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OF SUBSTITUTED 1,10-PHENANTHROLINES.

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INFRARED SPECTRA OF
SUBSTITUTED 1,10-PHENANTHROLINES

by

Robert Carl Smith

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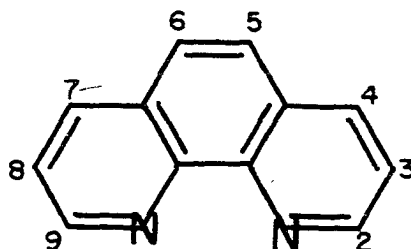
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I. INTRODUCTION

1,10-Phenanthroline and various substituted derivatives of 1,10-phenanthroline have been found to be very sensitive



and specific reagents for the colorimetric determination of iron and of copper. The ferrous derivatives of 1,10-phenanthroline and the various substituted 1,10-phenanthrolines have been employed also as oxidation-reduction indicators. The electrode potential varies in interesting and useful fashion with the nature of the substituent in the 1,10-phenanthroline molecule. These uses of 1,10-phenanthroline and its derivatives have brought about a considerable number of studies of these materials, notably by G. Frederick Smith of the University of Illinois, and Francis H. Case of Temple University. Case has synthesized over one hundred derivatives of 1,10-phenanthroline, and these compounds have been examined by Smith. From these efforts has emerged in particular two "super-sensitive" reagents: bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) for iron, and bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) for copper. There has also resulted a

series of oxidation-reduction indicators covering, in small steps, the potential range 0.9 to 1.3 volts.

The infrared spectrum of 1,10-phenanthroline has already been reported, but nothing has been done in the infrared with the numerous substituted 1,10-phenanthrolines. The purpose of this investigation was to make a detailed study of the infrared spectra of 1,10-phenanthroline and its derivatives to provide information relative to their identification and structure.

Two authors have previously studied the spectrum of 1,10-phenanthroline: Busch and Bailar (5) who obtained the spectrum of 1,10-phenanthroline monohydrate using a Nujol suspension and proposed tentative assignments of vibration modes of the molecules for eight of the absorption frequencies observed; and Schilt and Taylor (53) who obtained the spectra of anhydrous 1,10-phenanthroline, of the 1,10-phenanthroline monohydrate, of 1,10-phenanthrolium perchlorate, and of twenty-two metal-1,10-phenanthroline perchlorates, all using the Nujol mull technique.

In the following material, a review of the methods of synthesizing 1,10-phenanthrolines is first given. A section then follows noting the purity and purification required of compounds available, and the preparation of derivatives pre-

viously reported but not otherwise available. There follows then a section presenting the infrared spectra of over one hundred and thirty 1,10-phenanthrolines and a detailed discussion of absorption spectra of 1,10-phenanthroline and its derivatives in the spectral region 5000 to 650 cm^{-1} . In the next section are described correlations of the absorption frequencies observed with the type of substitution in the 1,10-phenanthroline molecule.

II. HISTORY OF SYNTHESIS OF 1,10-PHENANTHROLINES

The first 1,10-phenanthroline compound was reported in 1889 by Gerdeissen (26) who described the synthesis of 2-methyl-1,10-phenanthroline. No mention was made of any reaction of this material with iron, and not until 1938 when Pfeiffer and Christeleit (46) investigated and isolated several metal derivatives, was this particular compound studied for its ability to unite with metals.

The parent compound, 1,10-phenanthroline, was synthesized in 1898 by Blau (3) from glycerin and o-phenylenediamine by a double Skraup reaction. Blau observed the intense color formed by 1,10-phenanthroline with ferrous iron and investigated the iron derivative in great detail. Blau's claim of a 30 per cent yield in the synthesis of 1,10-phenanthroline was not substantiated for many decades. C. R. Smith (59), for example, failed to get any 1,10-phenanthroline by the method. Hieber and Muhlbauer (33) in 1928 were apparently successful but failed to report the yield obtained. Demand for 1,10-phenanthroline in the meantime prompted other studies on its synthesis. Smith and Getz (61), for example, in 1935 described a preparation starting with o-nitroaniline and proceeding through the route: 8-nitroquinoline (by the Skraup reaction), 8-aminoquinoline (iron and hydrochloric acid reduction), and 1,10-phenanthroline (second Skraup reaction).

Interest in obtaining substituted 1,10-phenanthrolines began in the early 1940's. Richter and Smith (51) in 1944 reported the preparation of several 5-substituted derivatives (5-methyl- , 5-chloro- , and 5-bromo-1,10-phenanthrolines) using two Skraup reactions. These workers also nitrated 1,10-phenanthroline which yielded the 5-nitro derivative. Nitration of 5-methyl-1,10-phenanthroline gave 5-nitro-6-methyl-1,10-phenanthroline. The first investigation of the nitration of 1,10-phenanthroline was that of Hammett et al. (31) in 1934. An improved synthesis of 5-nitro-1,10-phenanthroline was later described by Smith and Cagle (60) in 1947. Snyder and Freier (62) reported the synthesis of several dialkylaminoalkylamino-1,10-phenanthrolines in 1946. The preparation of several intermediates used for the synthesis of the above materials were noted also, the most important being 4,7-dihydroxy-1,10-phenanthroline (commonly called Snyder's reagent). The preparation of 2-chloro-1,10-phenanthroline was described in 1946 by Halcrow and Kermack (30). Using the above 2-chloro-derivative as starting material, Karrer and Pletscher (36) prepared 2-methoxy-1,10-phenanthroline in 1948.

At about this time Professor Case and his co-workers began their work on the 1,10-phenanthrolines. Since 1948, eleven papers have been published by Case describing the

synthesis of nearly eighty 1,10-phenanthroline compounds. The publications in chronological order and the types of derivatives synthesized in each are listed in Table 1.

Table 1. Publications of F. H. Case on the synthesis of 1,10-phenanthrolines

Case publica- tion number	Reference	Year of publication	Type of deriva- tives prepared
I	(7)	1948	Methyl
II	(8)	1949	Methyl
III	(9)	1949	Methyl
IV	(10)	1951	Bromo
V	(11)	1951	Phenyl
VI	(15)	1954	Chloro
VII	(13)	1954	Methyl
VIII	(17)	1955	Phenyl
IX	(12)	1956	Cycloalkeno
X	(16)	1957	Ethyl
XI	(14)	1959	Aza

Approximately thirty other 1,10-phenanthroline derivatives have been synthesized by Case and co-workers which have not as yet been reported in the literature.

Other 1,10-phenanthroline derivatives have been reported by various authors (4, 23, 34, 36, 39, 40, 43, 63, 64), but these will not be listed here as they do not represent any major group of 1,10-phenanthrolines.

III. COMPOUNDS AND APPARATUS

A. Sources and Purification of 1,10-Phenanthrolines and Other Compounds

The majority of the compounds investigated in this project were supplied by Professor F. H. Case of Temple University. In most instances these compounds were pure materials which had been previously submitted for analysis to the Huffman Microanalytical Laboratories, Wheatridge, Colorado. Many of the compounds, however, required further purification (see Table 2). Several 1,10-phenanthroline derivatives were available commercially from the G. Frederick Chemical Company, Columbus, Ohio (27). In some instances the supply of a compound available was too small, and additional amounts were prepared, usually by the procedures of Professor Case. Descriptions of these syntheses are given in section B.

In Table 2 a summary of information is given on each 1,10-phenanthroline derivative for which infrared spectra were obtained. In the reference noted, the synthesis and the melting point of the purified compound are recorded. If further purification of the sample available was necessary, the solvent used in the recrystallization is indicated in the column labeled "purification." The Skelly solvents (A, E, and D), which were used in many purifications, are petroleum ether fractions with the following boiling point ranges:

Table 2. Properties of 1,10-phenanthroline and its derivatives

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
1,10-Phenanthroline (anhydrous)	3	(3)	Skelly D	117°	118-120°
1,10-Phenanthroline (monohydrate)	2	(3)	Water	102°	100-101°
1,10-Phenanthrolium chloride	3	(--)	None	---	222-228°
1,10-Phenanthrolium perchlorate	3	(53)	Water	None	None
2-Methyl-	3	(26)	Skelly B	75-76°	75-78°
3-Methyl-	1	(7)	Ethanol-water	158-159°	159-161°

^aThe following numbers indicate the sources of these 1,10-phenanthroline compounds:

1. Professor F. H. Case, Temple University, Philadelphia, Pa.
2. G. Frederick Smith Chemical Co., Columbus, Ohio
3. This author's preparation
4. Professor H. P. Snyder, University of Illinois, Urbana, Ill.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
4-Methyl-	3	(7)	Benzene-Skelly B	144-145°	143.5-145°
5-Methyl-	2	(51)	Skelly B	114°	111.5-112.5°
2,4-Dimethyl-	1	(13)	Water	123-124°	124-126°
2,9-Dimethyl-	2	(7)	Skelly D	159-160°	162-164.5°
3,4-Dimethyl	1	(9)	None	234-235°	233.5-235°
3,5-Dimethyl-	1	(8)	None	169-170°	172-174°
3,6-Dimethyl-	1	(8)	None	117-118°	119-120°
3,7-Dimethyl-	1	(7)	None	136-137°	136-137.5°
3,8-Dimethyl-	1	(7)	Ethanol-water	212°	213-214°
4,5-Dimethyl-	1	(8)	None	151-152°	150.5-151.5°
4,6-Dimethyl-	1	(8)	None	161-162°	165-166.5°
4,7-Dimethyl-	1	(7)	None	194-195°	193-195°
5,6-Dimethyl-	1	(7)	None	265-266°	268-270°

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
2,3,4-Trimethyl-	1	(--) ^b	None	173.5-174.5 ^o	174-175 ^o
3,4,6-Trimethyl-	1	(9)	None	217-218 ^o	220-221 ^o
3,4,7-Trimethyl-	1	(9)	None	221-222 ^o	221-224 ^o
3,4,8-Trimethyl-	1	(9)	None	211-212 ^o	213-215 ^o
3,5,6-Trimethyl-	1	(7)	None	196-197 ^o	197-198.5 ^o
3,5,7-Trimethyl-	1	(8)	None	201-202 ^o	203-204 ^o
3,5,8-Trimethyl-	1	(8)	None	185-186 ^o	187-189 ^o
3,6,7-Trimethyl-	1	(8)	None	177-178 ^o	178-181 ^o
4,5,7-Trimethyl-	1	(8)	None	184-185 ^o	186-189 ^o
2,3,8,9-Tetramethyl-	1	(13)	None	225-226 ^o	222-225 ^o
2,4,7,9-Tetramethyl-	1	(13)	Ethanol-water	199-200 ^o	200-202 ^o
2,5,6,9-Tetramethyl-	1	(13)	Ethanol-water	171-172 ^o	171-173 ^o

^bThe synthesis of the derivative has not been published; the melting point was reported in a private communication from F. H. Case of Temple University, Philadelphia, Pa., in November, 1960.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
3,4,6,7-Tetramethyl-	1	(9)	None	229-230 ^o	227-230 ^o
3,4,6,8-Tetramethyl-	1	(9)	None	189-190 ^o	192-194 ^o
3,4,7,8-Tetramethyl-	1	(9)	Ethanol-water	275-276 ^o	273-276 ^o
3,5,6,8-Tetramethyl-	1	(7)	None	260-261 ^o	262-264 ^o
2,3,4,7,8,9-Hexamethyl-	1	(--) ^b	None	247-248 ^o	240-248 ^o
3-Ethyl-	1	(16)	Benzene-Skelly B	144-145 ^o	145.5-147.5 ^o
4-Ethyl-	1	(16)	None	108-109 ^o	105-106 ^o
5-Ethyl-	1	(16)	None	80-81 ^o	None ^c
3,8-Diethyl-	1	(16)	None	112-113 ^o	112.5-114.5 ^o
4,6-Diethyl-	1	(16)	None	130-131 ^o	127-130 ^o
4,7-Diethyl-	1	(16)	Skelly B	116-117 ^o	115-116 ^o
5,6-Diethyl-	1	(16)	Skelly B	161-162 ^o	165-167 ^o
4-n-Propyl-	1	(--) ^b	None	82-85 ^o	92-94 ^o

^cOnly an oil was available.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting Point	
				Reported	Observed
5-Fluoro-	1	(--) ^b	None	143°	144-146°
2-Chloro-	3	(30)	Skelly B-chloroform	129-130°	127-129°
3-Chloro-	1	(15)	None	170°	170-172°
4-Chloro-	4	(62)	Chloroform	180-230° (for crude)	158-164°
5-Chloro-	2	(51)	None	123°	123-125°
3,5-Dichloro-	1	(15)	None	226-227°	227.5-229.5°
3,8-Dichloro-	1	(15)	None	268-269°	268-270°
4,7-Dichloro-	4	(62)	Skelly D	249-250°	251-253°
5,6-Dichloro-	1	(15)	None	234-235°	234-236°
3,5,6-Trichloro-	1	(15)	None	207-208°	209-211°
3-Bromo-	1	(10)	Chloroform	169-170°	172-174.5°
4-Bromo-	1	(10)	None	157°	153.5-155.5°
5-Bromo-	3	(51)	Skelly A	119°	107-110°
3,5-Dibromo-	1	(10)	None	225-226°	228-231°

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
3,6-Dibromo-	1	(10)	None	247-248 ^o	249.5-252 ^o
4,7-Dibromo-	3	(10)	None	236 ^o	233-234 ^o
5,6-Dibromo-	1	(10)	Benzene	215-216 ^o	217-220 ^o
3,5,6-Tribromo-	1	(10)	Benzene	251-252 ^o	255-257 ^o
3,5,6,8-Tetrabromo-	1	(10)	None	356-357 ^o	355-356 ^o
2-Phenyl-	1	(17)	None	104 ^o	103.5-105 ^o
3-Phenyl-	3	(17)	Chloroform	None ^d	None ^c
3-Phenyl-1,10-phenanthrolium chloride	1	(17)	Absolute ethanol	210-211 ^o	210-211.5 ^o
4-Phenyl-	1	(11)	None	105-106 ^o	106-108 ^o
5-Phenyl-	1	(11)	None	202-203 ^o	206-207.5 ^o
2,9-Diphenyl-	1	(17)	None	185-186 ^o	186-187 ^o
3,8-Diphenyl-	1	(17)	Benzene-Skelly B	190-191 ^o	192-193 ^o
4,6-Diphenyl-	1	(11)	None	245 ^o	248-249.5 ^o

^dCompound isolated as an oil only.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
4,7-Diphenyl-	2	(17)	None	216-217 ^o	217-219 ^o
2,4,7,9-Tetraphenyl-	1	(17)	None	318-319 ^o	322-325 ^o
2-Methoxy-	3	(36)	None	88-89 ^o	70-72 ^{oe}
5-Methoxy-	1	(22)	None	104-105 ^o	109-111 ^o
4,7-Dimethoxy	1	(--) ^b	None	209-210 ^o	207-210 ^o
5,6-Dimethoxy-	1	(--) ^b	None	125-126 ^o	124-126 ^o
4,7-Diphenoxy-	1	(--) ^b	None	179-180 ^o	178-180 ^o
1,10-Phenanthroline- 5,6-dione	3	(34)	Methanol	256-257 ^o	255-258 ^o
2-Hydroxy-	1	(--) ^b	None	159.5-160.6 ^o	160-162 ^o
5-Hydroxy-	1	(--) ^b	None	None noted up to 340 ^o	None ^f
2,4-Dihydroxy-	1	(--) ^b	None	315-316 ^{og}	303-309 ^o

^eMelting point for the monohydrate material.

^fNo melting observed up to 350^o.

^gMelting point after previous sintering.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
4,5-Dihydroxy-	1	(--) ^b	None	229-230°	229.5-231.5°
4,7-Dihydroxy-	3	(62)	None	475° ^h	None ^f
4,7-Dihydroxy- 1,10-phenanthrolium chloride	2	(52)	None	None given	None ^f
5,6-Dihydroxy-	1	(--) ^b	None	390° ^h	None ^f
2-Methyl-4-hydroxy-	1	(--) ^b	None	213.5-215°	215-217°
3-Phenyl-4-hydroxy-	1	(17)	None	235-236°	239.5-240°
3-Carbethoxy-4-hydroxy-	4	(62)	None	237-241°	240-244°
3-Carboxy-4-hydroxy-	4	(62)	None	300-305° ^h	315-321° ^h
4-Hydroxy-5-methoxy- (monopicrate)	4	(62)	None	215-221°	216-219°
2-Methyl-4,5-dihydroxy-	1	(--) ^b	None	237-237.5°	238-240°
2-Methyl-4-hydroxy- 5-methoxy-	1	(--) ^b	None	241.5-243°	241.5-243.5°
2,4-Dihydroxy- 5-methoxy-	1	(--) ^b	None	249.5-251°	243-245°

^hWith decomposition.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
3-Carbethoxy-4-hydroxy-5-methoxy-	4	(62)	None	217-220 ^o	221-222 ^o
3-Carboxy-4-hydroxy-5-methoxy-	4	(62)	None	278-284 ^{oh}	288-296 ^{oh}
3-carboxy-4-hydroxy-5,6-dimethoxy-	1	(--) ^b	None	273-274.5 ^{oh}	268-269.5 ^o
3,8-Diphenyl-4,7-dihydroxy-	1	(17)	None	337-338 ^o	333-336 ^o
3,8-Dicarbethoxy-4,7-dihydroxy-	4	(62)	None	264-265 ^o	267-269 ^o
3,8-Dicarboxy-4,7-dihydroxy-	4	(62)	None	300-310 ^{oh}	None ^f
3,3-Chlorobenzene-(3,4b)4-hydroxy-	4	(63) ⁱ	Glacial acetic acid	315-320 ^o	315-319 ^o
5-Nitro	2	(31)	Chloroform	202 ^o	200-202.5 ^o
5-Nitro-6-methyl-	3	(51)	Ethanol	268-270 ^o	269.5-272.5 ^o
5-Amino-	1	(--) ^b	None	253-254 ^o	254-256 ^o
4,7-Diamino-1,10-phenanthrolium dichloride	1	(--) ^b	None	359-360 ^{oh}	None ^f

ⁱProfessor Snyder named this compound as an acridine derivative; 10-chloro-7-hydroxy-pyrid-(3,2 c)-acridine.

Table 2. (Continued)

Compound	Source of Compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
2-Aza-	1	(14)	None	170.5-171.5°	172-176°
3-Aza-	1	(14)	None	171.5-172.5°	173-176°
4-Aza-	1	(14)	None	146.5-147.5°	150-153°
5-Aza-	1	(14)	Skelly A	152-153°	153-155°
4,7-Diaza-	1	(14)	None	242° ^j	252-254°
4-Hydroxy-2-aza-	1	(14)	None	263° ^j	265-267° ^j
4-Chloro-2-aza-	1	(--) ^b	None	212-213°	204-205°
5,6-Dioxime-	2	(34)	None	189°	190-193°
4-(3-Diethylamino-propylamino)-	4	(62)	None	166-168°	170-172°
4,7-Bis-(3-diethylamino-propylamino)-	4	(67)	Skelly D-Chloroform	170-175°	183.5-192°
4,7-Bis-(4-diethylamino-1-methylbutylamino)-	4	(62)	None	152-155°	146-153°

^jMelting point taken with a sealed tube.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
3-Methyl-7-chloro-	1	(7)	None	178-179 ^o	174-178 ^o
3-Phenyl-4-chloro	1	(17)	None	149-150 ^o	150-151 ^o
3-Phenyl-4-bromo-	1	(17)	None	158-159 ^o	159-161 ^o
2,9-Dimethyl- 4,7-diphenyl-	1	(13)	None	282-283 ^o	278-282 ^o
2,9-Diphenyl- 4,7-dimethyl-	1	(17)	Benzene	259-260 ^o	259-263 ^o
3,8-Diphenyl- 4,7-dichloro-	3	(17)	Benzene- Skelly D	235-236 ^o	229-232 ^o
3,8-Diphenyl- 4,7-dibromo-	1	(17)	None	240-241 ^o	240-242.5 ^o
4-Chloro-5-methoxy- (monopicrate)	4	(62)	None	218-220 ^o	217-218 ^o
2,3-Benzo-	1	(--) ^b	Water	116-117 ^o ^k	138-141 ^o
3,4-Cyclopenteno-	1	(12)	None	207-208 ^o	204-208 ^o
3,4-Cyclohexeno-	1	(12)	None	208-209 ^o	203-205 ^o

^kMelting point for the dihydrate material.

Table 2. (Continued)

Compound	Source of compound ^a	Ref.	Purification	Melting point	
				Reported	Observed
3,4-Cyclohepteno-	1	(12)	None	164-165 ^o	165-166 ^o
3,4-Cycloocteno-	1	(12)	None	145-146 ^o	145-147 ^o
5,6-Cyclohexeno-	1	(--) ^b	None	223-224.5 ^o	223-224.5 ^c
5,6-Benzo-	1	(--) ^b	None	180-181 ^o	183.5-185 ^c
5,6-Pyrido-(2,3 f)-	1	(--) ^b	None	199-200 ^o	198-199.5 ^c
(3,4),(7,8)-Dicyclo- pento-	1	(12)	None	282-283 ^o	277-280 ^o
(3,4),(7,8)-Dicyclo- hexeno-	1	(12)	None	259-260 ^o	255-257 ^o
2-Bromo-1,10-phenan- throline methbromide	3	(--) ¹	Absolute ethanol	--	216-219 ^o
1,10-Phenanthroline methiodide	3	(30)	Ethanol	210-213 ^o	203-207 ^o
1-Methyl-2- (1,10)-phenanthrolone	3	(30)	Benzene	123-124 ^o	124-126 ^o

¹See section III, B, of this thesis for the preparation of this compound.

Skelly A 28-60°
 Skelly B 60-70°
 Skelly D 77-115°

These solvents are referred to as Skelly A, B, or D without any reference to the boiling ranges in the remainder of this work. Melting points were obtained using a constant immersion thermometer dipped into an electrically heated oil bath (Dow Corning 550 Silicone Fluid) equipped with rapid stirring.

Sources and purifications of compounds other than 1,10-phenanthrolines of which spectra were obtained and used in this study for comparisons are listed in Table 3.

Table 3. Properties of miscellaneous compounds other than 1,10-phenanthrolines used in this study

Compound	Source ^a	Purification	Melting point or boiling point		Ref. ^b
			Reported	Observed	
Phenanthrene	1	Recrystallized from ethanol	100°	97-101°	(18)
Quinoline	2	Distillation	237.7°/760 mm	229°/735 mm	(18)
Naphthalene	3	Recrystallized from water	80.22°	80-82°	(18)
2,2'-Biquinoline	4	None	196°	194-195°	(58)
2,2'-Binaphthyl	5	None	187-188°	184-186°	(18)

^aThese numbers correspond to the following sources:

1. Reilly Tar and Chemical Corp., Indianapolis, Indiana
2. Eastman Organic Chemicals Dept., Rochester, New York
3. J. T. Baker Chemical Co., Phillipsburg, New Jersey
4. G. Frederick Smith Chemical Co., Columbus, Ohio
5. Dr. Gilman organic group, Iowa State University, Ames, Iowa
6. Matheson Coleman and Bell Division, East Rutherford, New Jersey.

