,3.49,3.51
MS- 3 Cyclopentane	3.37,3.45,3.48,3.51
MS- 4 Cyclohexane	3.42,3.51
MS- 5 Diethylether	3.37,3.41,3.51
MS- 6 Tetrahydrofuran	3.36,3.50
MS- 7 2,3-Dihydropyran	3.27,3.41,3.48,3.50
MS- 8 1,4-Dioxane	3.38,3.43,3.46,3.51
MS- 9 N-Benzyl-3,3-diphenylpyrrolidine ·HCl	3.27,3.30,3.42,3.51
MS-10 N-Methyl-2-pyrrolidinone	3.26,3.42,3.47,3.50
MS-11 N-Phenyl-3-pyrrolidinol	3.32,3.40,3.43,3.51
MS-12 N-Benzyl-3-pyrrolidinol methyl bromide	3.39 (No others)

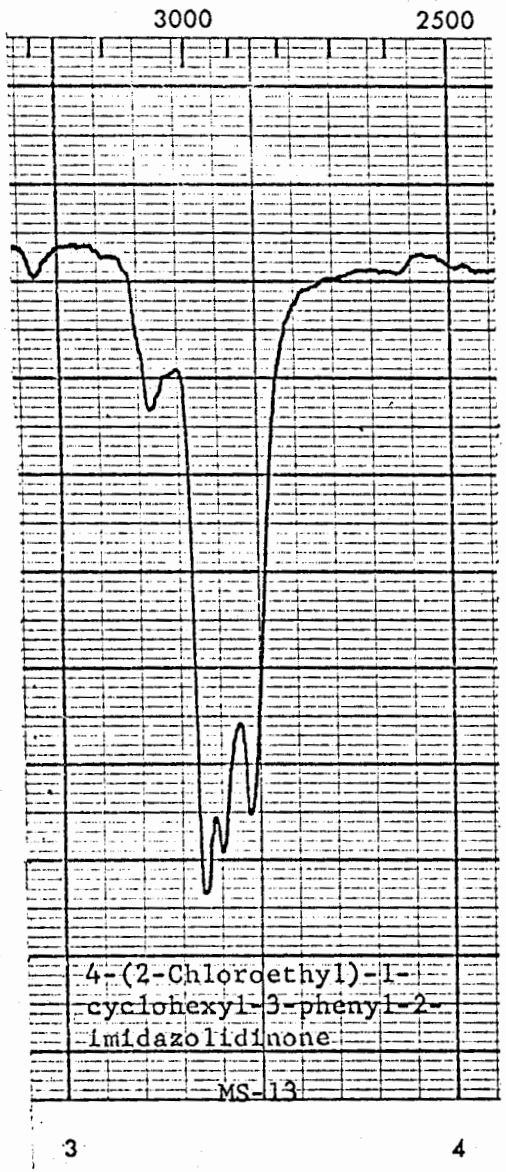
TABLE 8
(continued)

COMPOUND		PROMINENT ABSORPTION BANDS (MICRONS)
MS-13	4-(2-Chloroethyl)-1-cyclohexyl-3-phenyl-2-imidazolidinone	3.23,3.36,3.40,3.47
MS-14	1-Cyclohexyl-4-(2-morpholinylethyl)-3-phenyl-2-imidazolidinone	3.37,3.40,3.45,3.49,3.56,3.61
MS-15	N-Methyl-3-pyrrolidinol	3.41,3.45,3.53,3.61
MS-16	5-(2-Chloroethyl)-3-methyl-2-oxazolidinone	3.36,3.41,3.48
MS-17	3-(p-Chloroanilino)-1-ethyl-pyrrolidine	3.28,3.37,3.42,3.48,3.60
MS-18	4-(2-Chloroethyl)-3-(p-chlorophenyl)-1-ethyl-imidazolidinone	3.26,3.28,3.30,3.41,3.49
MS-19	3-[1-(2-Phenylethyl)-2-oxo]-pyrrolidinyl-diphenylmethanol	3.26,3.30,3.38,3.41,3.48
MS-20	1-(2-Phenylethyl)-3-pyrrolidinyldiphenyl-methanol	3.24,3.26,3.30,3.41,3.48,3.57,3.62
MS-21	(1-Benzyl-3-pyrrolidinyl)-diphenylmethanol	3.27,3.30,3.39,3.41,3.48,3.52,3.59
MS-22	3-Pyrrolidinyldiphenylmethanol	3.24,3.27,3.31,3.37,3.39,3.48