^bReference in which the literature value for the melting points and boiling points were obtained.

Table 3. (Continued)

Compound	Source ^a	Purification	Melting point or boiling point		Ref. ^b
			Reported	Observed	
Pyridine	6	Distillation	115.3°/ 760 mm	122°/739 mm	(18)
Benzene	3	Distillation	80.1°/ 760 mm	79°/745 mm	(18)
2,2'-Bipyridine	4	None	70°	69-71°	(2)
Biphenyl	6	None	69-71°	69-71°	(18)
2,2',2''-Terpyridyl	4	None	88-89°	85-88°	(27)
m-Terphenyl	2	Recrystallized from Skelly A	86-87°	85-87°	(18)

Other 1,10-phenanthroline derivatives have been reported which were not available and were not prepared in this study. These derivatives and the references in which they were reported are listed in Table 4.

B. Preparation of 1,10-Phenanthrolines

Several derivatives of 1,10-phenanthroline reported in the literature were not available in this laboratory. In cases where starting materials could be obtained, these compounds were synthesized following procedures previously described. All Skraup reactions were performed in a three necked flask containing a stirring device at the center and thermometer and condenser at the side arms. Heat was applied

Table 4. Reported 1,10-phenanthroline derivatives which were not investigated in this study

Compound	Reference
2-Anilino-	(30)
5-Phenoxy-	(30)
4-Hydroxy-	(62)
5-Ethoxy-	(43)
4-Chloro-5-methoxy-	(62)
2-Hydroxy-4-methyl-	(4)
2-Chloro-4-methyl-	(4)
2-Methyl-4-chloro-	(23)
2-Methyl-4-phenoxy-	(23)
2-Methyl-4-chloro-5-methoxy-	(39)
2-Methyl-4-hydroxy-5-methoxy-	(39)
3,8-Dinitro-	(64)
3,5,8-Trinitro-	(64)
1,10-Phenanthroline-3,8-dione	(64)
3,5-Diphenyl-4-hydroxy-	(17)
1,10-Phenanthroline-1-oxide	(40)

using a Glas-Col brand heating mantle controlled with a power-statt. Purified samples were analyzed at Huffman Microanalytical Laboratories, Wheatridge, Colorado. Brief accounts of these preparations are given below.

1. Anhydrous 1,10-phenanthroline

This material was obtained by dissolving 1,10-phenanthroline monohydrate in hot Skelly D which contained a few drops of chloroform. This solution was concentrated and cooled, producing white crystals which melted at $118-120^{\circ}$. The reported value was 117° (3).

2. 1,10-Phenanthrolium chloride

An excess of hydrochloric acid was added to a solution of 1,10-phenanthroline monohydrate dissolved in water. The acid solution was evaporated to near dryness, and the last trace of excess hydrochloric acid removed under vacuum. No heat was applied in this process. The resulting light brown material melted at $222-228^{\circ}$. It was analyzed for chloride by dissolving a weighed sample in water, adjusting the pH to 1.5 with a small amount of nitric acid, passing the solution through a strongly acidic cation column (Amberlite IR-120 in the H^{+} form) to remove the 1,10-phenanthrolium cation, washing the chloride from the column with water, adjusting the pH of the eluent to 5.5 with 1 N sodium hydroxide, and titrating the eluted chloride with standard silver nitrate using dichlorofluorescein as indicator. Calculated for $C_{12}H_8N_2 \cdot HCl$: Cl, 16.36. Found, Cl, 15.80.

3. 1,10-Phenanthrolium perchlorate

Following the method outlined by Schilt and Taylor (53),

this acid salt was prepared by the addition of a slight excess of perchloric acid to a water solution of 1,10-phenanthroline. The acid solution was concentrated and cooled yielding white crystals. This material was then recrystallized from water. Calculated for $C_{12}H_8N_2 \cdot HClO_4$: C, 51.35; H, 3.23; N, 9.98; Cl, 12.63. Found: C, 50.62; H, 3.21; N, 9.64; Cl, 13.15.

4. 2-Methyl-1,10-phenanthroline

The preparation of this compound was first described in detail by Gerdeissen (26) and later by Pfeiffer and Christel-eit (46). Quinaldine (2-methylquinoline) was nitrated following essentially a procedure used by Johnson and Hamilton (35) for nitrating lepidine (4-methylquinoline). The two isomers produced, 2-methyl-5-nitroquinoline and 2-methyl-8-nitroquinoline, in this nitration were separated by repeated batch extractions with warm Skelly A. The extraction removed the 5-nitro-isomer leaving reasonably pure 2-methyl-8-nitroquinoline which melted at 135-140°. The literature value was 137° (26). This nitroquinoline was reduced to the corresponding amine using a reduction procedure described by Case (7) in which the material was refluxed in ethanol containing stannous chloride. After removing the alcohol and making the residue basic with ammonia, the amine was extracted batchwise with diethyl ether. The ether was then removed with distillation leaving a dark oil. No further purification

of the 2-methyl-8-aminoquinoline was carried out as was suggested by Pfeiffer and Christeleit (46). The amine was converted to 2-methyl-1,10-phenanthroline by a Skraup reaction using a similar procedure and molar proportions of reactants specified by Case (7) in the preparation of other methyl-1,10-phenanthroline derivatives. The reaction mixture was poured into water and made alkaline with ammonia leaving a black tar and a dark solution. The solution was decanted from the tar and extracted several times with hot benzene. This benzene was then used to extract the tar, yielding a reddish solution. The solvent was evaporated leaving a dark red oil. The yellow solution obtained by heating this dark oil with Skelly B was concentrated and cooled giving white crystals which melted at 75-78°. The literature value for the anhydrous material was 75-76° (26). Calculated for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.43. Found: C, 78.17; H, 5.27; N, 13.97. Assuming the nitrogen analysis was correct, the calculated ratios were $C_{13.05}H_{10.48}N_{2.00}^{(0.32)}$. Apparently the material which was analyzed was $C_{13}H_{10}N_2 \cdot \frac{1}{3}H_2O$.

5. 4-Methyl-1,10-phenanthroline

This derivative was prepared as described by Case (7). Lepidine (4-methylquinoline) was nitrated following the method of Johnson and Hamilton (35) producing 4-methyl-8-nitroquinoline. This material was reduced to the corresponding

amine by refluxing with stannous chloride in ethanol (7). The alcohol was removed, the residue made alkaline with ammonia, and the amine extracted with diethyl ether. Removal of the ether by distillation yielded a black, oily material. Repeated batch extractions by heating of this oil with Skelly A gave a yellow solution. The Skelly A was removed under vacuum leaving the amine as a yellow solid melting at 76-80°. The literature value was 84° (35). This product was then converted to 4-methyl-1,10-phenanthroline by a Skraup reaction using the method and molar proportions of reactants given by Case (7). The 1,10-phenanthroline derivative was recovered from the reaction mixture as outlined in the Case procedure as a black tar and oil. The tarry material was heated with small portions of Skelly B giving a yellow solution which upon concentration and cooling yielded a light brown solid. This material was dissolved in benzene, concentrated, and cooled. With the addition of Skelly B, a light brown solid precipitated which melted at 143.5-145°. The literature value was 144-145° (7). Calculated for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19, N, 14.43, Found: C, 80.41; H, 5.10; N, 14.55.

6. 2-Chloro-1,10-phenanthroline

The synthesis of this derivative using 1,10-phenanthroline as the starting material was described by Halcrow and Kermack (30). Using their procedure, methyl iodide was added to a solution of 1,10-phenanthroline monohydrate dissolved in ni-

trobenzene. The solution was held at 37° for 24 hours producing yellow crystals of 1,10-phenanthroline methiodide. After recrystallization from 95 per cent ethanol, this product melted at $203-207^{\circ}$. The literature value was $210-213^{\circ}$ (30). The above material was treated with potassium ferricyanide and sodium hydroxide producing 1-methyl-2-(1,10)-phenanthrolone. The light brown precipitate was extracted and recrystallized with benzene yielding light brown crystals which melted at $124-126^{\circ}$. The literature value was $123-124^{\circ}$ (30). This product was refluxed with a phosphorous pentachloride and phosphorous oxychloride mixture for 8.5 hours. After removal of the phosphorous oxychloride by distillation with reduced pressure, the light brown solid remaining was recrystallized from Skelly B (to which had been added a few drops of chloroform) yielding light brown crystals of 2-chloro-1,10-phenanthroline which melted at $127-129^{\circ}$. The literature value was $129-130^{\circ}$ (30). Calculated for $C_{12}H_7N_2Cl$: N, 13.05; Cl, 16.52. Found: N, 13.01; Cl, 16.92.

7. Attempted preparation of 2-bromo-1,10-phenanthroline

This derivative had not been reported previously. A similar reaction to that used above in the synthesis of 2-chloro-1,10-phenanthroline was employed. Case (10) described the use of a mixture of phosphorous tribromide and phosphorous oxybromide for converting hydroxy-1,10-phenan-

throlines to the corresponding bromo derivatives. Here 1-methyl-2-(1,10)-phenanthrolone prepared above was used as starting material. Phosphorous oxybromide was obtained from the K and K Laboratories, Inc., Jamaica, N. Y. Five grams of 1-methyl-2-(1,10)-phenanthrolone, 19 grams of phosphorous tribromide, and 4 grams of phosphorous oxybromide were heated at 108-110° for 6.5 hours. The reaction mixture was added to ice. The solution obtained was made alkaline with ammonia, and a light brown solid precipitated. Recrystallization from absolute ethanol yielded light brown crystals melting at 216-219°. This material did not analyze correctly for a monobromo-1,10-phenanthroline derivative, however. It appeared that a higher bromination product had been obtained. Calculated for a dibromo derivative: $C_{12}H_6N_2Br_2$; C, 42.63; H, 1.78; N, 8.29; Br, 47.29. Found: C, 44.09; H, 2.28; N, 7.93; Br, 45.6. Assuming the nitrogen analysis was correct, the calculated ratios were: $C_{12.89}H_{10.03}N_{2.00}Br_{2.00}$. The molecular weight calculated using the nitrogen analysis was 351.1, (the molecular weight for $C_{12}H_6N_2Br_2$ was 338.0). In comparing these molecular weights and noting the calculated ratios from the analysis, it appeared that the methyl group must still be present in this compound. When including one methyl group, the calculated molecular weight was 353.0 compared to 351.1 as calculated from the nitrogen analysis. The compound obtained was apparently 1-methyl-2,(?)-dibromo-

1,10-phenanthroline or 2-bromo-1,10-phenanthroline methbromide (see section IV, C, for discussion of this latter possibility.

8. 5-Bromo-1,10-phenanthroline

The preparation of this derivative was described by Richter and Smith (51) using 6-bromo-8-nitroquinoline as the starting material. Halcrow and Kermack (30) reported the synthesis of the same 1,10-phenanthroline derivative starting with 5-bromo-8-nitroquinoline. However, neither of these quinolines was readily available.

Using a mild bromination procedure described by Kosalappoff (37), o-nitroaniline was brominated producing 4-bromo-2-nitroaniline. This latter material was converted to 6-bromo-8-nitroquinoline by a Skraup reaction using the molar proportions of reactants and procedure described by Case (7) in the preparation of methylquinolines. This above quinoline was reduced with stannous chloride following the procedure by Case (7) yielding 6-bromo-8-aminoquinoline. With a Skraup reaction using molar proportions of reactants and procedure reported by Case (7), this quinoline was converted to 5-bromo-1,10-phenanthroline. The product was isolated by making the reaction mixture basic and extracting with benzene. Removal of benzene yielded a reddish-brown oil. This oil was heated to remove any traces of water from the melted 5-bromo-1,10-phenanthroline and was repeatedly batchwise extracted

with Skelly A. Concentration and cooling of the Skelly A solution yielded a white solid which melted at 107-111°. The literature value was 119° for anhydrous 5-bromo-1,10-phenanthroline (51). Calculated for $C_{12}H_7N_2Br$: C, 55.62; H, 2.73; N, 10.81; Br, 30.85. Found: C, 55.59; H, 2.89; N, 10.83; Br, 30.88.

9. 4,7-Dibromo-1,10-phenanthroline

The starting material, 4,7-dihydroxy-1,10-phenanthroline (see preparation below), was converted to 4,7-dibromo-1,10-phenanthroline using the procedure of Case (10). This hydroxy compound was heated with a mixture of phosphorous tribromide and phosphorous oxybromide (obtained from K and K Laboratories, Inc., Jamaica, New York) at 113-116° for 7.5 hours. The reaction mixture was poured on ice, and the resulting solution made basic with ammonia. The brown to gray solid which was precipitated was extracted with benzene yielding a reddish solution. With concentrating and cooling, a light brown solid was obtained which melted at 233-234°. The literature value was 236° (10). Calculated for $C_{12}H_6N_2Br_2$: C, 42.63; H, 1.78; N, 8.29; Br, 47.29. Found: C, 43.17; H, 8.29; Br, 45.50. Assuming the nitrogen analysis was correct, the ratios calculated were: $C_{12.15}H_{6.44}N_{2.00}Br_{1.92}^{(0.24)}$. The material which was analyzed was apparently: $C_{12}H_6N_2Br_2 \cdot 1/4 H_2O$.

10. 3-Phenyl-1,10-phenanthroline

The compound, 3-phenyl-1,10-phenanthroline chloride (17), was available in our laboratory. This material was dissolved in water, made basic with ammonia, and then extracted with chloroform. Removal of chloroform yielded a light brown oil which was used for obtaining infrared spectra. Case had previously reported (17) that the free base was obtained only as a viscous oil and was not solidified.

11. 2-Methoxy-1,10-phenanthroline

The synthesis of this derivative was described by Karrer and Pletscher (36) using 2-chloro-1,10-phenanthroline as the starting material. Sodium metal was dissolved in absolute methanol, and this solution was added to the solid 2-chloro-1,10-phenanthroline. The mixture was heated to a slight boil and the temperature held at this level for eight hours. The solvent was removed, and the oil which remained was extracted with a Skelly A-chloroform mixture. The extract was concentrated and cooled, yielding a white solid which melted at 70-72°. The literature value was 88-89° (36). Calculated for $C_{13}H_{10}N_2O$: C, 75.35; H, 3.41; N, 13.52; O, 7.72. Found: C, 68.54; H, 4.99; N, 12.38; O, (14.09). Assuming the nitrogen analysis was correct, the calculated ratios were: $C_{12.92}H_{11.20}N_{2.00}O_{1.99}$. From the analysis this material appeared to be a monohydrate, and this fact probably accounted for the discrepancy noted above in the observed melting point

with that reported in the literature.

12. 5-Nitro-6-methyl-1,10-phenanthroline

Richter and Smith (51) reported a nitration procedure for obtaining this compound. Following their method this material was synthesized by adding concentrated sulfuric acid and fuming nitric acid to 5-methyl-1,10-phenanthroline and heating at 120° for two hours. The reaction product was neutralized with sodium hydroxide precipitating a light yellow solid. The 5-nitro-6-methyl-1,10-phenanthroline was then recrystallized from 95 percent ethanol, and the pure product melted at 269.5-272.5°. The literature value was 268-270° (51). Calculated for $C_{13}H_9N_3O_2$: C, 65.26; H, 3.79; N, 17.57. Found: C, 65.29; H, 3.88; N, 17.33.

13. 4,7-Dihydroxy-1,10-phenanthroline

This material was prepared from G. Frederick Smith Chemical Co. commercial 4,7-dihydroxy-1,10-phenanthroline hydrochloride (27). The acid salt was dissolved in water and neutralized with ammonia. The solution was concentrated until a light brown solid began to precipitate. The solution was cooled, filtered, and the retained solid washed thoroughly. This material was used for obtaining the infrared spectrum without further purification.

14. 1,10-Phenanthroline-5,6-dione

This compound was first reported by Smith and Cagle (60)

as a by-product in the preparation of 5-nitro-phenanthroline. Druey and Schmidt (22) gave details for the synthesis of this compound from 5-methoxy-1,10-phenanthroline. Following the procedure of the latter authors, 5-methoxy-1,10-phenanthroline (obtained from Professor Case) was dissolved in concentrated sulfuric acid, fuming nitric acid was added, and the mixture heated for 1.5 hours at 120°. The reaction product was made basic with sodium hydroxide and then extracted with chloroform. The yellow chloroform solution was evaporated to dryness leaving a yellow solid. Recrystallization from absolute methanol yielded orange-yellow crystals which melted at 255-258°. The literature values were 256-257° (34, 60) and 250° (22). Calculated for $C_{12}H_6N_2O_2$: C, 68.57; H, 2.88; N, 13.33. Found: C, 67.83; H, 2.91; N, 12.92.

15. 3,8-Diphenyl-4,7-dichloro-1,10-phenanthroline

This compound was prepared following the scheme reported by Case (17). The available derivative, 3,8-diphenyl-4,7-dihydroxy-1,10-phenanthroline, was converted to the desired product by refluxing with a mixture of phosphorous pentachloride and phosphorous oxychloride. The reaction mixture was poured on ice. After isolation of the product from the solution by precipitation with the addition of sodium hydroxide, the material was recrystallized from a benzene-Skelly D mixture. The pure compound melted at 229-232°. The

literature value was 235-236° (17). Calculated for $C_{24}H_{14}N_2Cl_2$: C, 71.63; H, 3.52; N, 6.98; Cl, 17.67. Found: C, 71.63; H, 3.61; N, 6.85; Cl, 17.58.

C. Recording of Infrared Spectra

Preliminary studies of the infrared spectra of 1,10-phenanthrolines were made using spectra obtained with the Baird Associates Model B Double Beam Infrared Spectrophotometer. A polystyrene spectrum was superimposed on all spectra for calibration.

All spectra reproduced in this thesis were recorded on the Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with sodium chloride optics. The abscissa recording for this instrument was linear with wavelength (micron units). In all discussions the micron wavelength values were converted to frequency units in wave numbers (cm^{-1}) using a reciprocal table found in Bellamy (1).

Solution spectra were obtained for all compounds which were soluble in chloroform and carbon tetrachloride. Many of the 1,10-phenanthrolines were not soluble enough in carbon tetrachloride to give useful spectra, however. For this reason chloroform was the general solvent used in obtaining solution spectra. The cell thickness was 0.51 mm in most

cases, and the solutions contained approximately 10 mg. of the 1,10-phenanthroline derivative in 0.5 ml. of solvent (or about 2 per cent solutions). In instances where a 0.1 mm cell was used, saturated solutions of derivatives were many times required to obtain useful spectra. A variable space cell containing chloroform or carbon tetrachloride was used as the compensating cell in the reference beam in each case. In addition to recording the normal spectra, the 2000-1667 cm^{-1} region of the solution spectra was magnified using the x5 ordinate expansion on the Model 21 instrument (19).

Spectra were also obtained for all the solid derivatives using the potassium bromide disk technique. Here approximately three mg. of each of the 1,10-phenanthrolines was ground with approximately 100 mg. of potassium bromide in an agate mortar. This mixture was pressed into a disk using a 0.5 inch diameter Beckman die which was evacuated and pressed with a Loomis Engineering and Manufacturing Company 20-ton hydraulic press. The pressure applied was 15,000 ton/square inch (the press meter reading) for approximately three minutes. The potassium bromide used was a special infrared grade from the Harshaw Chemical Company of Cleveland, Ohio. A blank potassium bromide disk was placed in the reference beam in order to blank out water bands.

In cases where the 1,10-phenanthroline derivative was

available only as an oil, a demountable cell (cap cell) was used to obtain spectra. Here a drop of the oil was placed on a sodium chloride plate, another plate placed on top, and the cell mounted and positioned in the light beam.

All of the spectra recorded in this thesis were traced from the originals, and reduced and reproduced by a photostat process. In most cases the spectra recorded are a combination of chloroform solution spectra in the $5000-1667\text{ cm}^{-1}$ or $2.0-6.0$ micron range and the potassium bromide solid state spectra in the $1667-650\text{ cm}^{-1}$ or $6.0-15.4$ micron range. The dividing point, which usually occurred near 1667 cm^{-1} or 6.0 microns is indicated on each spectrum. In cases where the 1,10-phenanthroline derivative was insoluble in the solvents, the entire spectrum which was reproduced was taken from the potassium bromide disk spectrum. In a few instances the $1667-650\text{ cm}^{-1}$ region consisted of a cap cell spectrum.

IV. INFRARED SPECTRA

A. 1,10-Phenanthroline and Related Compounds

Bellamy (1) has indicated that little is known about the vibrational frequencies of heterocyclic compounds. Some information on the infrared spectra of pyridine and quinoline compounds has appeared in the literature. However, little infrared data has been previously reported for the various phenanthrolines. Absorption frequencies from spectra of 1,10-phenanthroline obtained using the Nujol mull technique have been listed (5, 53) and a few tentative assignments proposed.

The infrared spectra of anhydrous and monohydrated 1,10-phenanthroline were obtained, Figures 1 and 2. Four regions of strong absorption were observed for both of these materials; these regions will be discussed individually below. The spectra of 1,10-phenanthrolium chloride and 1,10-phenanthrolium perchlorate are reproduced in Figures 3 and 4. These acid salts are distinguished from the free base by shifts to higher frequencies of bands in the $1620\text{-}1400\text{ cm}^{-1}$ region. These shifts and other characteristic absorptions for the acid salts will be considered below.

1. The four regions of strong absorption in the 1,10-phenanthroline spectrum

a. Absorption near 3000 cm^{-1}

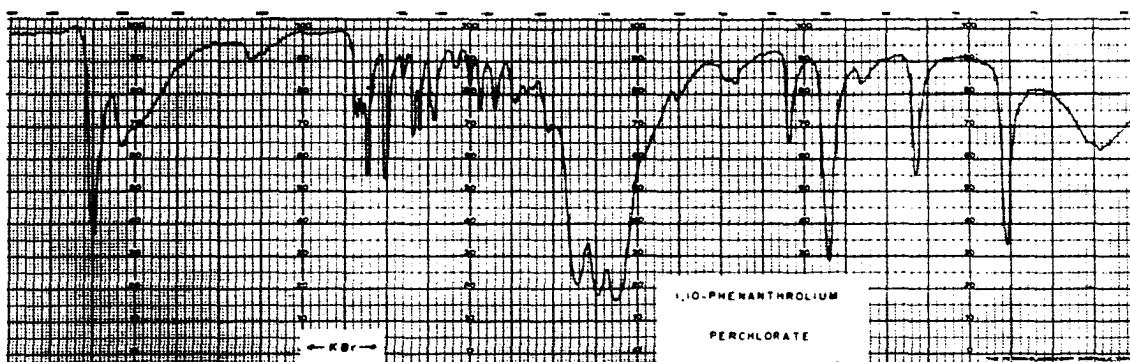
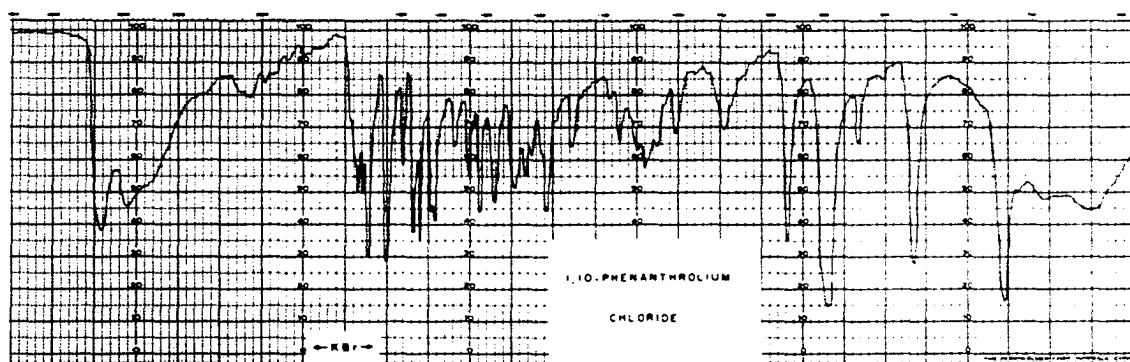
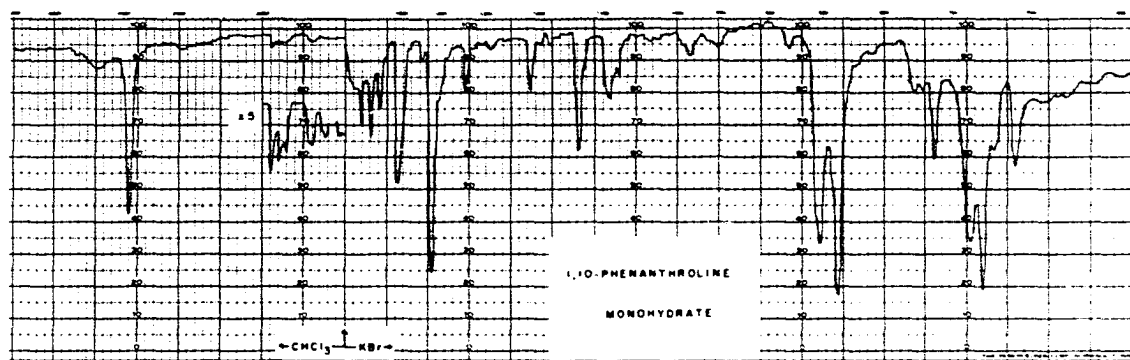
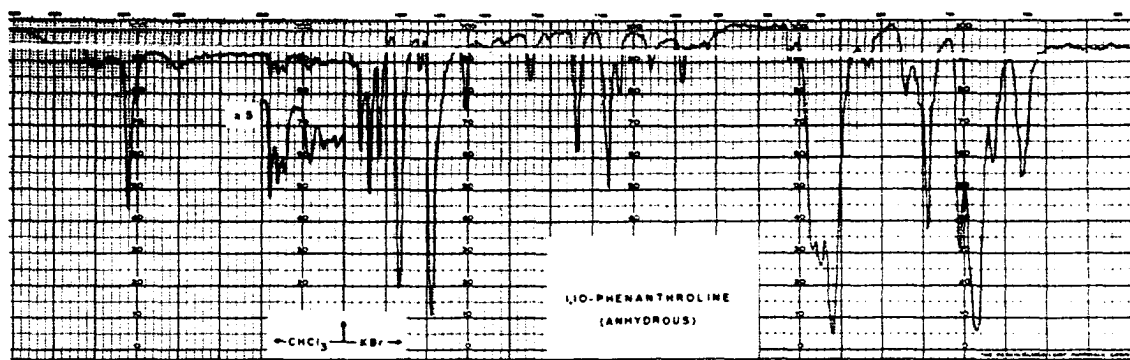
The first region of strong

Figure 1. Infrared spectrum of 1,10-phenanthroline
(anhydrous)

Figure 2. Infrared spectrum of 1,10-phenanthroline
monohydrate

Figure 3. Infrared spectrum of 1,10-phenanthrolium
chloride

Figure 4. Infrared spectrum of 1,10-phenanthrolium
perchlorate



absorption in the 1,10-phenanthroline spectrum, which occurs near 3000 cm^{-1} , was attributed to the aromatic C-H stretching mode reported by Bellamy (1) as a sharp band near 3030 cm^{-1} in aromatic compounds. In general the resolution obtained in this region in the 1,10-phenanthroline spectrum was not too good owing to the low dispersion with sodium chloride optics. With lithium fluoride or calcium fluoride optics, better detail and more definite information on the characteristic bands in this region could be obtained (68). The absorptions observed in the 3000 cm^{-1} region with 1,10-phenanthroline are recorded in Table 5.

Table 5. The aromatic C-H stretching vibration region in spectra of 1,10-phenanthroline

Data source	Frequency (cm ⁻¹)	
1,10-Phenanthroline ^a		
KBr disk spectrum	3425 ^b	3021 ^b
CCl ₄ solution spectrum	--	3049
CHCl ₃ solution spectrum	--	2959
1,10-Phenanthroline monohydrate		
KBr disk spectrum	3390	3012 ^b
CCl ₄ solution spectrum	--	3049
CHCl ₃ solution spectrum	--	2941

^a Anhydrous material.

^b A band of weak intensity.

The absorptions in the potassium bromide disk spectra of 1,10-phenanthroline and of all the substituted derivatives are not resolved too well in the 5000-1667 cm^{-1} range. A broad water band near 3400 cm^{-1} is usually present with varying intensity. The aromatic C-H stretching absorption appears as a broad peak of medium to weak intensity. With the monohydrate material, an intense water band occurs at 3390 cm^{-1} . The aromatic C-H stretching absorption obtained with carbon tetrachloride as the solvent is much sharper and of greater intensity, and this peak is found at slightly higher frequency than that observed in the potassium bromide disk spectrum.

Chloroform was reported to absorb (68) in the 3.31-3.34 micron (3021-2985 cm^{-1}) range, hence it would be expected that the C-H stretching vibration absorption would be nearly or totally blanked out when using this solvent. However, with a solution of 1,10-phenanthroline in chloroform, the C-H stretching absorption is observed as a very intense and sharp peak at a much lower frequency than is noted in the potassium bromide and carbon tetrachloride spectra. This shift to lower frequency with chloroform solution spectra is observed with all the 1,10-phenanthrolines which were soluble in this solvent. Apparently interaction between 1,10-phenanthroline and chloroform occurs which causes this large shift to lower frequency. A similar shift is found in pyridine and quinoline spectra when these liquids are diluted with chloroform.

b. Absorptions in the 1620-1400 cm^{-1} region The second region of strong absorption in the 1,10-phenanthroline spectrum occurs between 1620-1400 cm^{-1} . Within this range fall the characteristic ring vibrational frequencies for aromatic compounds (1). In the case of nitrogen heterocyclic compounds, such as pyridine and quinoline, these absorptions have been associated with the C=C and C=N stretching vibrations. As in quinoline, both heterocyclic and carbocyclic rings are present in 1,10-phenanthroline. Three strong absorptions were observed within this region. The first of these bands was a triplet absorption with well resolved components. The frequencies are recorded in Tables 6 and 7 for the anhydrous and monohydrate materials, respectively. Each peak of the triplet (band A) was at slightly lower frequency in the potassium bromide spectra compared to spectra obtained using the two solvents. This slight shift to lower frequency in the potassium bromide spectra was found in general in spectra of all the substituted 1,10-phenanthrolines. The intensities of the second and third absorptions (bands B and C) are much stronger than the first (band A) in both the solid state and solution spectra.

Assignments have been previously proposed for the absorptions in the 1620-1400 cm^{-1} region with nitrogen heterocyclic compounds. Randall et al. (49) assigned the absorption at 6.33 microns (1580 cm^{-1}) of pyridine to a C=N ring vibra-

Table 6. Absorptions in the 1620-1400 cm^{-1} region in the spectra of anhydrous 1,10-phenanthroline

Data source	Frequency (cm^{-1})				
	A ^a (triplet)			B	C
KBr disk spectrum	1616	1587	1558	1502	1416
CCl_4 solution spectrum	1618	1592	-- ^b	1504	1416
CHCl_3 solution spectrum	1621	1595	1563	1499	1416
Schilt and Taylor (53) ^c	1615	1591	1558	1505	1423

^aThe letters A, B, and C designate the three strong absorptions in the region.

^bBand blanks out in this instance by absorption of the carbon tetrachloride solvent.

^cSpectrum obtained using the Nujol mull technique.

Table 7. Absorptions in the 1620-1400 cm^{-1} region in the spectra of 1,10-phenanthroline monohydrate

Data source	Frequency (cm^{-1})				
	A ^a (triplet)			B	C
KBr disk spectrum	1616	1585	1558	1508	1418
CCl_4 solution spectrum	1618	1592	--- ^b	1504	1416
CHCl_3 solution spectrum	1618	1592	1560	1502	1416
Schilt and Taylor (53) ^c	1618	1590	1565	1508	1427
Busch and Bailar (5) ^c	1623 ^d	1592 ^e	1567 ^e	1511 ^e	--

^aThe letters A, B, and C designate the three strong absorptions in this region.

^bBand blanks out in this instance by absorption of the carbon tetrachloride solvent.

^cSpectrum obtained using the Nujol mull technique.

^dThis absorption was assigned to the aryl C=N ring vibration.

^eThis absorption was assigned to the C=C ring vibration.

tion. Withop (69) concluded, however, that the assignment of this peak to the C=N vibration in pyridine or in other heterocyclics was a simplification convenient for comparison purposes and that no absolute assignment could be made with certainty. Bellamy (1) preferred not to differentiate between the C=N and C=C vibrations in pyridines and quinolines, but rather to consider the absorptions in this region as due to both vibrations. He indicated that the frequencies of the two vibrations were so similar that in ring systems like these, neither would retain its individual character, and interactions between the C=N and C=C vibrations would probably occur. Cook and Church (21) followed Bellamy's assignments in their discussion of this region in a study of substituted pyridines. Shindo and Ikekawa (56) did not distinguish the C=C and C=N vibrations with several methyl- and ethylpyridines.

Busch and Bailar (5) gave tentative assignments for each of the absorptions in this region with 1,10-phenanthroline monohydrate, and these were noted above in Table 7. The first component of the triplet absorption (band A) was associated with the C=N vibration. The next two components of the triplet and second strong absorption (band B) were all designated as due to C=C vibrations. These authors did not make any reference to the third strong absorption (band C) in this region, however. Schilt and Taylor (53) did not give any individual assignments to bands observed in this region with

1,10-phenanthroline. They suggested that the second strong absorption (band B) was associated with the carbocyclic ring since the 2,2'-bipyridine spectrum did not contain a strong band near 1500 cm^{-1} .

In order to test the validity of the above proposed assignments and to investigate the possibility of distinguishing an absorption associated with the C=N vibration in the presence of C=C vibrations, the spectra of a series of nitrogen heterocyclic ring compounds were compared with spectra of corresponding ring structures which contained no nitrogen atom. In Figure 5 the position and relative intensity of absorptions obtained with these compounds are recorded in a line graph. In Table 8 the frequencies for these absorptions are tabulated. The third component of the triplet absorption (band A) found in 1,10-phenanthroline is observed to be absent in the phenanthrene spectrum. This observation would imply that the 1558 cm^{-1} band of 1,10-phenanthroline could possibly be assigned to the C=N ring vibration rather than the 1616 cm^{-1} peak as proposed by Busch and Bailar (5). A band corresponding to the first component of the 1,10-phenanthroline spectrum appeared only as a weak shoulder in the phenanthrene spectrum. The absence of a medium peak here would tend to support the assignment of the C=N vibration in the 1,10-phenanthroline spectrum to the first component as was proposed by Busch and Bailar (5). A more convincing confirmation of the above as-

Figure 5. Absorptions in the $1660\text{-}1300\text{ cm}^{-1}$ region in spectra of various heterocyclic and carbocyclic compounds

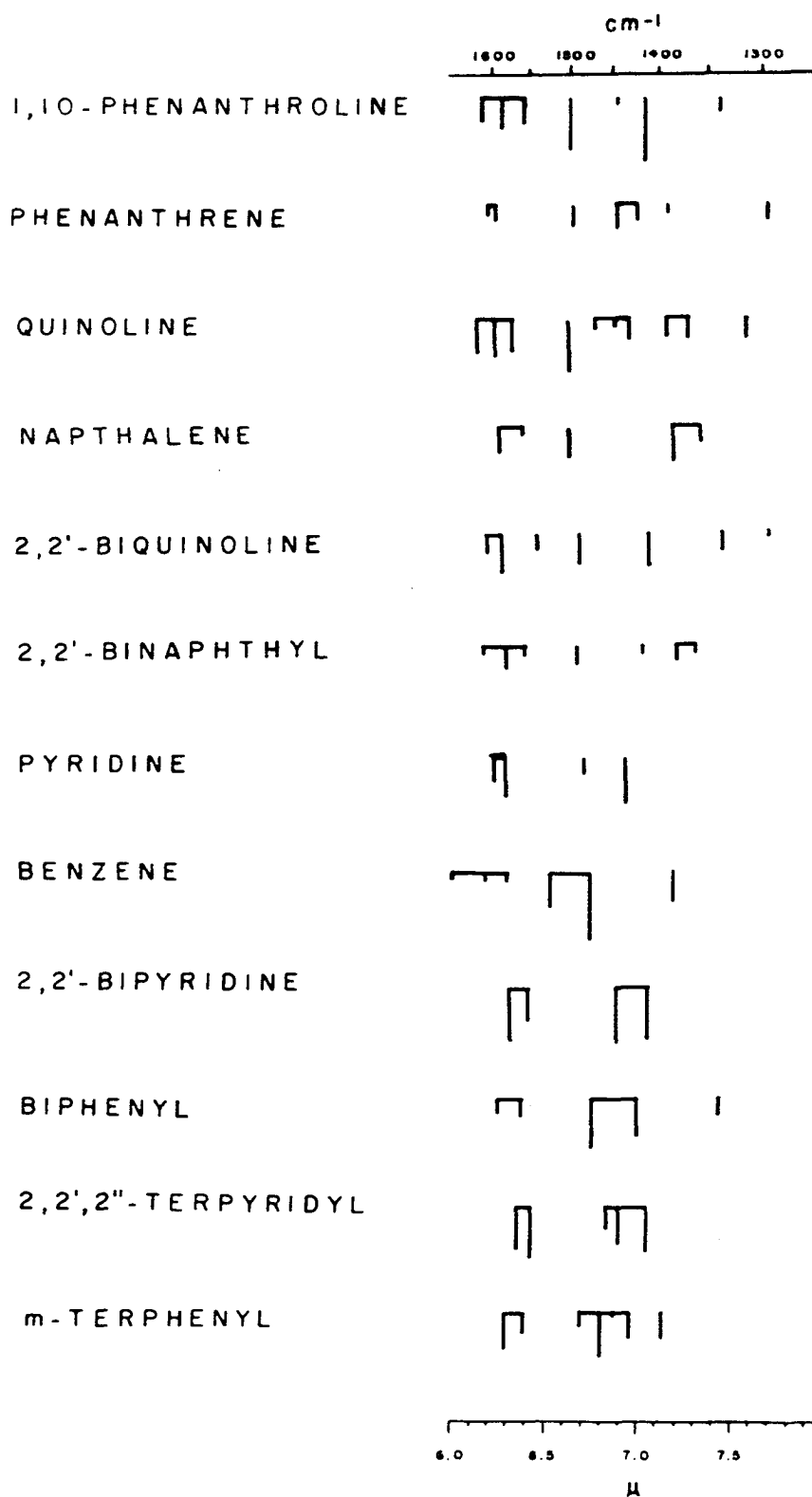


Table 8. Absorptions in the 1660-1300 cm^{-1} region of various heterocyclic and carbocyclic compounds

Compound	Frequency (cm^{-1}) ^a					
	A (triplet)			B	C	
1,10-Phenanthroline ^{b,c}	1616	1587	1558	1502	1447 1416	1340
Phenanthrene ^c	1608	1595		1497	1447 1425	1395 1295
Quinoline ^d	1621	1595	1572	1502	1471 1449 1433	1393 1370 1312
Naphthalene ^c		1592	1558	1502		1385 1359
2,2'-Biquinoline ^c	1613	1595	1565	1495	1414	1323 1295
2,2'-Binaphthyl ^c	1621	1592	1565	1497	1425	1389 1370
Pyridine ^d	1597	1582		1484	1437	
Benzene ^d	1661	1613	1582	1527	1477	1389
2,2'-Bipyridine ^c		1577	1553		1447 1412	
Biphenyl ^c		1595	1567	1477	1427	1340
2,2',2''-Terpyridyl ^c		1577	1558	1466	1453 1420	
m-Terphenyl ^c		1592	1567	1490	1473 1456 1437	1403

^aThese frequencies correspond to absorptions reproduced in line graph of Figure 5.

^bAnhydrous material.

^cData from the potassium bromide disk spectrum.

^dData from the cap cell spectrum.

signment by these authors was found when comparing the quinoline spectrum (which was very similar to that of 1,10-phenanthroline in this region) with naphthalene. In this instance the first component of the triplet was not present in the naphthalene spectrum. However, in comparing 2,2'-biquinoline with 2,2'-binaphthyl, the assignment of Busch and Bailar (5) was questioned since the first component of the triplet appears in the spectra of both compounds. If the assignment of the C=N vibration to the first component of the triplet is correct, this peak should have been absent in the 2,2'-binaphthyl spectrum.

The comparison of various pyridines with their corresponding benzene ring compounds gave further reasons for possible general assignment of the C=N ring vibration frequency in these nitrogen heterocyclic ring compounds. In the pyridine spectrum the first absorption appears as a doublet, where with 1,10-phenanthroline and the two quinolines three peaks are present in this region. In the 2,2'-biquinoline spectrum, the third peak is a separate absorption, however, and not a component of a triplet as observed with 1,10-phenanthroline and quinoline. The first triplet absorption with benzene is quite weak, and the designation of these stronger peaks in pyridine to the C=N vibration appears possible. As noted above, Pandall et al. (49) assigned the 6.33 micron (1580 cm^{-1}) band to the ring C=N vibration of pyridine. This as-

signment corresponds to the second component of the first doublet in the pyridine spectrum. In the 2,2'-bipyridine and 2,2',2''-terpyridyl spectra, the first doublet was at lower frequency than found in the pyridine spectrum.

These following observations were made for possible verification of the assignment by Schilt and Taylor (53) of the 1502 cm^{-1} band of 1,10-phenanthroline to the ring vibrations of the carbocyclic ring. As Schilt and Taylor had observed previously, no peak near 1500 cm^{-1} was found in the 2,2'-bipyridine spectrum. This compound contains no carbocyclic ring. The first component of the second doublet in the biphenyl spectrum is at 1477 cm^{-1} . This peak could have corresponded to the doublet absorption in 2,2'-bipyridine which was at lower frequency, however. The m-terphenyl spectrum contains a peak at 1490 cm^{-1} which is not present in the spectrum of 2,2',2''-terpyridyl. A weak band is observed at 1484 cm^{-1} in the pyridine spectrum but its intensity is much weaker compared to the benzene absorption at 1477 cm^{-1} . Absorption near 1500 cm^{-1} is found with all the nitrogen heterocyclic compounds which contained a carbocyclic ring (1,10-phenanthroline, quinoline, and 2,2'-biquinoline).

From this investigation it was apparent that the assignment of the C=N vibration of 1,10-phenanthroline to the first component of the triplet absorption (band A) was very uncertain.

A general assignment of the C=N vibration to the entire triplet absorption in 1,10-phenanthroline seemed more reasonable rather than designating one component of this triplet. This assignment seemed more realistic since the 2,2'-bipyridine spectrum did not even contain the first component.

The association of the 1502 cm^{-1} band to the carbocyclic ring in 1,10-phenanthroline by Schilt and Taylor seemed to be substantiated in most instances in these comparisons. This band was present in the spectra of all compounds containing the carbocyclic ring (with some shifts), and in general was not present (at least not as a strong band as in pyridine) in the heterocyclic compounds which contained no carbocyclic ring.

No definite assignment to the third strong absorption (band C) in the 1,10-phenanthroline spectrum has been reported. The above comparisons do not assist much in this task. However, this absorption appears to be another ring vibration. It was shifted to higher frequency upon co-ordination of 1,10-phenanthroline with a proton (see the discussion below on the acid salts of 1,10-phenanthroline). Also the position and the strong intensity of the peak remained relatively constant with substitution in the majority of the 1,10-phenanthroline derivatives.

c. Absorptions in the 1150-1060 cm^{-1} region A third region of strong absorption in the spectrum of 1,10-phenanthroline is observed in the region from 1150 to 1060 cm^{-1} . Two sharp bands of medium intensity appear at 1134 cm^{-1} and 1088 cm^{-1} with a medium shoulder on the low frequency side of the second band. Quinoline gave similar strong absorptions in this spectral region. In the pyridine spectrum the strong peaks were found at a lower frequency in the 1030 to 980 cm^{-1} range.

Bellamy (1) indicated that the strong absorptions in this region with pyridines were either ring vibrations or hydrogen deformation modes. Schilt and Taylor (53) have suggested that the bands in the 1250-1125 cm^{-1} region of the 1,10-phenanthroline spectrum were probably due to in-plane hydrogen deformation modes or due to ring vibrations.

d. Absorptions in the 900-700 cm^{-1} region In the spectrum of 1,10-phenanthroline, a fourth region of strong absorption occurs at 900-700 cm^{-1} . Two very strong bands are found in this region, at 839 cm^{-1} and 733 cm^{-1} , and in addition many other shoulders and medium peaks are present.

Bellamy (1) reported that the out-of-plane C-H deformations occur in the 1000-650 cm^{-1} range for aromatic compounds and in the 900-700 cm^{-1} region with pyridines and quinolines. Schilt and Taylor (53) assigned the lower frequency band (at

733 cm^{-1}) to the out-of-plane motion of the hydrogen atoms on the heterocyclic rings, and the higher frequency band (at 839 cm^{-1}) to the motions of the hydrogens on the center benzene rings of 1,10-phenanthroline. They attributed the multiple splittings exhibited by these strong bands to out-of-plane hydrogen motions not in phase and to possible overtones of fundamental vibrations of lower frequency.