3000
2500
Heptane
MS-1
3
4
3000
2500
Isooctane
MS- 2
3
4
3000
2500
Cyclopentane
MS- 3
3
4
3000
2500
Cyclohexane
MS- 4
3
4

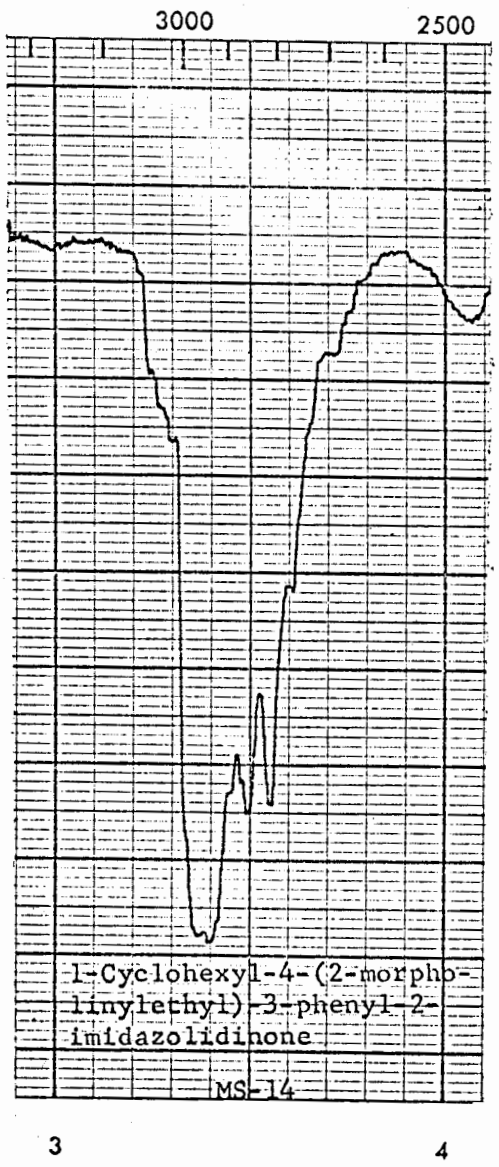

3000
2500
Diethyl ether
MS- 5
3
4
3000
2500
Tetrahydrofuran
MS- 6
3
4
3000
2500
2,3-Dihydropyran
MS- 7
3
4
3000
2500
1,4-Dioxane
MS- 8
3
4


3000
2500
N-Benzyl-3,3-diphenyl-pyrrolidine hydrochloride
MS- 9
3
4
3000
2500
N-Methyl-2-pyrrolidinone
MS-10
3
4
3000
2500
N-Phenyl-3-pyrrolidinol
MS-11
3
4
3000
2500
N-Benzyl-3-pyrrolidinol methyl bromide
MS-12
3
4