2. Spectra of the acid salts of 1,10-phenanthroline

As briefly discussed earlier, shifts of the strong absorptions in the 1620-1400 cm^{-1} region to higher frequency were observed on comparing the spectra of the acid salts of 1,10-phenanthroline with that of the free base. Withop (69) observed the shift to shorter wavelength (higher frequency) for the first ring vibration absorption in pyridine compounds upon passing from the >C=N- group to the cation, >C=N^+_{H} . The first ring vibration for pyridines was reported at 6.24-6.28 microns (1603-1593 cm^{-1}) and the shifted absorption at 6.07-6.13 microns (1647-1631 cm^{-1}) for the pyridine acid salts. Schilt and Taylor (53) have reported shifts to higher frequencies for the ring vibration absorptions in the 1,10-phenanthroline spectrum upon co-ordination with a metal atom or with a proton. The proton can be either from water or from acids. With water the shifts are small as noted in Table 9 where the absorptions with 1,10-phenanthroline mono-

hydrate were compared with those of the anhydrous compound. The effect of the co-ordination of a proton of an acid is observed by comparing the spectra of two acid salts in Figures 3 and 4 with the spectra of anhydrous 1,10-phenanthroline in Figure 1. The frequencies and the shifts observed with these acid salts are recorded in Table 9. The third strong band (band C) usually observed in the 1,10-phenanthroline spectrum, appears as a doublet absorption with both acid salts. This split peak was apparently not observed by Schilt and Taylor (53) owing to the presence of the interfering Nujol band in the vicinity of this absorption.

Withop (69) observed that salts of heterocyclic compounds as pyridine, quinoline, isoquinoline, etc., which contain the cation, $\text{>C}=\overset{\text{H}}{\underset{\text{H}}{\text{N}}^+}$, showed one or several bands in the 4.5-5.5 micron or 2222-1818 cm^{-1} region. He termed these absorptions as the "immonium bands" (the group, $\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{N}}^+}$, in other compounds showed absorption in the 4.0-4.3 micron or 2500-2326 cm^{-1} range which was called the "ammonium band"). In Figures 3 and 4 a very weak and broad absorption is detected near 2100 cm^{-1} in the potassium bromide spectra of the two acid salts of 1,10-phenanthroline which can be related to the "immonium band." Closer examination of the potassium bromide and Nujol mull spectra using the x5 ordinate expansion reveals two peaks (the second being of weaker intensity) at frequencies recorded in Table 10. These peaks were somewhat better defined with

Table 9. Shifts to higher frequency in the 1630-1400 cm^{-1} region upon co-ordination with a proton

Data source	Frequency (cm ⁻¹)					
1,10-Phenanthroline ^a						
	<u>A^b (triplet)</u>			<u>B</u>	<u>C</u>	
KBr disk spectrum	1616	1587	1558	1502	1416	
Schilt and Taylor(53) ^c	1615	1591	1558	1505	1423	
1,10-Phenanthroline monohydrate						
KBr disk spectrum	1616	1585	1558	1508	1418	
Δv (cm ⁻¹) ^d	0	-2	0	6	2	
Schilt and Taylor (53) ^c	1618	1590	1565	1508	1427	
Δv (cm ⁻¹) ^e	3	1	7	3	4	
1,10-Phenanthrolium chloride						
KBr disk spectrum	1626	1610	1595	1543	1466	1449 ^f
Δv (cm ⁻¹) ^d	10	23	37	41	50	33
1,10-Phenanthrolium perchlorate						
KBr disk spectrum	1629	1613	1595	1543	1466	1449 ^f
Δv (cm ⁻¹) ^d	13	26	37	41	50	33
Schilt and Taylor (53) ^c	1635	1618	1599	1544	1473	
Δv (cm ⁻¹) ^e	20	27	41	39	50	

^aAnhydrous material.

^bThe letters A, B, and C designate the three strong absorptions in this region.

^cThe spectrum was obtained using the Nujol mull technique.

^dShifts calculated from frequencies of the potassium bromide disk spectrum of anhydrous 1,10-phenanthroline.

^eShifts calculated from frequencies of the Nujol mull spectrum of anhydrous 1,10-phenanthroline.

^fDoublet absorption.

Table 10. Absorptions observed in the spectra of two acid salts of 1,10-phenanthroline corresponding to the "immonium bands"

Data source	Frequency (cm ⁻¹) ^a	
1,10-Phenanthrolium chloride		
KBr disk spectrum	2066	1992
Nujol mull spectrum	2132	1992
1,10-Phenanthrolium perchlorate		
KBr disk spectrum	2066	1992
Nujol mull spectrum	2028	1976

^aAll frequency values were observed using the x5 ordinate expansion.

the Nujol mull spectra in both cases, however the intensity of the absorptions is still very weak.

B. Alkyl Derivatives of 1,10-Phenanthroline

The spectra of 32 methyl derivatives, seven ethyl derivatives and one propyl derivative were obtained and are reproduced in Figures 6 through 45. In general the spectra of correspondingly substituted compounds are very similar. The main differences lie in the 900-650 cm⁻¹ region.

1. Infrared spectra of methyl-1,10-phenanthrolines

Bellamy (1) has discussed the absorptions which are associated with the methyl group. Hydrocarbons containing

methyl groups show two bands which occur at 2962 cm^{-1} and 2872 cm^{-1} . The first of these peaks corresponds to the asymmetrical C-H stretching vibration; the second to the symmetrical C-H stretching mode of the methyl group.

The spectra of methyl derivatives of 1,10-phenanthroline are recorded in Figures 6 through 37. In the methyl-1,10-phenanthrolines, these above absorptions which were associated with the methyl group, are not resolved too well, neither in solution nor in potassium bromide. In addition to the C-H stretching absorption near 3030 cm^{-1} , shoulders and inflections are found in the potassium bromide and carbon tetrachloride spectra, which are not observed in the 1,10-phenanthroline spectrum. However, in most cases the resolution is too poor to make definite assignments to the methyl bands. In chloroform spectra of the methyl-1,10-phenanthrolines, the asymmetric vibrational absorption at 2962 cm^{-1} is not observed owing to the overlap with the strong aromatic C-H stretching vibration which occurs at $2959\text{-}2924\text{ cm}^{-1}$. In most instances a very weak shoulder or inflection could be detected in the chloroform spectra in the range of $2874\text{-}2857\text{ cm}^{-1}$ which could correspond to the symmetric stretching mode discussed above.

Bellamy (1) has reported that the methyl group generally produces an absorption near 1460 cm^{-1} which is due to hydrogen bending vibrations about the carbon atom. The absorption

Figure 6. Infrared spectrum of 2-methyl-1,10-phenanthroline

Figure 7. Infrared spectrum of 3-methyl-1,10-phenanthroline

Figure 8. Infrared spectrum of 4-methyl-1,10-phenanthroline

Figure 9. Infrared spectrum of 5-methyl-1,10-phenanthroline

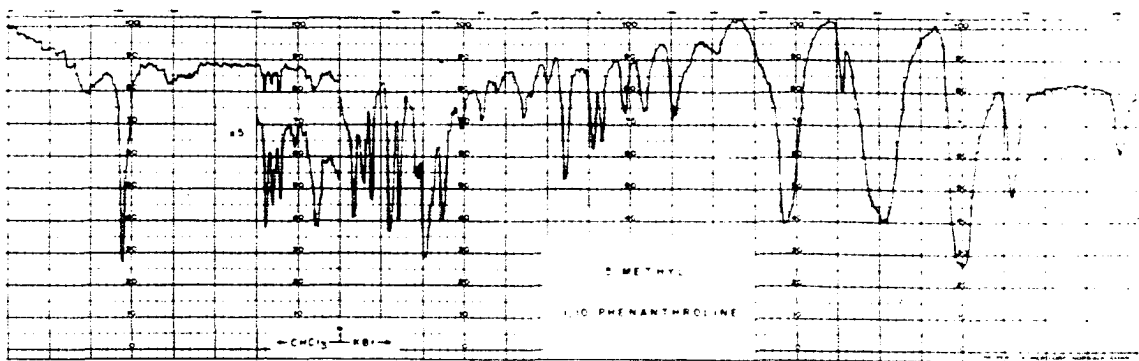
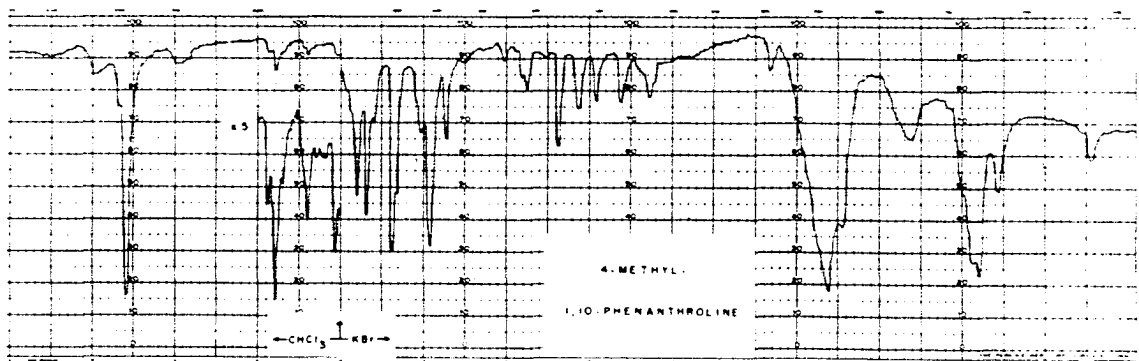
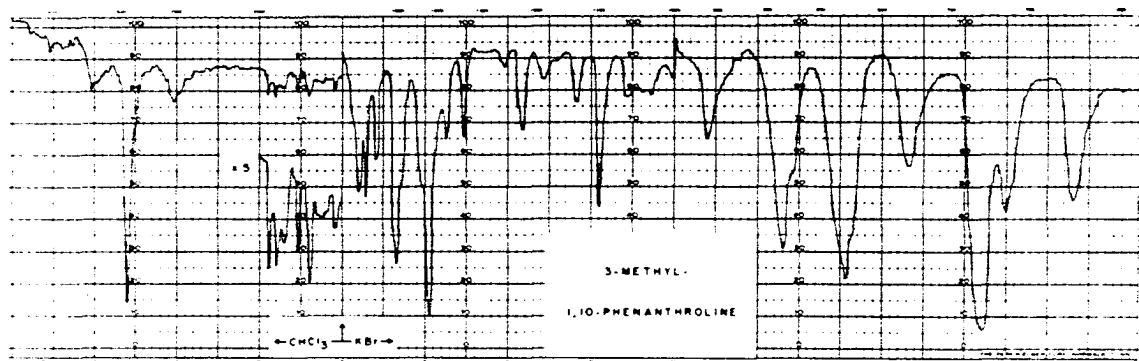
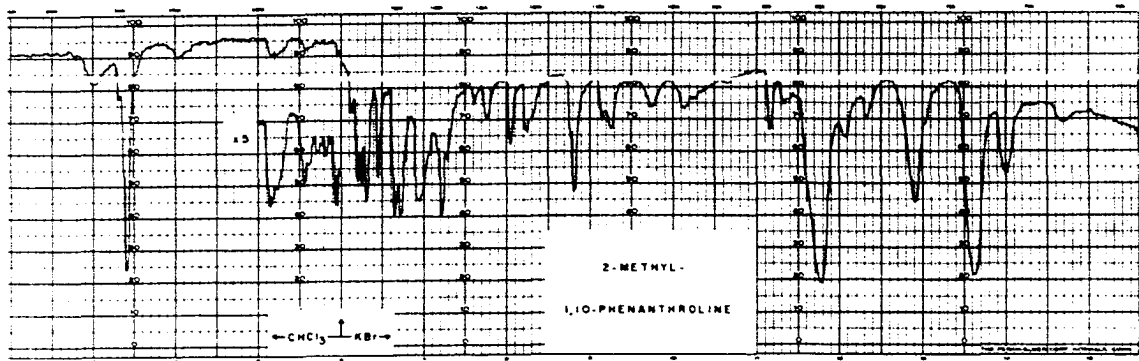


Figure 10. Infrared spectrum of 2,4-dimethyl-1,10-phenanthroline

Figure 11. Infrared spectrum of 2,9-dimethyl-1,10-phenanthroline

Figure 12. Infrared spectrum of 3,4-dimethyl-1,10-phenanthroline

Figure 13. Infrared spectrum of 3,5-dimethyl-1,10-phenanthroline

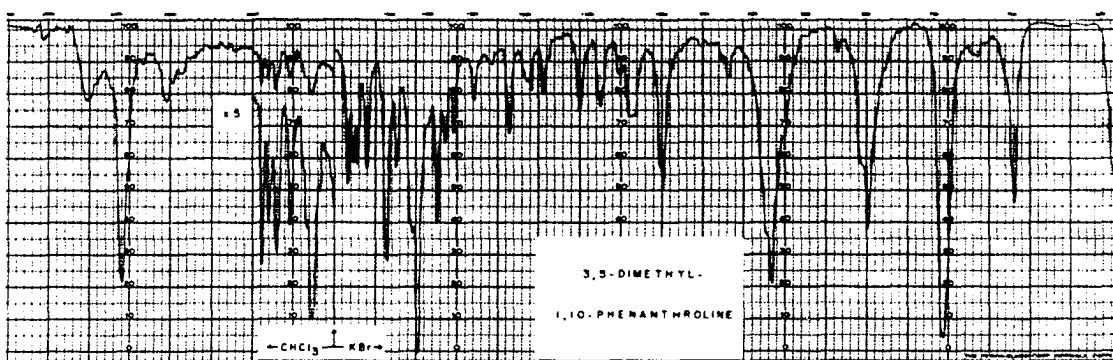
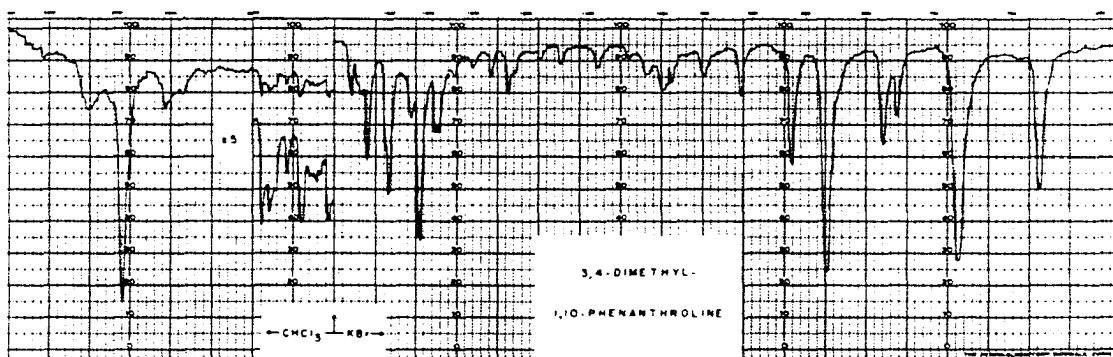
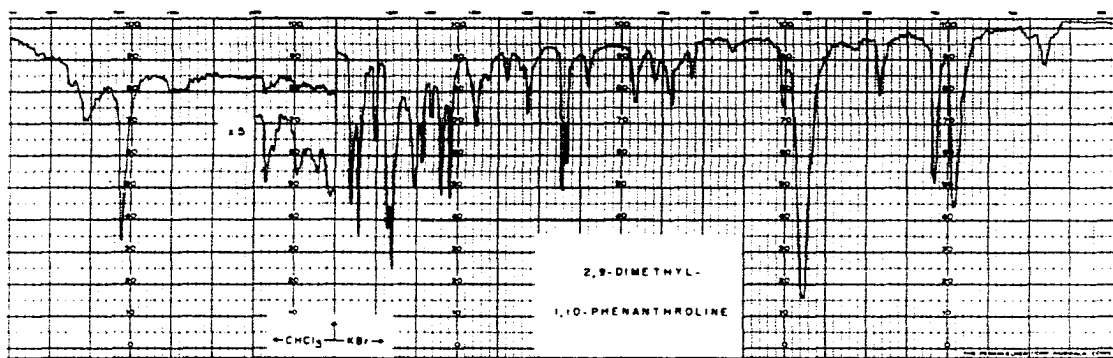
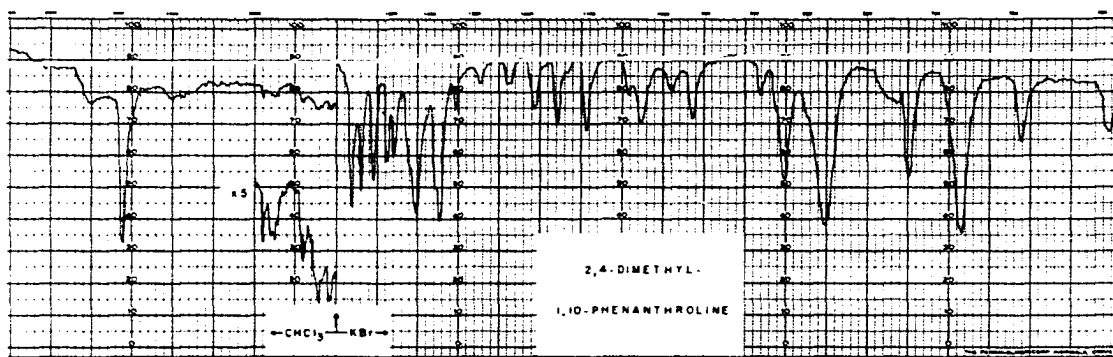


Figure 14. Infrared spectrum of 3,6-dimethyl-1,10-phenanthroline

Figure 15. Infrared spectrum of 3,7-dimethyl-1,10-phenanthroline

Figure 16. Infrared spectrum of 3,8-dimethyl-1,10-phenanthroline

Figure 17. Infrared spectrum of 4,5-dimethyl-1,10-phenanthroline

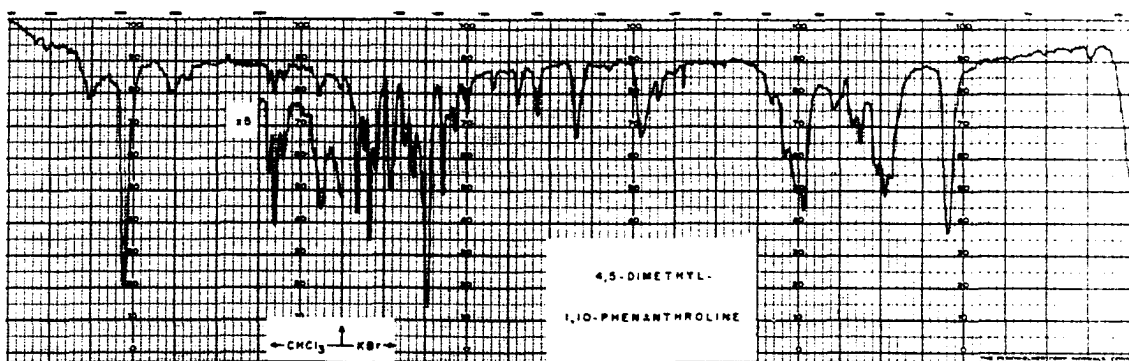
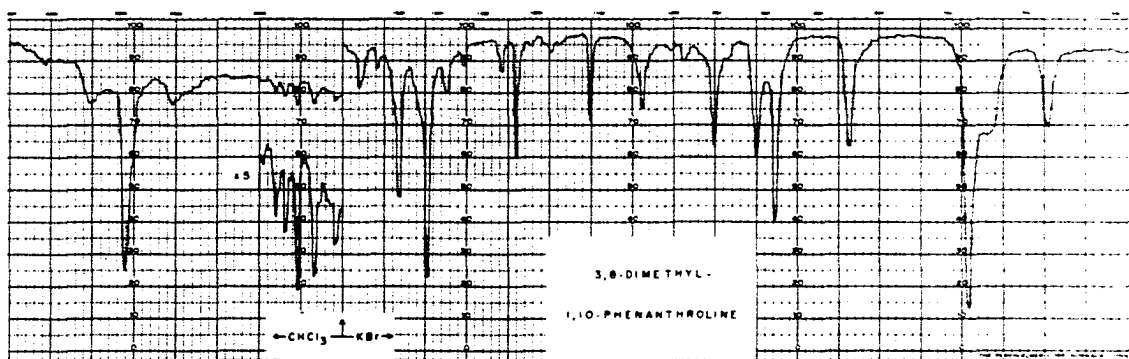
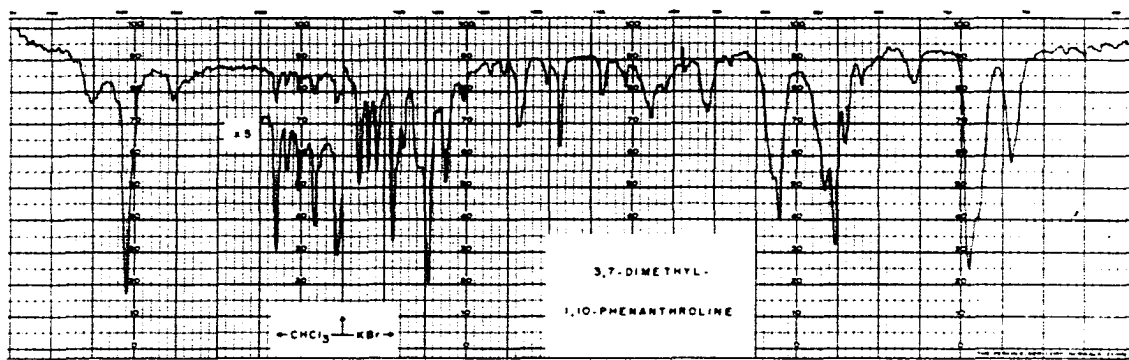
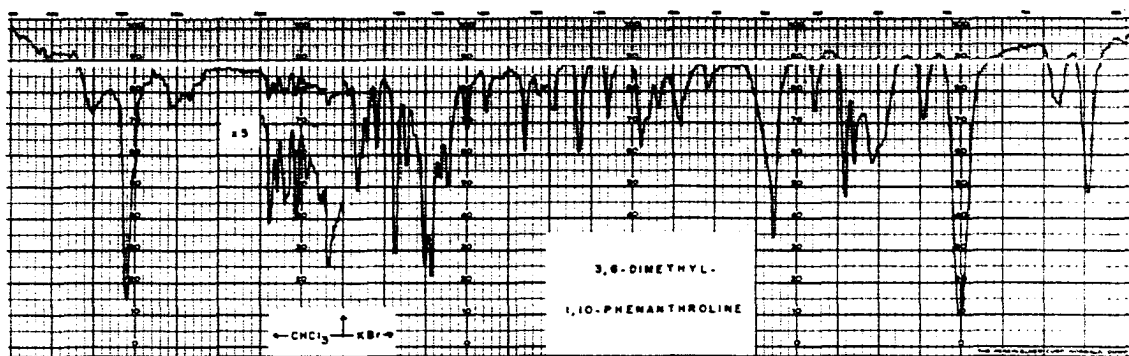