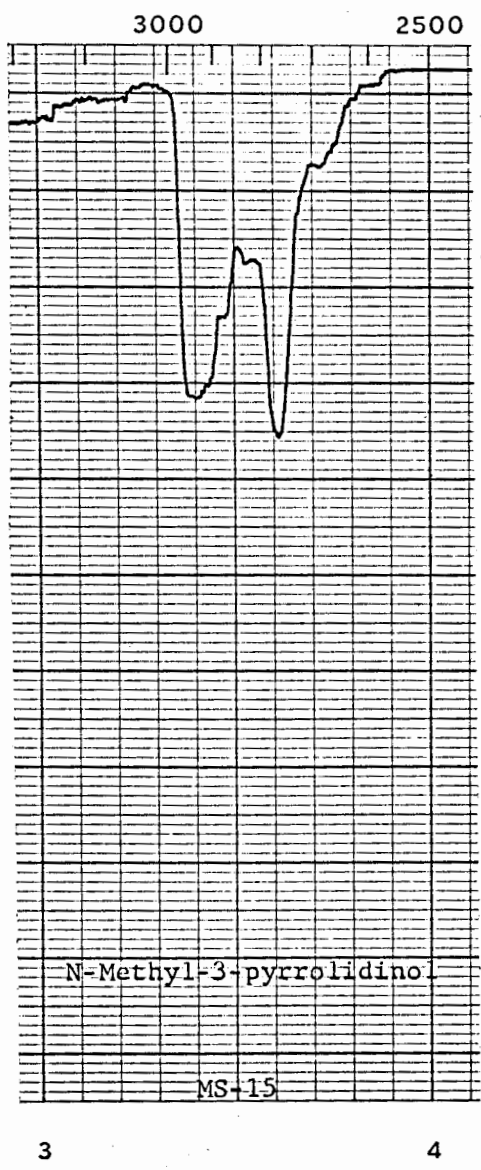
4-(2-Chloroethyl)-1-cyclohexyl-3-phenyl-2-imidazolidinone

MS-13



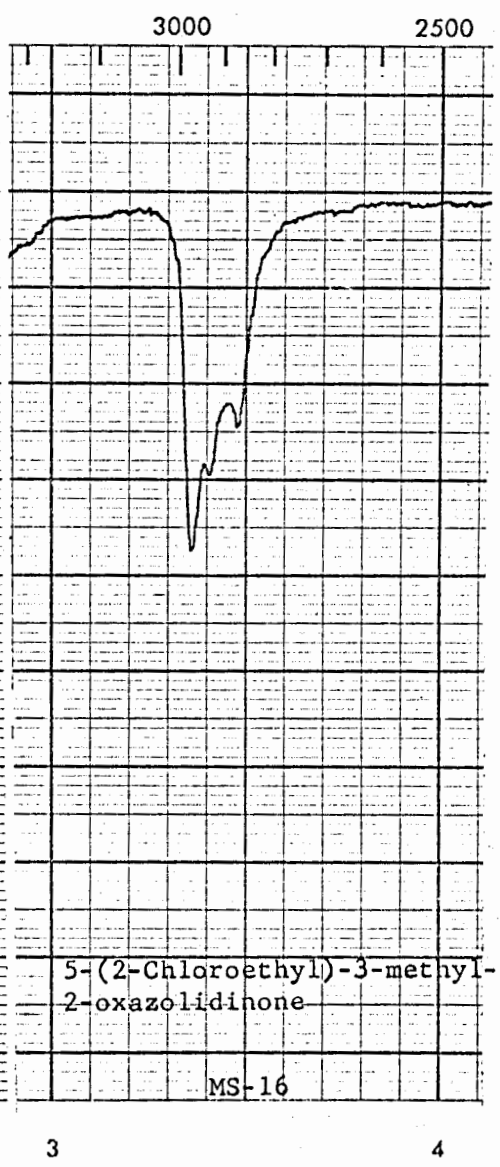
1-Cyclohexyl-4-(2-morpholinylethyl)-3-phenyl-2-imidazolidinone