Figure 18. Infrared spectrum of 4,6-dimethyl-1,10-phenanthroline

Figure 19. Infrared spectrum of 4,7-dimethyl-1,10-phenanthroline

Figure 20. Infrared spectrum of 5,6-dimethyl-1,10-phenanthroline

Figure 21. Infrared spectrum of 2,3,4-trimethyl-1,10-phenanthroline

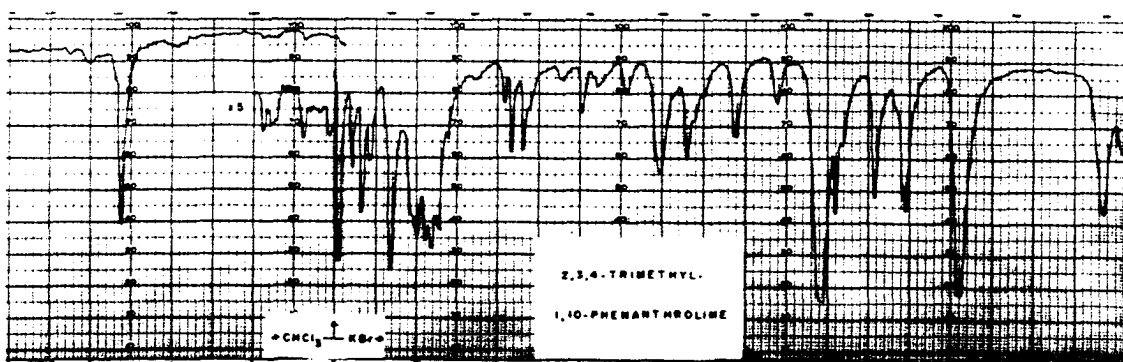
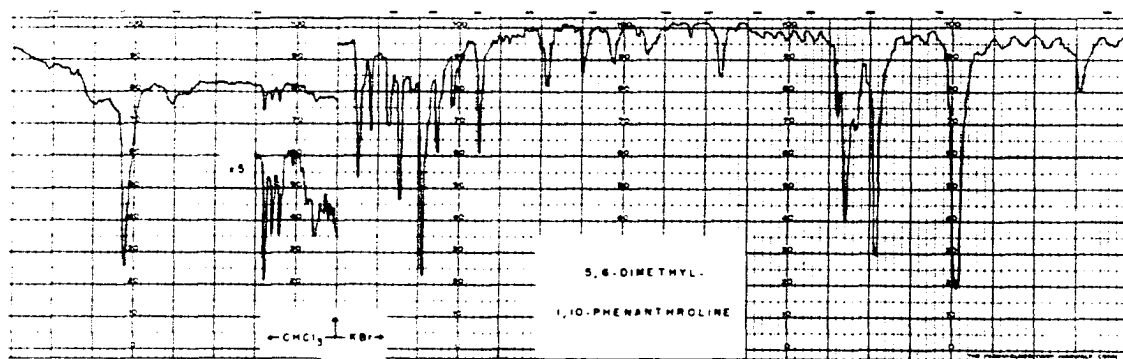
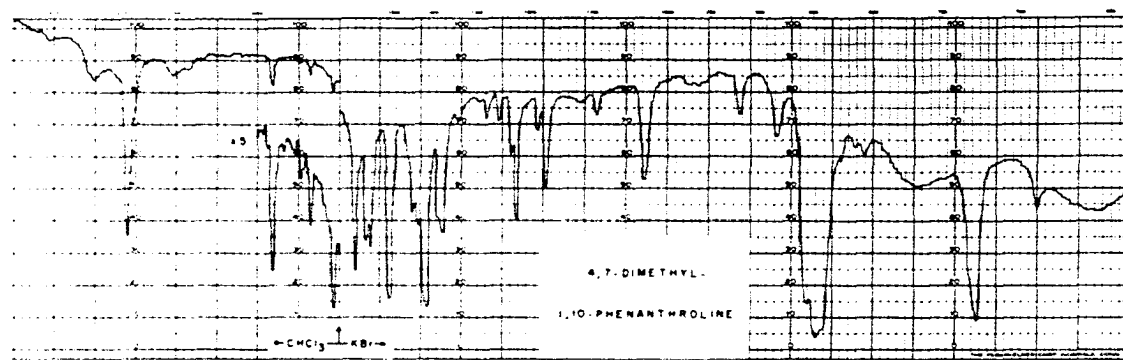
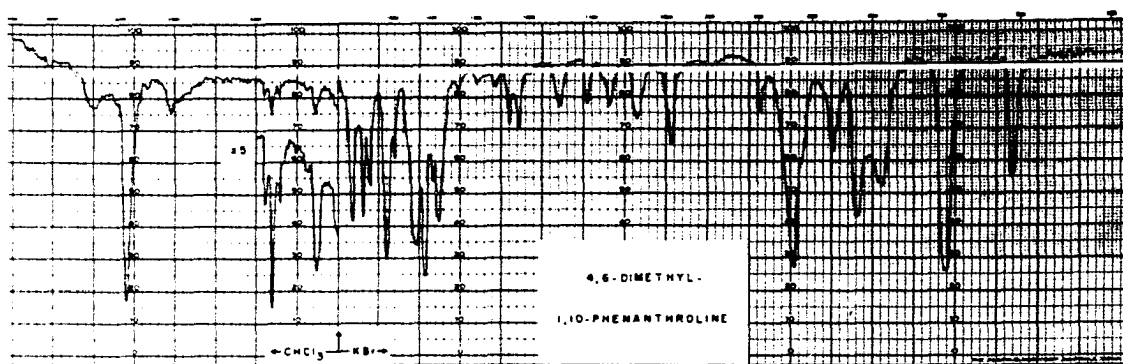


Figure 22. Infrared spectrum of 3,4,6-trimethyl-1,10-phenanthroline

Figure 23. Infrared spectrum of 3,4,7-trimethyl-1,10-phenanthroline

Figure 24. Infrared spectrum of 3,4,8-trimethyl-1,10-phenanthroline

Figure 25. Infrared spectrum of 3,5,6-trimethyl-1,10-phenanthroline

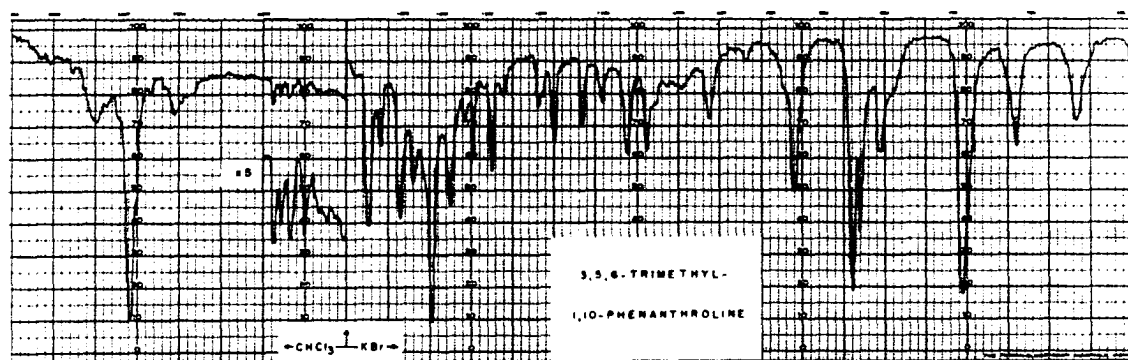
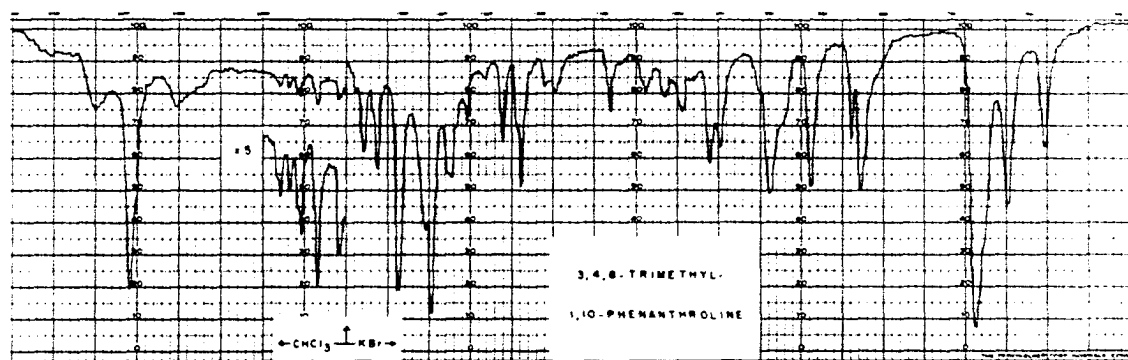
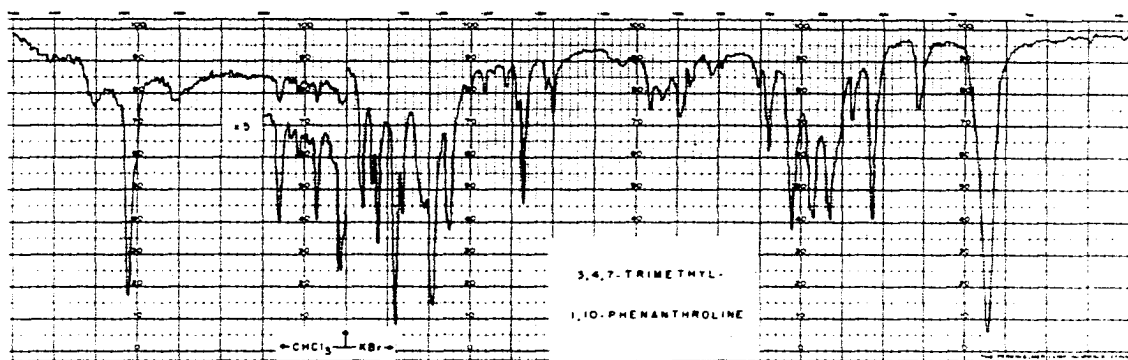
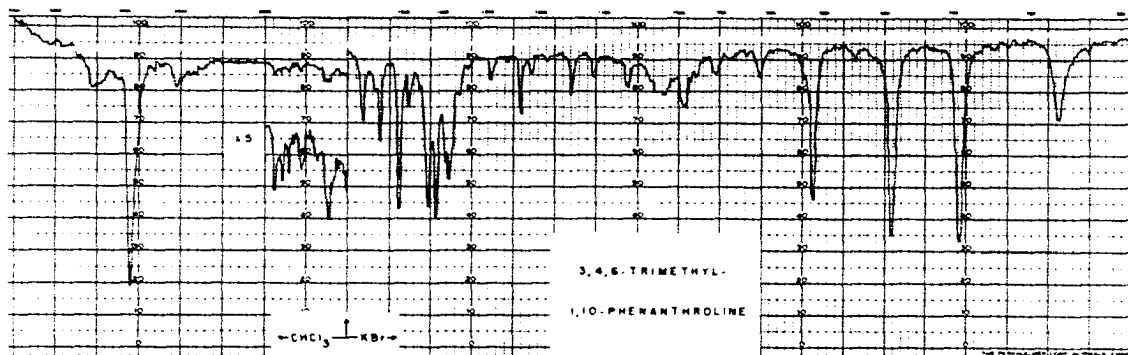


Figure 26. Infrared spectrum of 3,5,7-trimethyl-1,10-phenanthroline

Figure 27. Infrared spectrum of 3,5,8-trimethyl-1,10-phenanthroline

Figure 28. Infrared spectrum of 3,6,7-trimethyl-1,10-phenanthroline

Figure 29. Infrared spectrum of 4,5,7-trimethyl-1,10-phenanthroline

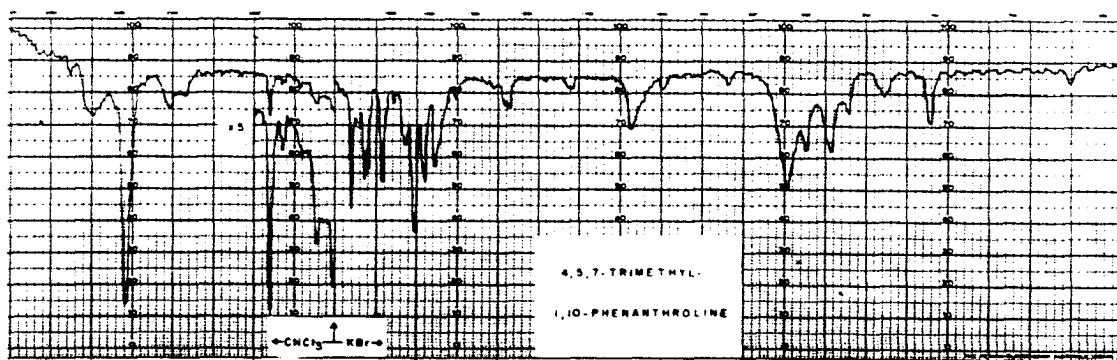
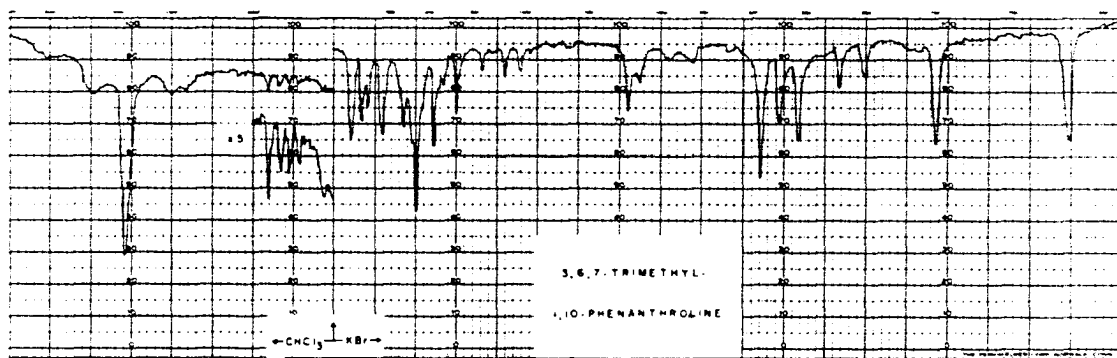
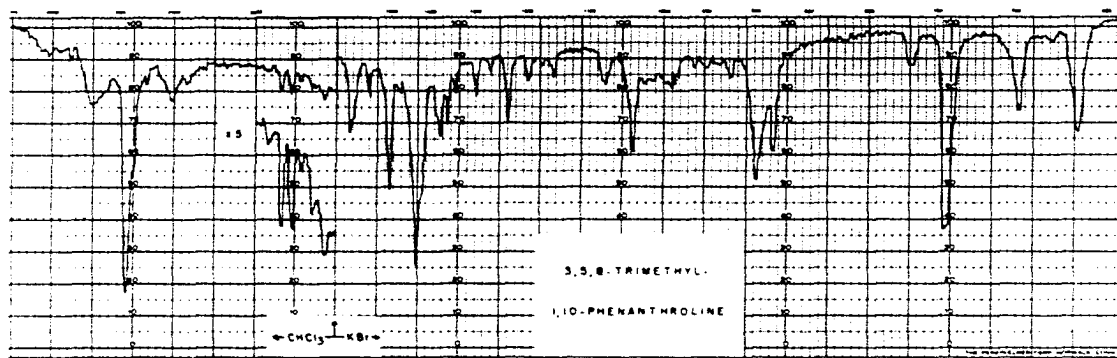
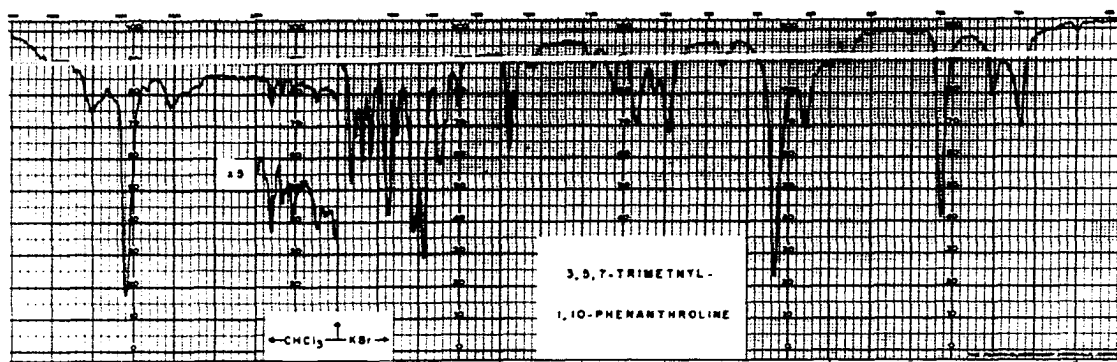


Figure 30. Infrared spectrum of 2,3,8,9-tetramethyl-1,10-phenanthroline

Figure 31. Infrared spectrum of 2,4,7,9-tetramethyl-1,10-phenanthroline

Figure 32. Infrared spectrum of 2,5,6,9-tetramethyl-1,10-phenanthroline

Figure 33. Infrared spectrum of 3,4,6,7-tetramethyl-1,10-phenanthroline

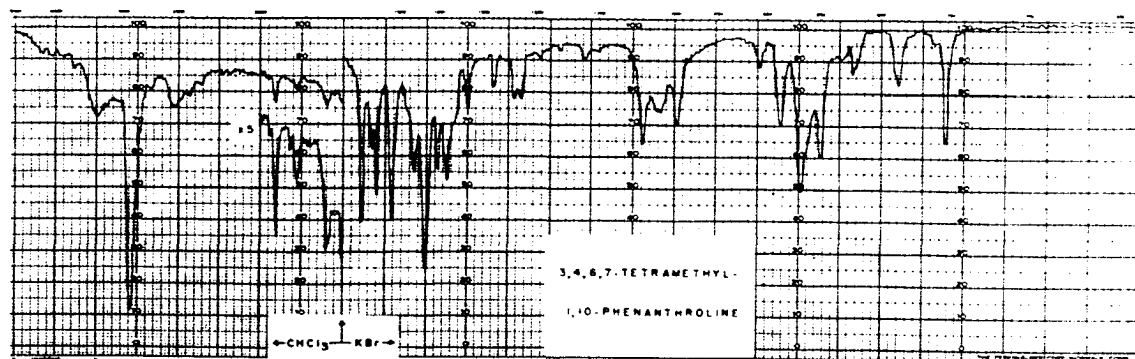
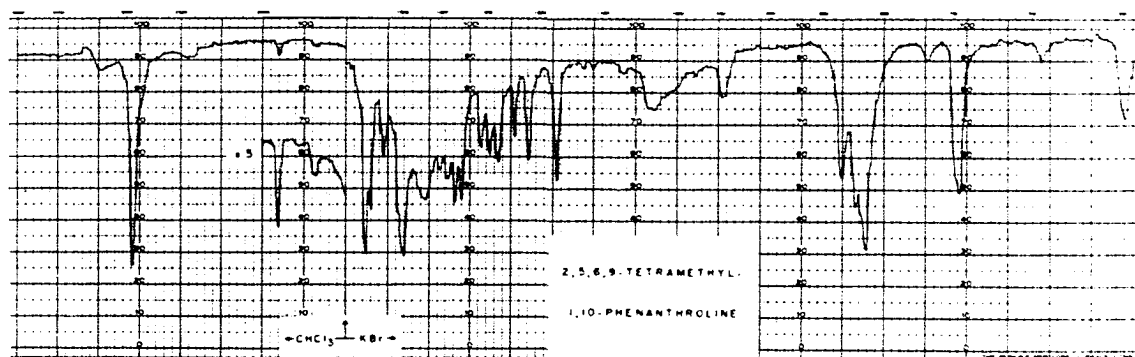
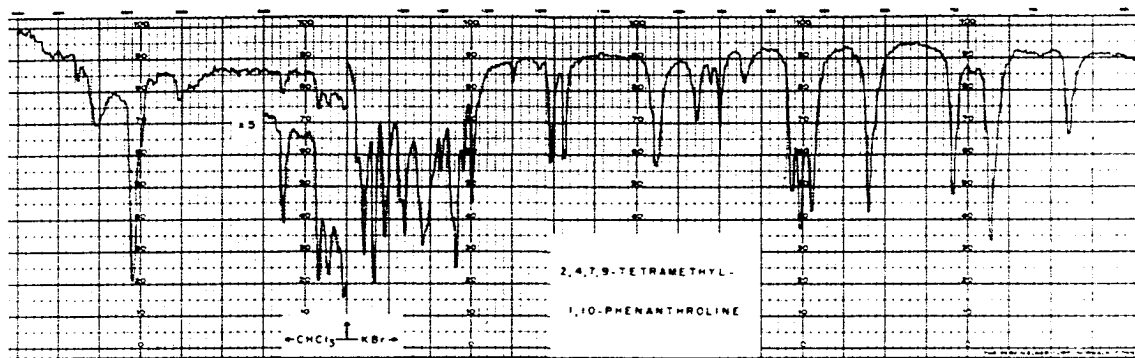
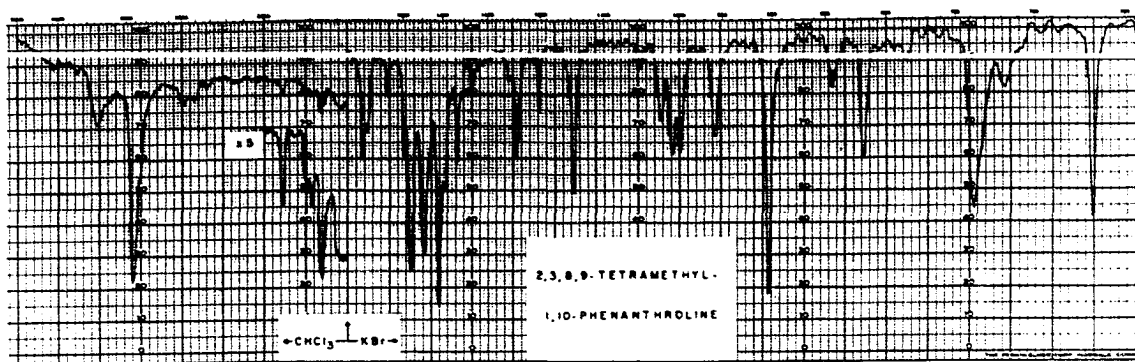
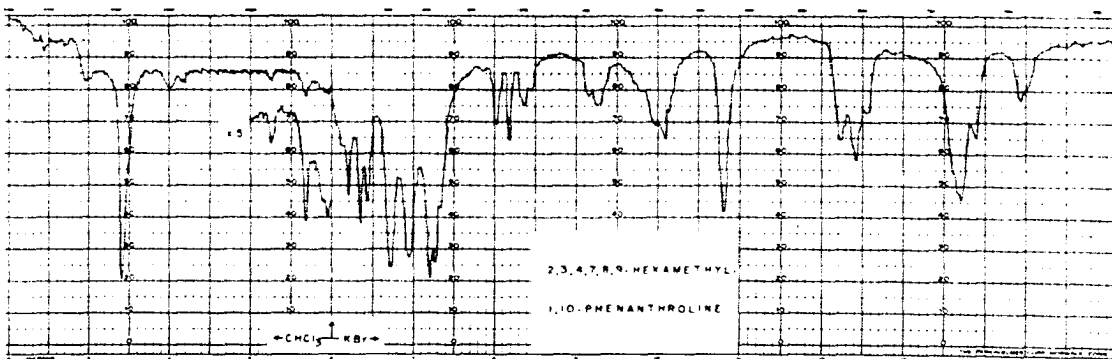
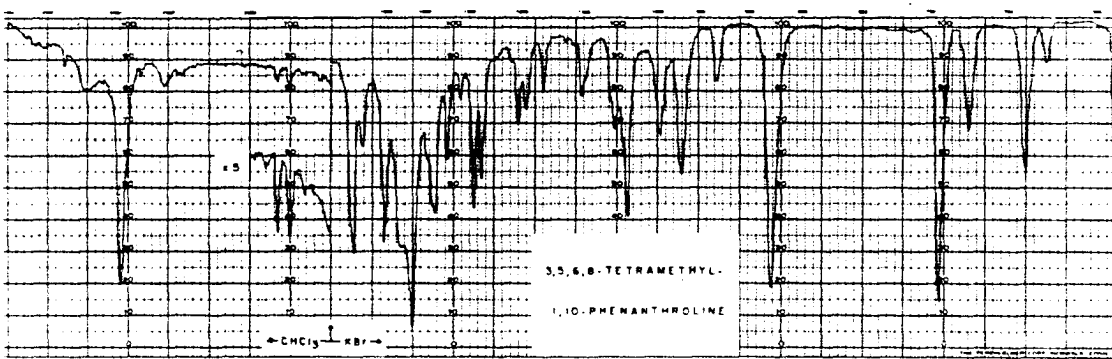
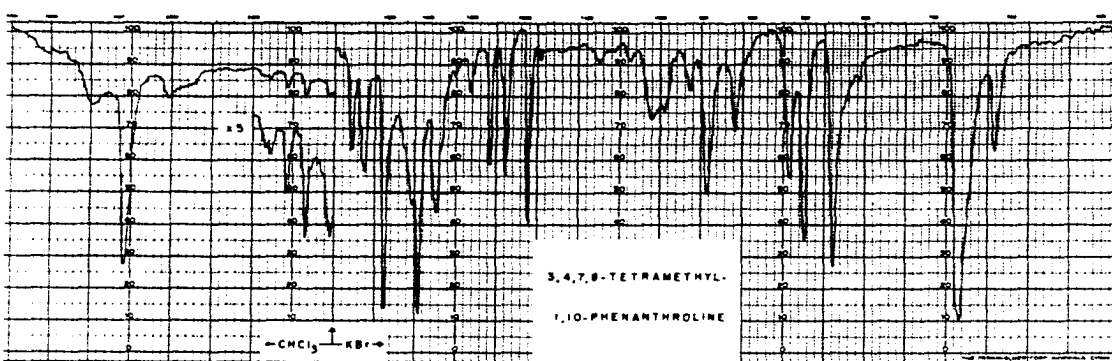
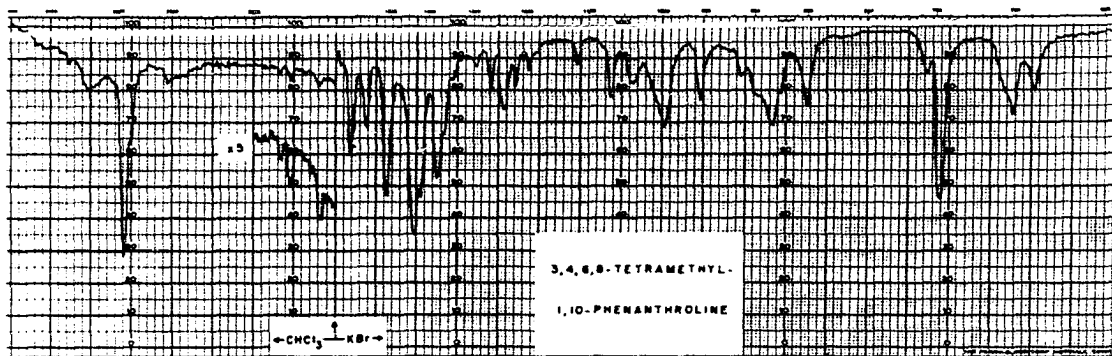


Figure 34. Infrared spectrum of 3,4,6,8-tetramethyl-1,10-phenanthroline

Figure 35. Infrared spectrum of 3,4,7,8-tetramethyl-1,10-phenanthroline

Figure 36. Infrared spectrum of 3,5,6,8-tetramethyl-1,10-phenanthroline

Figure 37. Infrared spectrum of 2,3,4,7,8,9-hexamethyl-1,10-phenanthroline



at 1450 cm^{-1} has been associated with the asymmetrical deformation mode of the hydrogen atoms of the methyl group. Another absorption near 1375 cm^{-1} has been related to the symmetrical deformation mode.

In the potassium bromide spectra of the methyl-1,10-phenanthrolines, the asymmetric deformation band of the methyl group is observed in the $1449\text{-}1431\text{ cm}^{-1}$ range. This absorption appears as a shoulder on the high frequency side of the third strong ring vibration (band C in 1,10-phenanthroline at 1416 cm^{-1}) in the majority of the spectra of the mono- and disubstituted compounds. In some instances this peak is quite intense, as in the spectra of 2-methyl-, 2,9-dimethyl-, 3,6-dimethyl-, and 4,6-dimethyl-1,10-phenanthroline in Figures 6, 11, 14, and 18 respectively, for example. In general the asymmetric deformation band is found to be very intense with the tri-, tetra-, and hexasubstituted methyl compounds. The appearance of only a shoulder or a weak band in these higher substituted methyl derivatives is observed in several instances, as in the spectra of 2,3,4-trimethyl-, 3,4,7-trimethyl-, 3,4,8-trimethyl-, 3,6,7-trimethyl-, 2,5,6,9-tetramethyl-, and 3,4,7,8-tetramethyl-1,10-phenanthroline, recorded in Figures 21, 23, 24, 28, 32, and 35, respectively. In the spectra of methyl derivatives with substitution in the 5,6-positions (5,6-dimethyl-, 3,5,6-trimethyl-, and 3,5,6,8-tetramethyl-1,10-phenanthroline), this asymmetric deformation

absorption occurs at higher frequencies than generally observed in the $1449\text{--}1451\text{ cm}^{-1}$ range noted above. These peaks are still within the frequency range of $1450 \pm 20\text{ cm}^{-1}$ reported by Bellamy (1) for the asymmetric deformation vibration of the methyl group. In the 5,6-dimethyl-1,10-phenanthroline spectrum, the peak at 1451 cm^{-1} is very weak and poorly defined. The peak at 1471 cm^{-1} in 3,5,6-trimethyl-1,10-phenanthroline is weak but is sharp, and the absorption in the 3,5,6,8-tetramethyl-1,10-phenanthroline spectrum appears only as a poorly defined shoulder at 1458 cm^{-1} . The 2,5,6,9-tetramethyl-1,10-phenanthroline spectrum is an exception for the 5,6-substituted methyl derivatives in that the absorption with this compound is at 1437 cm^{-1} which is within the general range given before for the majority of the methyl-1,10-phenanthrolines. The symmetrical deformation mode for the methyl group was reported by Bellamy (1) in the $1385\text{--}1370\text{ cm}^{-1}$ range and is observed in the spectra of the methyl-1,10-phenanthrolines in the $1385\text{--}1366\text{ cm}^{-1}$ region as a medium intensity absorption in most cases. The strong ring vibration at 1416 cm^{-1} (band C) in 1,10-phenanthroline does not in any case interfere with the observation of this peak. Therefore, this absorption would appear to be much more useful in the verification of the presence of the methyl group than was the asymmetric band at higher frequency. A similar peak in this region is found with substituted 1,10-phenanthrolines containing other sub-

stituents, thus the appearance of this absorption is not positive proof of methyl substitution.

The 2,3,4-trimethyl-1,10-phenanthroline spectrum is unique. In contrast to other methyl compounds its spectrum contains an intense, sharp absorption at 1656 cm^{-1} . The spectra of 3,6-dimethyl- and 3,4,6,8-tetramethyl-1,10-phenanthroline display a very weak absorption at 1647 cm^{-1} . These three derivatives are the only methyl compounds which have absorption in this vicinity. This peak did not appear, however, in the spectra of any of the three compounds dissolved in chloroform.

In spectra of 5,6-substituted methyl compounds, the first component of the triplet absorption (band A of 1,10-phenanthroline) was observed at lower frequency than was found with the other methyl derivatives. These absorptions for the first component appear in the $1605\text{--}1595\text{ cm}^{-1}$ range with 5,6-substituted compounds compared to the $1623\text{--}1608\text{ cm}^{-1}$ region for the other methyl derivatives. This shift to lower frequency with substitution in the 5,6-positions is correlated to 5,6-substituted derivatives of 1,10-phenanthroline in Table 19 in Section V, C.

In spectra of ten methyl derivatives, an extra absorption appears in the $1610\text{--}1592\text{ cm}^{-1}$ range between the first and sec-

ond component of the usual triplet absorption (band A of 1,10-phenanthroline). This absorption is of medium intensity many times, and in some cases appears only as a weak shoulder or inflection. This peak is observed in the spectra of 2-methyl-, 3,4-dimethyl-, 3,5-dimethyl-, 3,6-dimethyl-, 4,5-dimethyl-, 3,5,7-trimethyl-, 3,5,8-trimethyl-, 4,5,7-trimethyl-, 2,3,8,9-tetramethyl-, and 3,4,7,8-tetramethyl-1,10-phenanthroline. This extra absorption appears also with other types of substituents, but not necessarily with substitution in the same positions as above with methyl compounds.

With methyl substitution in the 3,8-positions, the second component of the triplet absorption (band A of 1,10-phenanthroline) is absent. This peak appears at 1587 cm^{-1} in the 1,10-phenanthroline spectrum and in the $1592\text{--}1572\text{ cm}^{-1}$ range in spectra of other methyl substituted compounds. This observation is consistent for seven of the eight methyl derivatives substituted in the 3,8-positions as noted later in Table 21 in section V, C. The spectrum of 2,3,4,7,8,9-hexamethyl-1,10-phenanthroline contains a strong peak at 1575 cm^{-1} and is the only exception. Other methyl derivatives in which this absorption is absent or present only as a weak shoulder are found. In the spectrum of 3,4,6-trimethyl-1,10-phenanthroline, only a weak shoulder is detected at 1580 cm^{-1} . In the spectra of 5,6-substituted compounds, this band appears as a weak shoulder or is absent. Shoulders are noted at 1582 cm^{-1} and

1587 cm^{-1} in the spectra of 5,6-dimethyl- and 2,5,6,9-tetramethyl-1,10-phenanthroline respectively. With 3,5,6-trimethyl-1,10-phenanthroline, this peak is absent. It was possible that the first component of the triplet absorption (band A), which in the discussion above was noted to shift to lower frequency in 5,6-substituted compounds, had masked this vibration, and for this reason the peak was not observed in these above 5,6-substituted compounds. The absence of the second peak of the triplet absorptions occurs also with 3,8-substituted 1,10-phenanthrolines with other substituents. The correlation of the disappearance of this peak to the presence of 3,8-substitution will be discussed in detail in section V, C.

In the majority of the methyl derivatives (nine exceptions listed below) splitting of the second ring vibration (band B of 1,10-phenanthroline) occurs. In some cases the peaks appear as a strong doublet absorption, but in most instances the second peak at lower frequency is a shoulder of weak to medium intensity found in the 1497-1471 cm^{-1} range. In some instances only a weak shoulder or inflection is detected. The intense ring vibration absorption (band B of 1,10-phenanthroline) occurs between 1522-1488 cm^{-1} and in some cases is of less intensity than the "new" peak. The methyl derivatives which do not have this extra peak associated with the second ring vibration in their spectra are:

3,4-dimethyl-, 3,8-dimethyl-, 4,7-dimethyl-, 2,5,6,9-tetramethyl-, 3,4,6,7-tetramethyl-, 3,4,6,8-tetramethyl-, 3,4,7,8-tetramethyl-, and 2,3,4,7,8,9-hexamethyl-1,10-phenanthroline. The 3,6,7-trimethyl-1,10-phenanthroline spectrum does have an extra peak present in this region, but it appears at a lower frequency (1458 cm^{-1}) and seems to be associated with the third ring vibration absorption at 1437 cm^{-1} . In spectra of derivatives with other substituents, a similar extra peak appears in this region. This occurrence will be discussed further in section V, C as a possible correlation for characterization purposes.

This second ring vibration absorption (band B of 1,10-phenanthroline) is shifted 13 cm^{-1} or more from 1502 cm^{-1} , as found in the 1,10-phenanthroline spectrum, to higher frequencies with certain methyl substituted compounds. This strong peak appears in the $1522\text{-}1515\text{ cm}^{-1}$ range with 3,7-dimethyl-4,5-dimethyl-, 4,6-dimethyl-, 3,4,7-trimethyl-, 3,6,7-trimethyl-, 4,5,7-trimethyl-, and 3,4,6,7-tetramethyl-1,10-phenanthroline. Here in each case the substitution is in the 3,7-, 4,5-, and 4,6-positions. This trend will be noted later in Section V, C as a possible correlation for these types of substitution. In the spectra of other methyl derivatives as 5-methyl-, 4,7-dimethyl-, 3,4,6-trimethyl-, 3,4,8-trimethyl-, and 3,4,7,8-tetramethyl-1,10-phenanthroline, shifts to higher frequency are also found, but these were not

as large as with those derivatives noted above.

Randle and Whiffen (50) have discussed the appearance of the methyl rocking frequency near 1042 cm^{-1} in compounds in which the methyl group is attached to an aromatic ring. They reported a band of moderate intensity near this frequency in various methyl substituted benzene compounds. Shindo (54) reported the methyl rocking frequencies for 2-methyl-, 3-methyl-, and 4-methylpyridine at 1042 cm^{-1} , 1041 cm^{-1} , and 1039 cm^{-1} , respectively. Investigation of the spectra of the 32 methyl derivatives of 1,10-phenanthroline revealed that an absorption which possibly was due to this vibration is present in 18 compounds in the $1050\text{-}1036\text{ cm}^{-1}$ range. These bands vary in intensity, sometimes being quite weak and more often being of medium intensity.

2. Infrared spectra of ethyl- and propyl-1,10-phenanthrolines

The frequency ranges reported by Bellamy which were noted above for the methyl group apply to ethyl compounds also. In addition absorptions related to the methylene group (CH_2) are now important, and these bands were also discussed by Bellamy (1). The frequency ranges, which he reported are taken from a series of aliphatic and aromatic hydrocarbons. The methylene group is observed to give two peaks in the C-H stretching region. The first is at 2926 cm^{-1} and is related to the in-phase vibration of the hydrogen atoms of the

methylene group; the second is at 2853 cm^{-1} and is associated with the out-of-phase vibrations of those hydrogen atoms.

The spectra of seven ethyl derivatives and one propyl derivative of 1,10-phenanthroline were obtained and recorded in Figures 38 through 45. The absorptions in the chloroform spectra of the ethyl and propyl derivatives are not resolved too well in this region. Comparison of these spectra with the chloroform spectra of methyl-1,10-phenanthrolines reveal very few differences. A shoulder or inflection appears on the low frequency side of the strong aromatic C-H absorption in both groups of chloroform spectra. Bellamy has indicated that difficulty is sometimes encountered in resolving the separate bands associated with the methyl and methylene groups using sodium chloride optics. When using carbon tetrachloride as the solvent for obtaining spectra and with the potassium bromide disk spectra, more peaks are observed in this region than noted before with the chloroform spectra of the ethyl and propyl compounds. Also these absorptions are much better resolved than found in the carbon tetrachloride and potassium bromide spectra of corresponding methyl derivatives. The tentative assignment of peaks to the methyl and methylene absorptions appears possible using the carbon tetrachloride and potassium bromide spectra of the ethyl and propyl compounds. More definite assignments could probably be made with spectra obtained using lithium fluoride or calcium fluoride optics.

Figure 38. Infrared spectrum of 3-ethyl-1,10-phenanthroline

Figure 39. Infrared spectrum of 4-ethyl-1,10-phenanthroline

Figure 40. Infrared spectrum of 5-ethyl-1,10-phenanthroline

Figure 41. Infrared spectrum of 3,8-diethyl-1,10-phenanthroline

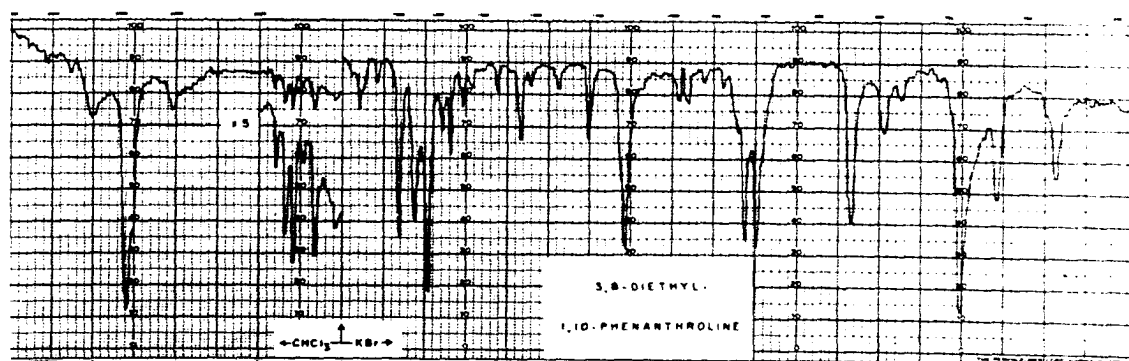
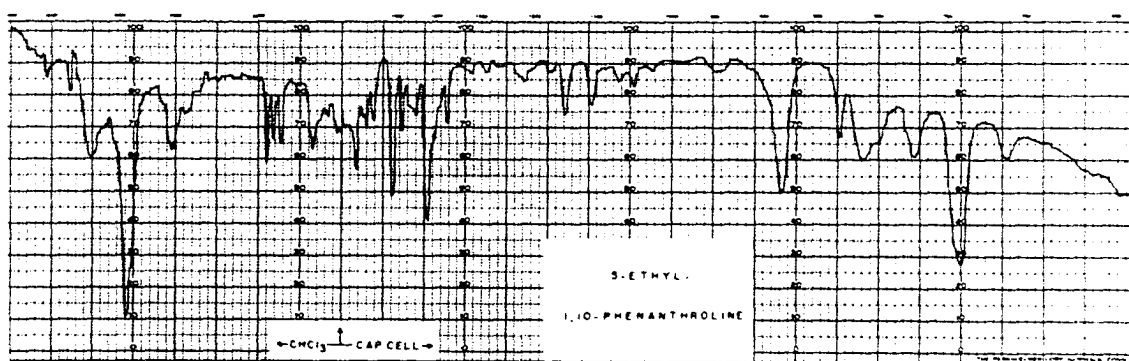
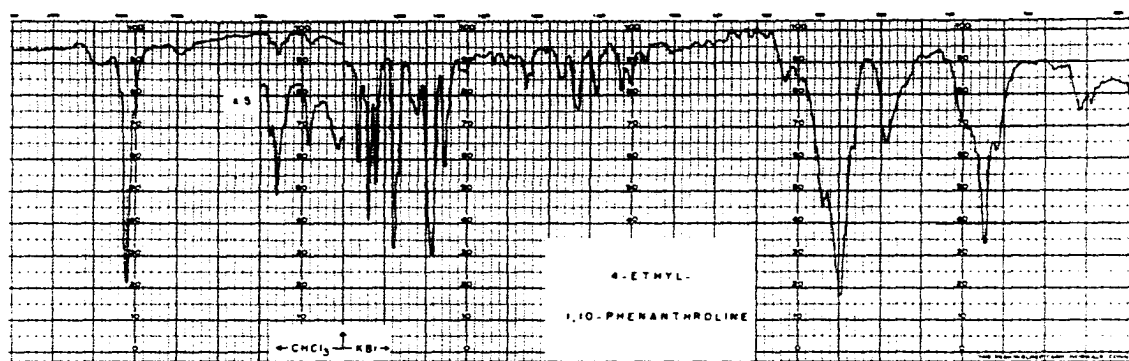
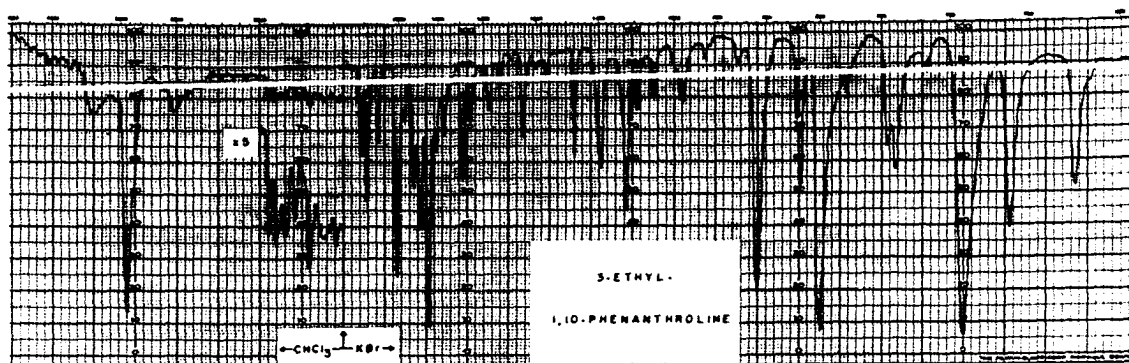
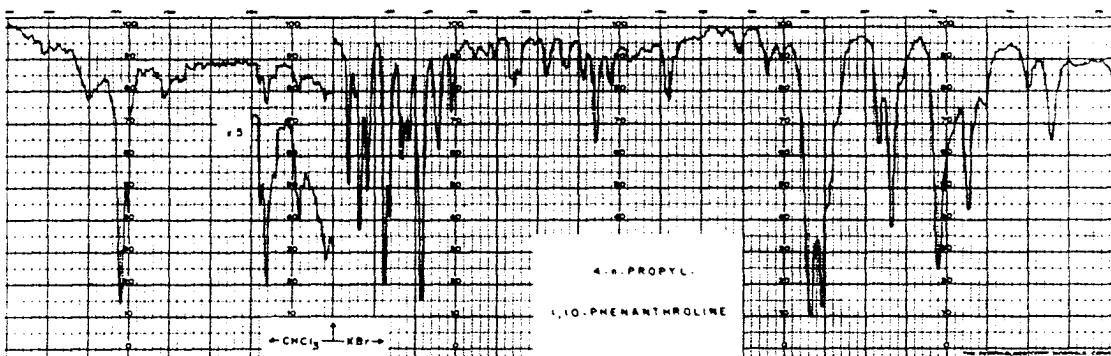
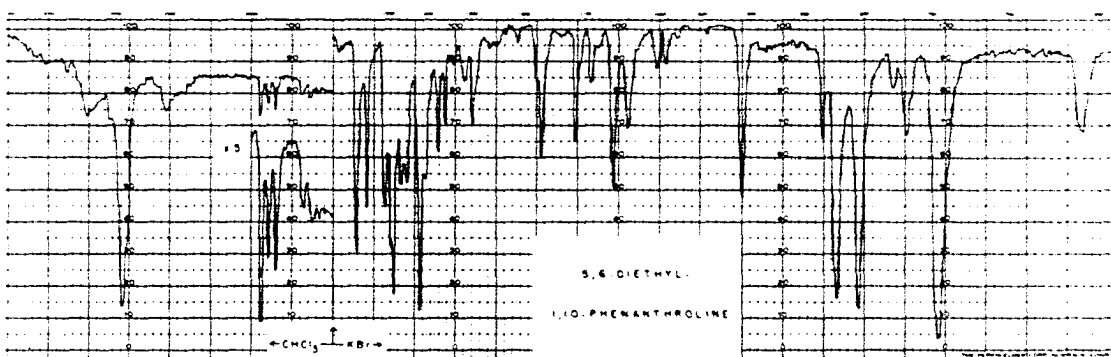
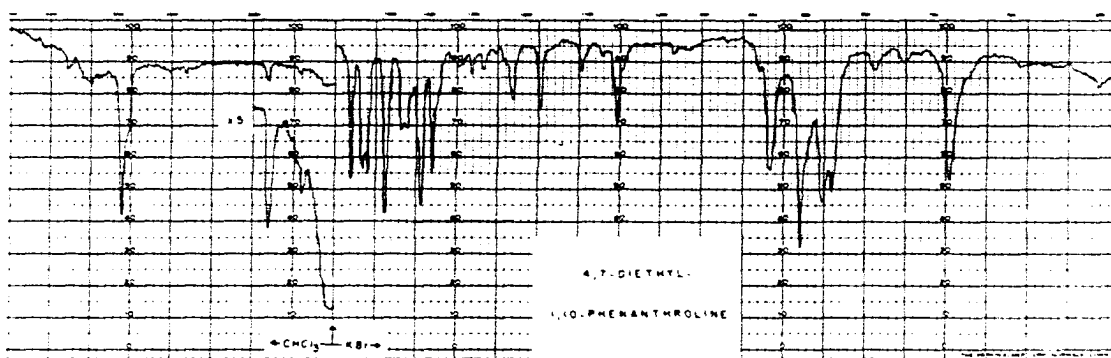
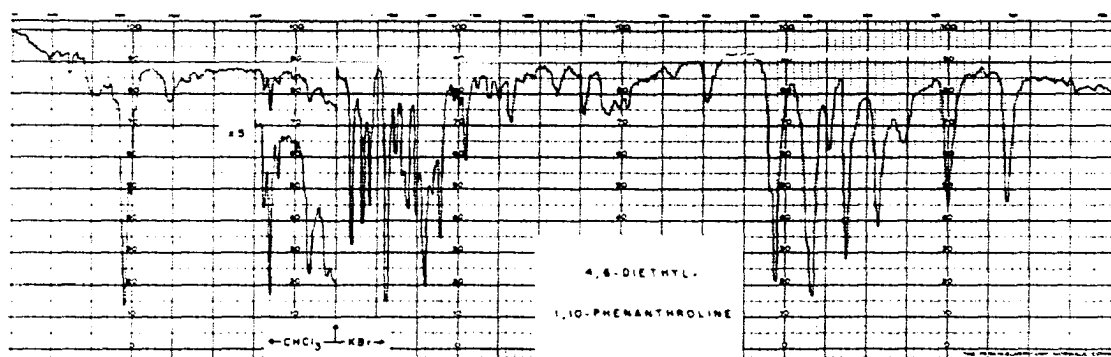