MS-14



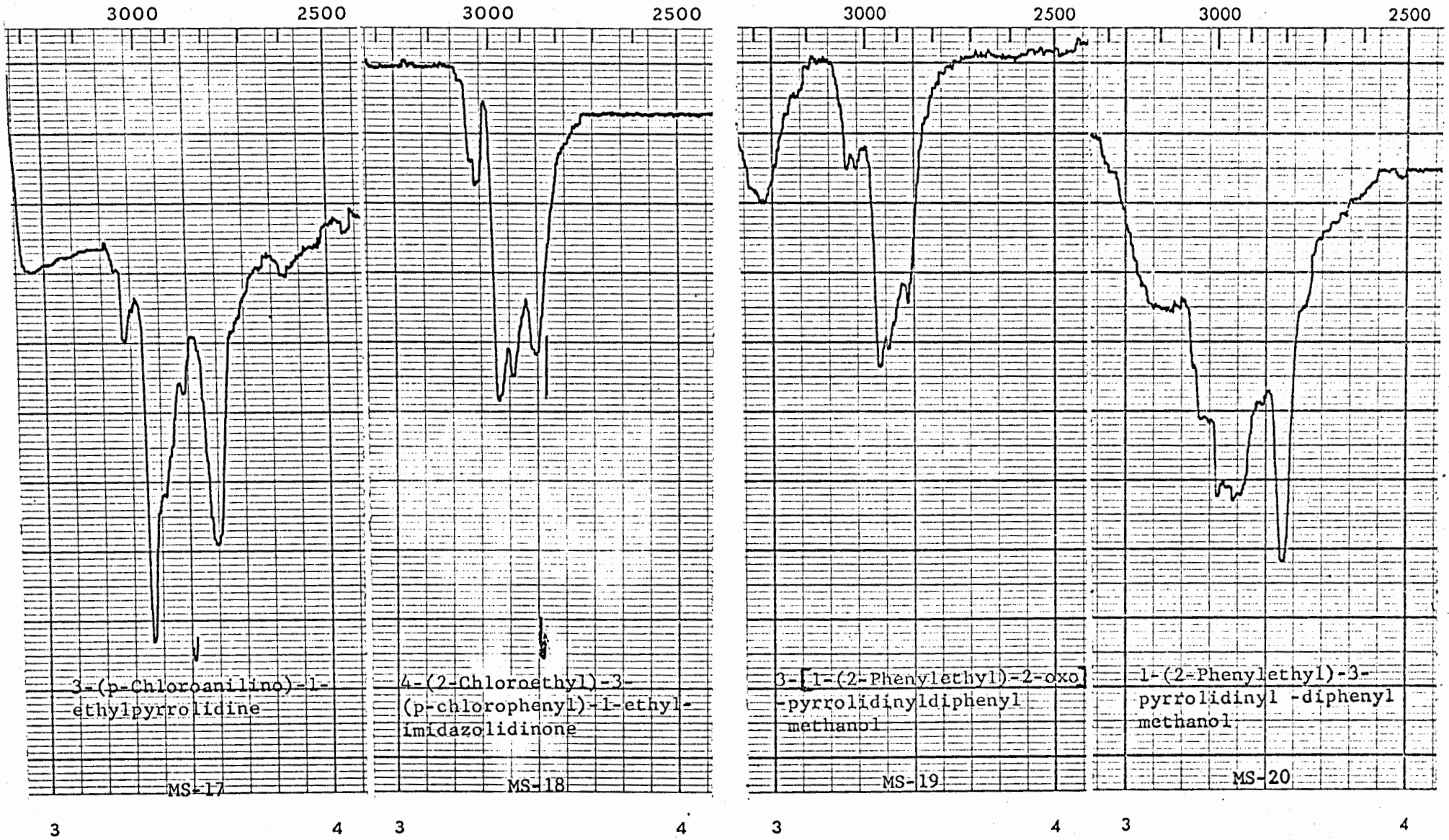
N-Methyl-3-pyrrolidinol

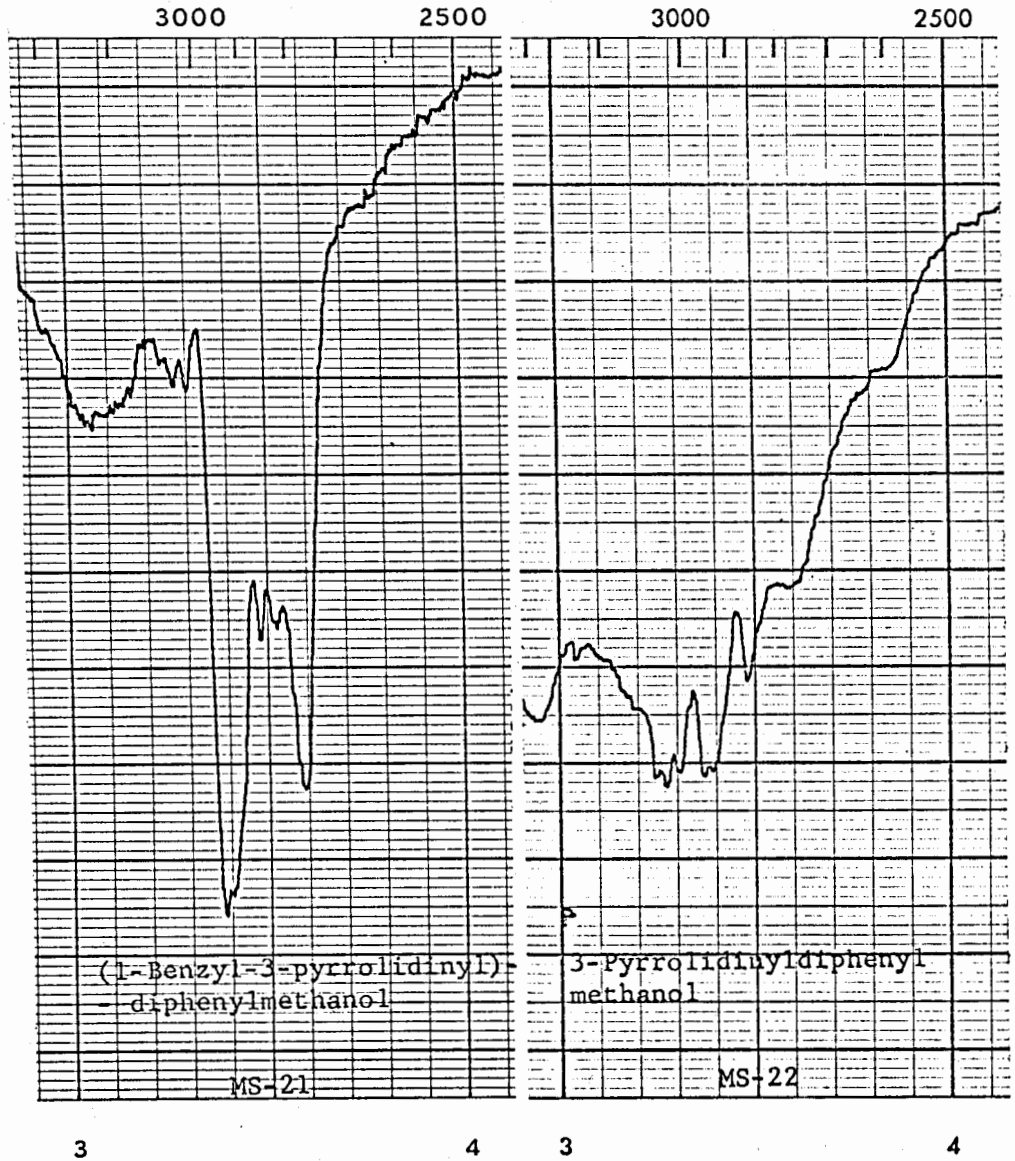
MS-15



5-(2-Chloroethyl)-3-methyl-2-oxazolidinone

MS-16


3000
2500
3000
2500
3000
2500
3000
2500
3-(p-Chloroanilino)-1-ethylpyrrolidine
MS-17
4-(2-Chloroethyl)-3-(p-chlorophenyl)-1-ethyl-imidazolidinone
MS-18
3-[1-(2-Phenylethyl)-2-oxo]-pyrrolidinyldiphenyl methanol
MS-19
1-(2-Phenylethyl)-3-pyrrolidinyl -diphenyl methanol
MS-20
3
4
3
4
3
4
3
4


3000
2500
(1-Benzyl-3-pyrrolidinyl)-
diphenylmethanol
MS-21
3
4
3000
2500
3-Pyrrolidinyldiphenyl
methanol
MS-22
3
4