Figure 42. Infrared spectrum of 4,6-diethyl-1,10-phenanthroline

Figure 43. Infrared spectrum of 4,7-diethyl-1,10-phenanthroline

Figure 44. Infrared spectrum of 5,6-diethyl-1,10-phenanthroline

Figure 45. Infrared spectrum of 4-n-propyl-1,10-phenanthroline



The frequencies of absorptions found in this region are given in Table 11. In most instances the peaks noted with the carbon tetrachloride spectra are found at slightly higher frequencies. The asymmetric C-H stretching frequency for the methyl group is observed as a strong peak with these compounds in the $2976\text{--}2959\text{ cm}^{-1}$ range. With the methyl-1,10-phenanthrolines this absorption is not in general noted in the carbon tetrachloride spectra, and the resolution is too poor in most potassium bromide spectra to observe this peak. No absorption which could be assigned to the out-of-phase C-H vibration (at 2853 cm^{-1}) for the methylene group is observed with carbon tetrachloride spectra. In some instances this absorption is noted in the potassium bromide spectra. In most cases the symmetrical C-H vibration (at 2872 cm^{-1}) for the methyl group is not observed in potassium bromide spectra. These two absorptions occur very close together, and when using sodium chloride optics it may not be possible to definitely distinguish between these bands. In the spectra of the ethyl and propyl derivatives the aromatic C-H band is of much less intensity than the asymmetric C-H stretching absorption of the methyl group, and it appeared in most instances as a shoulder or an inflection at the high frequency side of this methyl band.

As discussed before, the methyl and methylene groups have been reported by Bellamy (1) to give absorption near 1460 cm^{-1}

Table 11. The C-H stretching absorptions found in the carbon tetrachloride and potassium bromide spectra of ethyl- and propyl-1,10-phenanthrolines

Compound	Data source	Frequency (cm ⁻¹)				
		Aromatic C-H	Asym. CH ₃ ^a	In-phase CH ₂	Sym. CH ₃ ^b	Out-of-phase CH ₂
	Reported values ^c	3030	2962	2926	2872	2853
3-Ethyl-	CCl ₄ solution spectrum	3021 ^d	2967	2924 ^d	2874 ^d	--
	KBr disk spectrum	3003 ^e	2959	2915 ^e	--	2849 ^d
4-Ethyl-	CCl ₄ solution spectrum	3030 ^d	2967	2933 ^d	2874 ^d	--
	KBr disk spectrum	3030 ^d	2967	--	2882 ^e	--
5-Ethyl-	CCl ₄ solution spectrum	3021 ^d	2967	2933 ^e	2874 ^d	--
	Cap cell spectrum	3030	2959	2924 ^e	--	2857 ^d
3,8-Diethyl-	CCl ₄ solution spectrum	3040 ^e	2967	2941 ^e	2874 ^d	--
	KBr disk spectrum	3012 ^e	2967	2924 ^d	--	2857 ^d
4,6-Diethyl-	CCl ₄ solution-spectrum	3030	2967	2941 ^f	2874	--
	KBr disk spectrum	3012	2967	2933 ^e	2882 ^d	2833 ^d
4,7-Diethyl-	CCl ₄ solution spectrum	3040	2976	2950	2882	--
	KBr disk spectrum	3012 ^d	2967	2941 ^e	2874 ^d	--
5,6-Diethyl-	CCl ₄ solution spectrum	3030 ^e	2976	2941	2882	--
	KBr disk spectrum	3012	2959	--	--	2857 ^d
4-n-Propyl-	CCl ₄ solution spectrum	3030	2959	2941 ^e	2874	--
	KBr disk spectrum	3012 ^d	2959	2924 ^d	2865 ^d	--

^aAsymmetric C-H stretching frequency for the methyl group.

^bSymmetric C-H stretching for the methyl group.

^cAs noted by Bellamy (1).

^dShoulder.

^eInflection only.

which are related to hydrogen bending vibrations. The bands arising from these two groups in the 1460 cm^{-1} region were noted to be too close together to be readily distinguished with most materials. Bellamy also observed that the intensity in this region was proportional to the number of these groups present in the compound being investigated. Individual assignments for each group were made by him, however. The methylene deformation absorption was reported near 1465 cm^{-1} , and the asymmetrical methyl deformation was noted at 1450 cm^{-1} .

Examination of the spectra of the ethyl-1,10-phenanthrolines in the 1460 cm^{-1} region reveals that in most cases the methylene deformation and the methyl asymmetrical deformation absorptions could be differentiated. In some instances the peaks in this region are not resolved, however, and appear only as one weak to medium, broad band. In either case this region is found to be valuable in distinguishing the ethyl and propyl derivatives from the methyl compounds. In the potassium bromide spectra of 3-ethyl-, 3,8-diethyl-4,6-diethyl-, and 5,6-diethyl-1,10-phenanthroline, the methylene deformation absorption is observed in the $1464\text{-}1453\text{ cm}^{-1}$ range, and the methyl asymmetrical deformation absorption in the $1445\text{-}1435\text{ cm}^{-1}$ region. In the spectrum of 4-n-propyl-1,10-phenanthroline, the two sharp peaks are found within the above ranges.

The symmetrical methyl deformation mode was noted earlier

with the methyl-1,10-phenanthrolines to occur in 1385-1366 cm^{-1} range. In the ethyl- and propyl-1,10-phenanthrolines this peak is observed in the 1389-1368 cm^{-1} region.

Several of the general features of absorptions in the 1620-1400 cm^{-1} region found earlier with the methyl derivatives are observed with the ethyl and propyl derivatives also. In the spectrum of 5,6-diethyl-1,10-phenanthroline, the first component of the triplet absorption (band A with 1,10-phenanthroline) is shifted to lower frequency. An extra shoulder is found within the first ring absorption triplet with 5-ethyl-, 3,8-diethyl-, and 4-n-propyl-1,10-phenanthroline. In the 3,8-diethyl-1,10-phenanthroline spectrum, the second component of the triplet absorption is absent. Splitting of the second ring vibration absorption (band B of 1,10-phenanthroline) is observed with five of the ethyl derivatives and with the one propyl derivative. The spectra of 3,8-diethyl- and 4,7-diethyl-1,10-phenanthroline do not contain this extra peak.

C. Halogen Derivatives of 1,10-Phenanthroline

The spectra of one fluoro-, nine chloro-, and nine bromo-1,10-phenanthrolines were obtained and are recorded in Figures 46 through 64. These halogen derivatives have similar spectra. In the ring vibration region at 1620-1400 cm^{-1} and in regions of lower frequency, similar absorptions are found

appearing progressively at slightly lower frequencies on passing from the fluoro-, to the chloro-, and to the bromo-compound. The major differences in these spectra occur in the $900\text{--}650\text{ cm}^{-1}$ region where one or two peaks were of different intensity or were shifted to other frequencies.

Bellamy (1) has reported that the only absorption useful for characterization purposes produced by the halogens in the sodium chloride region are those resulting from the C-X stretching modes.

1. Infrared spectrum of 5-fluoro-1,10-phenanthroline

Bellamy (1) has reported that the C-F stretching absorptions may occur within a broad range, $1400\text{--}1000\text{ cm}^{-1}$. The intensity of this absorption is noted to be exceptionally great. With fluorine substitution, interaction effects are known to be large, and appreciable shifts in adjacent C-H, C=C, and C=O stretching vibration absorptions have been noted. For simple molecules with one fluorine atom present, Bellamy has reported a medium absorption in the $1100\text{--}1000\text{ cm}^{-1}$ range.

The spectrum of 5-fluoro-1,10-phenanthroline is recorded in Figure 46. In examining this spectrum, a strong triplet absorption is observed in the $1090\text{--}1010\text{ cm}^{-1}$ range with the center component at 1055 cm^{-1} which could be assigned to the C-F stretching vibration. In the C=C and C=N stretching ring vibration region at $1620\text{--}1400\text{ cm}^{-1}$, the first component of

Figure 46. Infrared spectrum of 5-fluoro-1,10-phenanthroline

Figure 47. Infrared spectrum of 2-chloro-1,10-phenanthroline

Figure 48. Infrared spectrum of 3-chloro-1,10-phenanthroline

Figure 49. Infrared spectrum of 4-chloro-1,10-phenanthroline

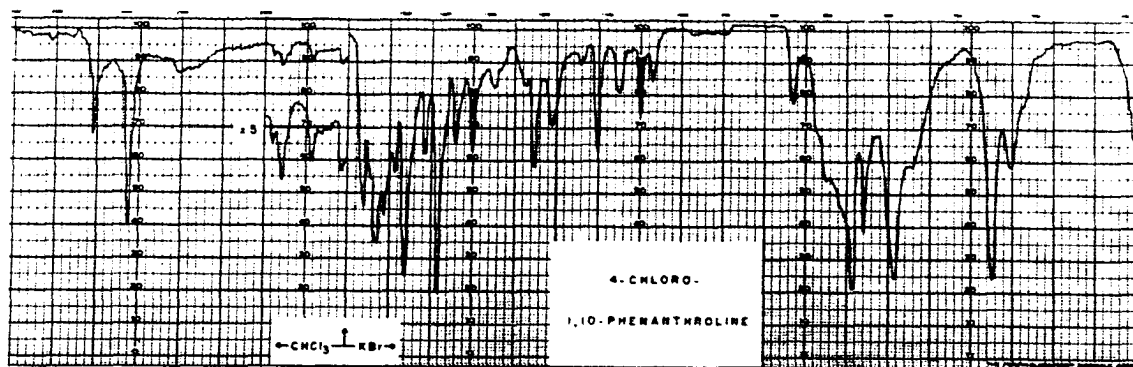
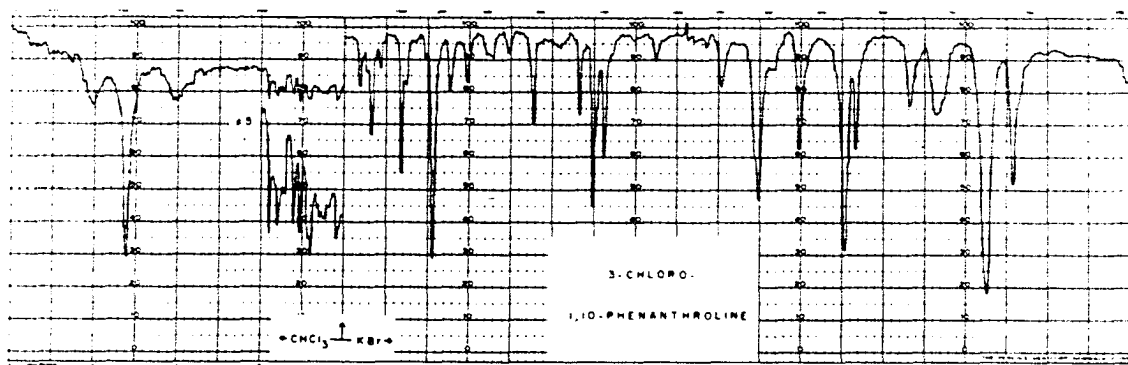
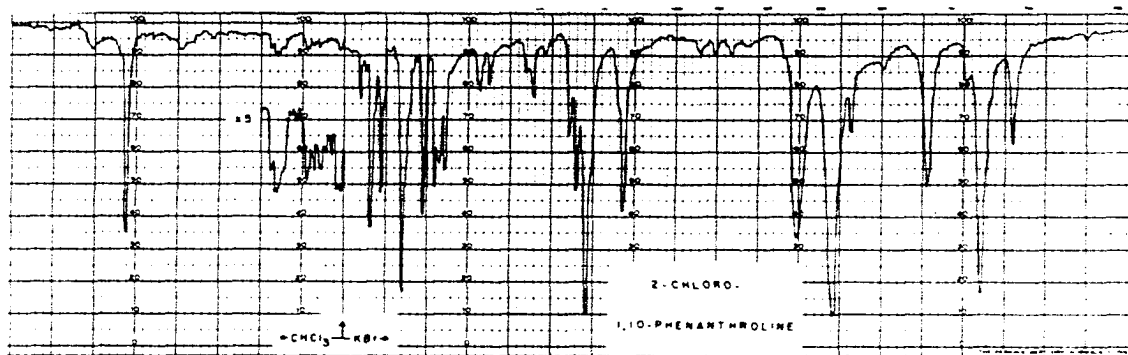
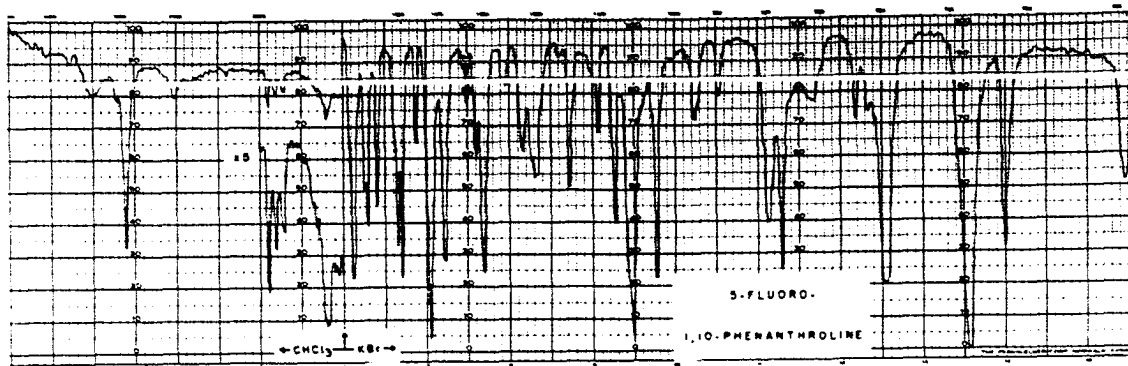


Figure 50. Infrared spectrum of 5-chloro-1,10-phenanthroline

Figure 51. Infrared spectrum of 3,5-dichloro-1,10-phenanthroline

Figure 52. Infrared spectrum of 3,8-dichloro-1,10-phenanthroline

Figure 53. Infrared spectrum of 4,7-dichloro-1,10-phenanthroline

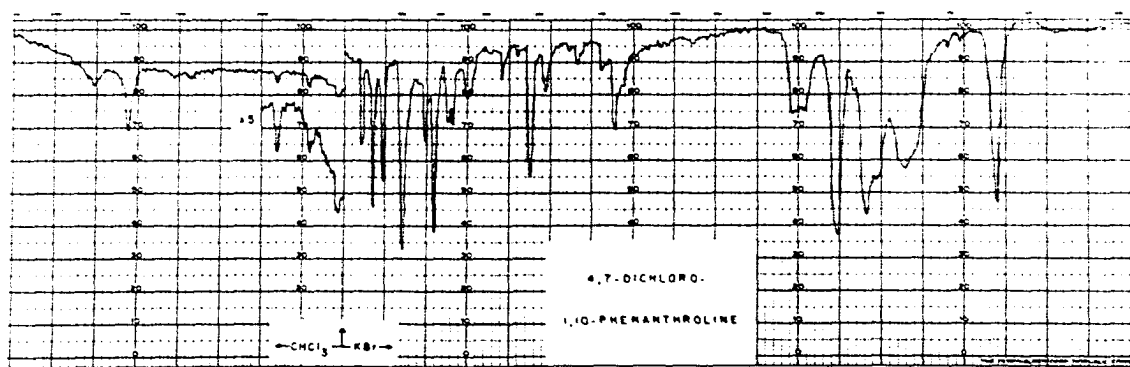
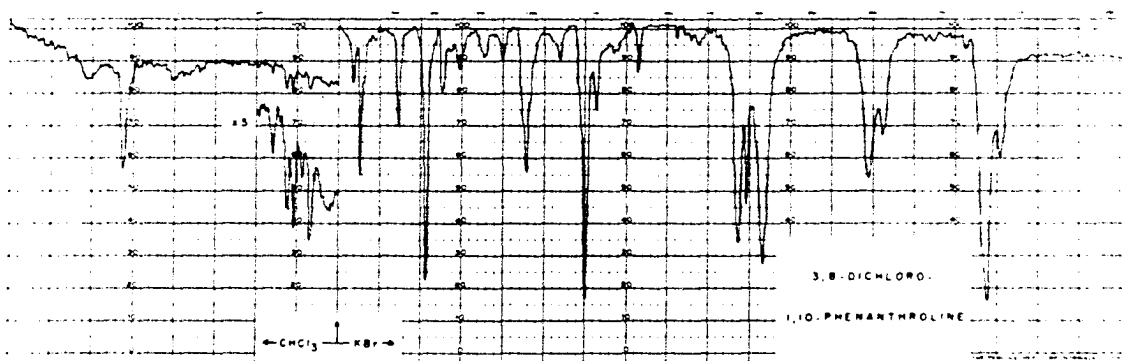
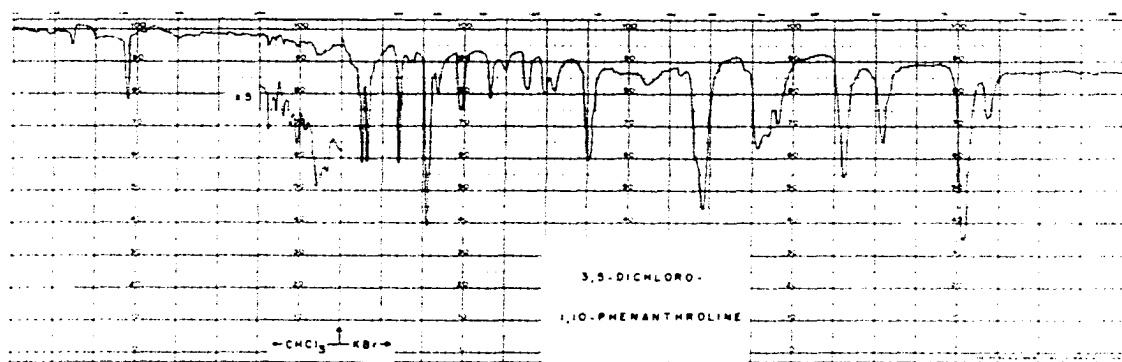
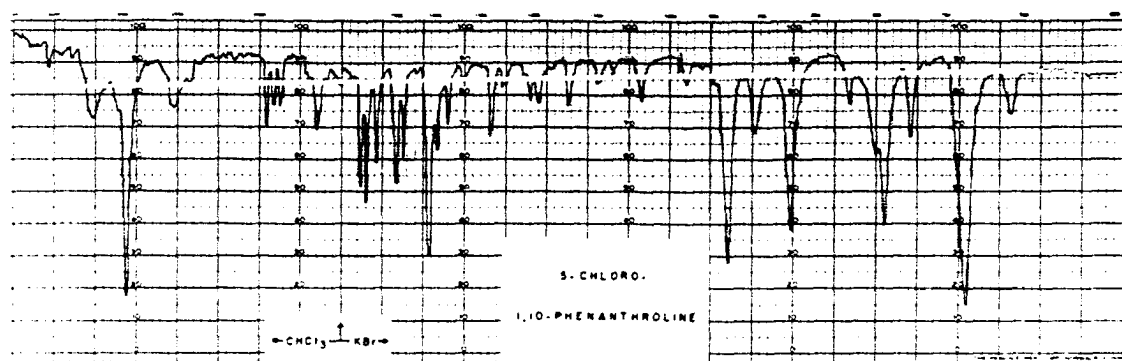


Figure 54. Infrared spectrum of 5,6-dichloro-1,10-phenanthroline

Figure 55. Infrared spectrum of 3,5,6-trichloro-1,10-phenanthroline

Figure 56. Infrared spectrum of 3-bromo-1,10-phenanthroline

Figure 57. Infrared spectrum of 4-bromo-1,10-phenanthroline

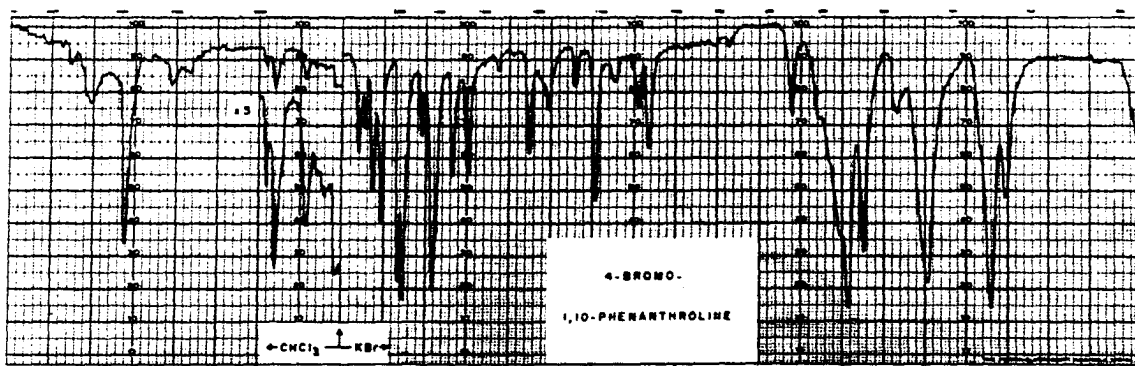
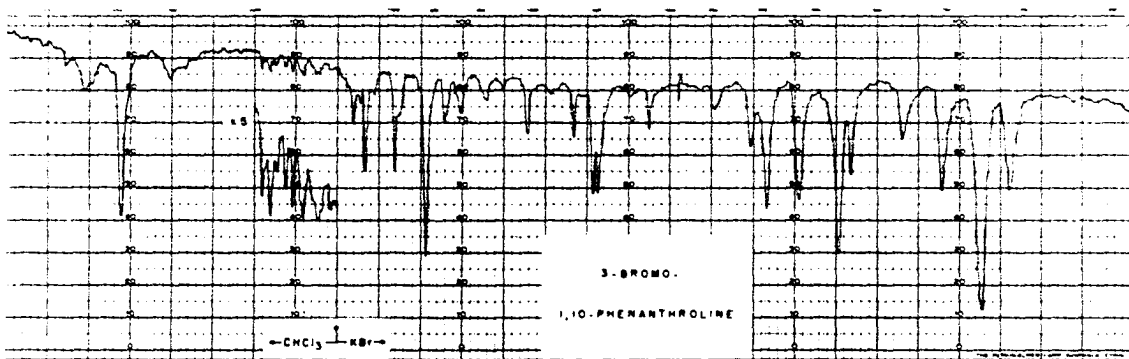
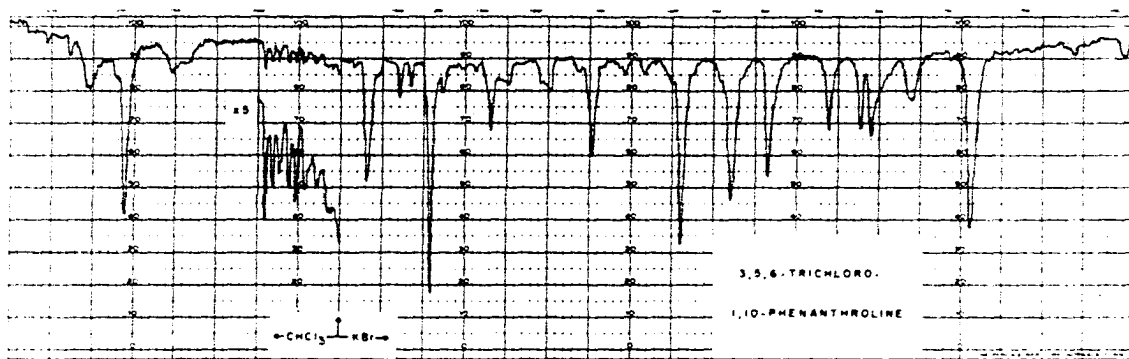
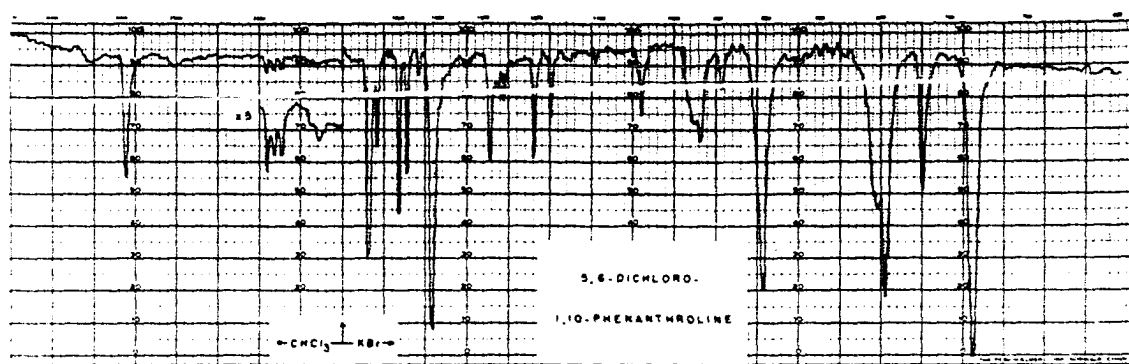


Figure 58. Infrared spectrum of 5-bromo-1,10-phenanthroline

Figure 59. Infrared spectrum of 3,5-dibromo-1,10-phenanthroline

Figure 60. Infrared spectrum of 3,6-dibromo-1,10-phenanthroline

Figure 61. Infrared spectrum of 4,7-dibromo-1,10-phenanthroline

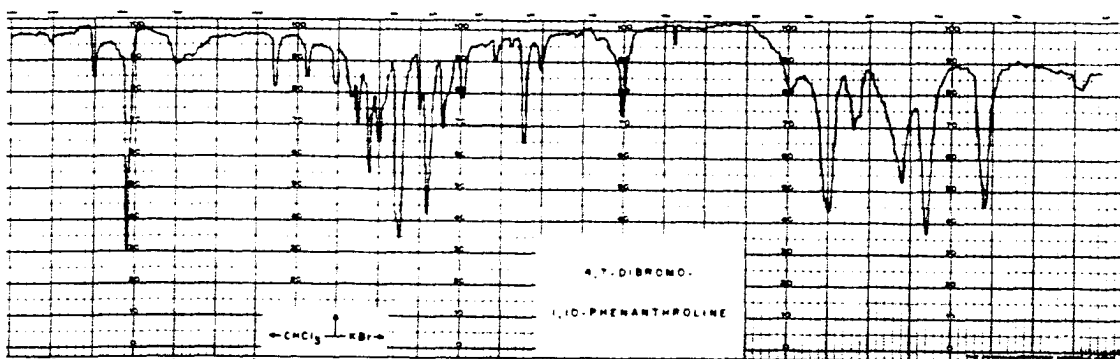
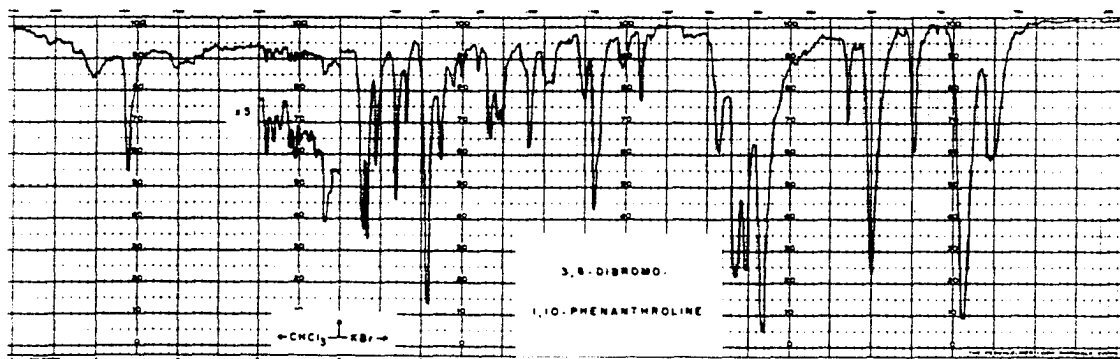
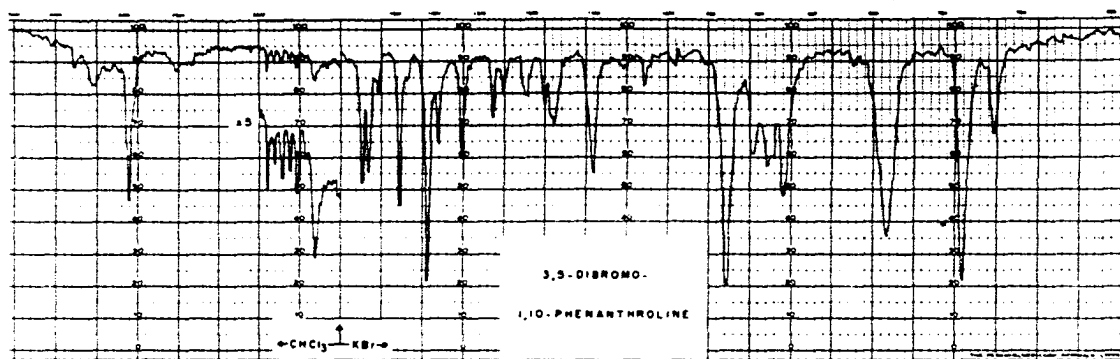
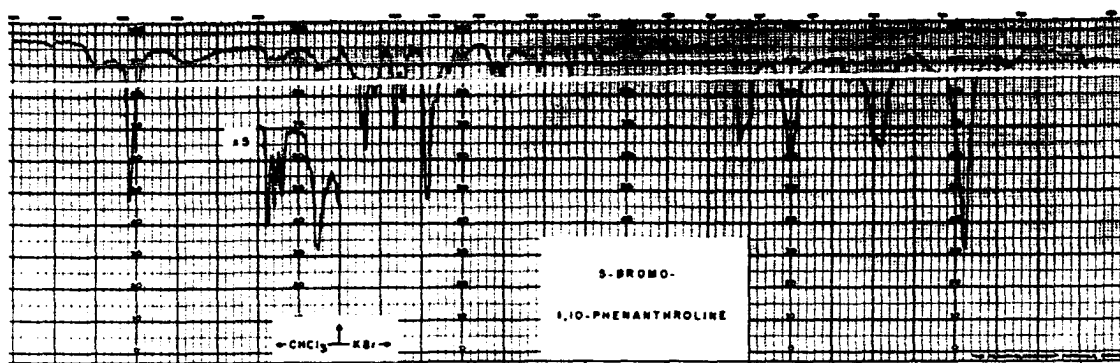
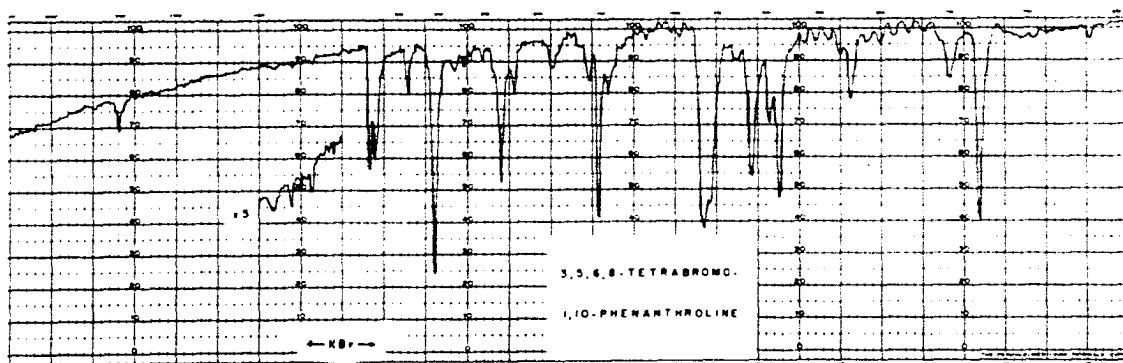
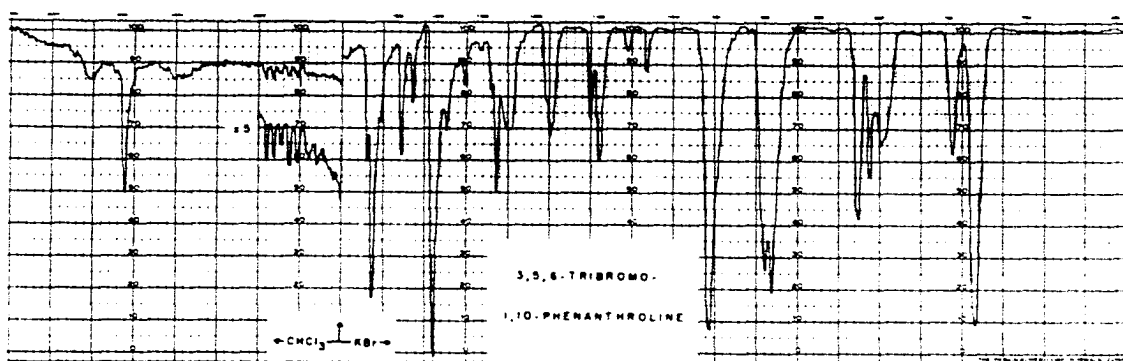
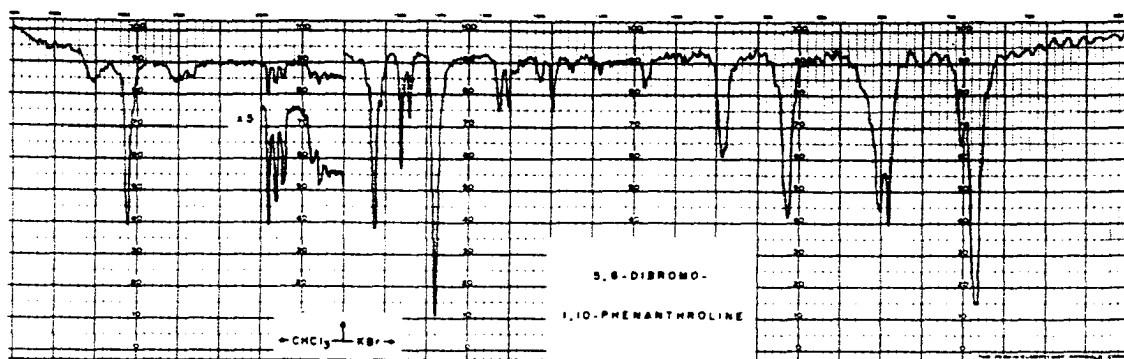


Figure 62. Infrared spectrum of 5,6-dibromo-1,10-phenanthroline

Figure 63. Infrared spectrum of 3,5,6-tribromo-1,10-phenanthroline

Figure 64. Infrared spectrum of 3,5,6,8-tetrabromo-1,10-phenanthroline



the triplet absorption (band A of 1,10-phenanthroline) is observed at a higher frequency (1634 cm^{-1}) than has been noted for any of the other substituted 1,10-phenanthrolines studied. This shift is probably due to the interaction effects accompanying fluoro substitution as was discussed above. The second component of this triplet contains a weak shoulder on the high frequency side which has been noted with other types of substitution before. The second ring vibration absorption (band B of 1,10-phenanthroline) is found to be split into two sharp components. This splitting has been noted before with other types of derivatives.

2. Infrared spectra of chloro-1,10-phenanthrolines

Bellamy (1) has reported a general range of $800\text{-}600\text{ cm}^{-1}$ for the C-Cl stretching absorption. Chlorine substitution reportedly gives interaction effects with groups as C=C and C=O also, but not as pronounced as with fluoro substitution. In compounds with only one chlorine substituted, the C-Cl stretching absorption is reported in a narrower frequency range ($750\text{-}700\text{ cm}^{-1}$) than quoted above.

The spectra for the nine chloro derivatives of 1,10-phenanthroline are recorded in Figures 47 through 55. No appreciable shifts are observed in the C=C and C=N stretching ring vibration region at $1620\text{-}1400\text{ cm}^{-1}$ with the chloro derivatives as noted with the 5-fluoro-1,10-phenanthroline

spectrum. Apparently, the interaction effects with the chloro group present are comparatively small in these compounds. Strong absorptions appear in the spectrum of 1,10-phenanthroline and in nearly all of the substituted derivatives in the $800\text{-}650\text{ cm}^{-1}$ region. Therefore, it is difficult to observe any band due to the C-Cl stretching vibration in this region. No peaks are found in the spectra of the chloro-1,10-phenanthrolines which could be definitely assigned to the C-Cl absorption. The spectra of three chloro derivatives, 5-chloro-, 5,6-dichloro-, and 3,5,6-trichloro-1,10-phenanthroline, contain a medium peak at 774 cm^{-1} , 768 cm^{-1} , and 775 cm^{-1} respectively which did not appear in the spectra of the corresponding bromo-1,10-phenanthrolines. This band did not appear consistently with the other chloro compounds, however. In the 3,5-dichloro-1,10-phenanthroline spectrum, a strong peak at 825 cm^{-1} is observed which is absent in the 3,5-dibromo-1,10-phenanthroline spectrum.

In the 5,6-dichloro- and 3,5,6-trichloro-1,10-phenanthroline spectra, the first component of the ring vibration triplet absorption (band A of 1,10-phenanthroline) is absent and not just shifted to lower frequency as noted earlier with other types of 5,6-substituted derivatives. In the 3,5-dichloro-1,10-phenanthroline spectrum only two strong peaks are observed rather than the usual triplet. The first

of these two bands (at 1597 cm^{-1}) appears at lower frequency than is generally found. In the spectra of four chloro compounds, a strong absorption (with 3,8-dichloro-1,10-phenanthroline) to weak shoulder (with 2-chloro-, 3-chloro-, and 4-chloro-1,10-phenanthroline) is found in the $1608\text{--}1592\text{ cm}^{-1}$ range between the first and second components of the first ring vibration triplet absorption. In the 3,8-dichloro-1,10-phenanthroline spectrum, the second component (at 1582 cm^{-1}) of this triplet appears as a weak shoulder. This peak has been noted before to be absent with other 3,8-substituted derivatives. Splitting of the second ring vibration absorption (band B of 1,10-phenanthroline) is observed with five of the nine chloro derivatives. The extra peak occurs on the low frequency side of the second ring vibration absorption. It appears as a weak shoulder in the spectra of 3-chloro- and 3,5-dichloro-1,10-phenanthroline, and as a strong doublet with this ring vibration absorption in the 5-chloro-, 5,6-dichloro-, and 3,5,6-trichloro-1,10-phenanthroline spectra. The spectra of 2-chloro-, 4-chloro-, 3,8-dichloro-, and 4,7-dichloro-1,10-phenanthroline do not contain an extra peak in this region. A weak band at 1522 cm^{-1} is observed in the 4-chloro-1,10-phenanthroline spectrum on the low frequency side of the triplet absorption (band A of 1,10-phenanthroline) and seems to be associated with these peaks rather than the strong second ring vibration absorption (band B of 1,10-phen-

anthroline). The spectrum of 4,7-dichloro-1,10-phenanthroline contains a medium shoulder at 1433 cm^{-1} on the high frequency side of the third strong ring vibration absorption at 1410 cm^{-1} .

3. Infrared spectra of bromo-1,10-phenanthrolines

Bellamy (1) has reported a range of $600\text{--}500\text{ cm}^{-1}$ for the C-Br absorption for simple molecules. He indicated that the C-Br absorption was difficult to observe unless several bromine atoms were substituted giving a greater intensity for this absorption.

The spectra of nine bromo-1,10-phenanthrolines are recorded in Figures 56 through 64. Using sodium chloride optics, absorptions in the region below 650 cm^{-1} could not be obtained, therefore, peaks associated with the C-Br stretching vibration were not observed in any of these bromo-1,10-phenanthrolines. The spectra of the bromo derivatives are very similar to that of the correspondingly substituted chloro compounds. In general, the peaks with bromo-1,10-phenanthrolines are at slightly lower frequencies. The usual shift of the first component of the triplet absorption (band A of 1,10-phenanthroline) to lower frequency is observed in the spectra of the 5,6-dibromo-, 3,5,6-tribromo-, and 3,5,6,8-tetrabromo-1,10-phenanthrolines. Shoulders at 1592 cm^{-1} and 1582 cm^{-1} are found in the 5,6-dibromo- and 3,5,6-

tribromo-1,10-phenanthroline spectra respectively, where in the spectra of the corresponding chloro derivatives, this first peak is absent. In the 3,5-dibromo- and 3,6-dibromo-1,10-phenanthroline spectra the first peak in the triplet absorption occurs at lower frequency (at 1595 cm^{-1} and 1592 cm^{-1} respectively) than generally noted with derivatives substituted in these positions. In the 3,5,6,8-tetrabromo-1,10-phenanthroline spectrum, the second component of the triplet absorption (band A of 1,10-phenanthroline), which usually was missing for 3,8-substituted derivatives, is present as a strong band. The 3-bromo-, 4-bromo-, and 4,7-dibromo-1,10-phenanthroline spectra all contain an extra peak in the $1603\text{--}1592\text{ cm}^{-1}$ range between the first and second component of the triplet absorption. Splitting of the second ring vibration (band B of 1,10-phenanthroline) is observed for seven of the nine bromo derivatives. This peak, which is on the low frequency side of the strong ring vibration absorption, appears as a weak shoulder in the 3-bromo- and 3,5-dibromo-1,10-phenanthroline spectra and as a medium to strong band in the 4-bromo-, 5-bromo-, 3,6-dibromo-, 5,6-dibromo-, and 3,5,6-tribromo-1,10-phenanthroline spectra. A weak shoulder appears on the high frequency side of the third strong ring vibration absorption (band C of 1,10-phenanthroline) in the 4,7-dibromo-1,10-phenanthroline spectrum. The spectra of 3,5,6,8-tetrabromo-1,10-phenanthroline does not

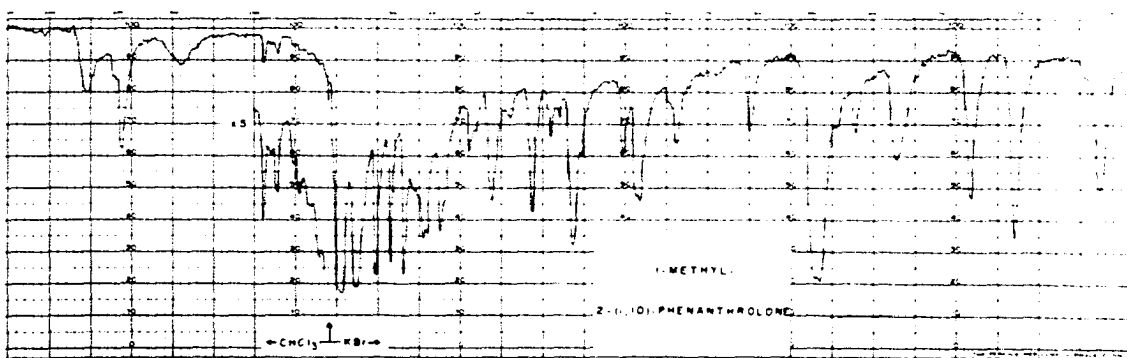
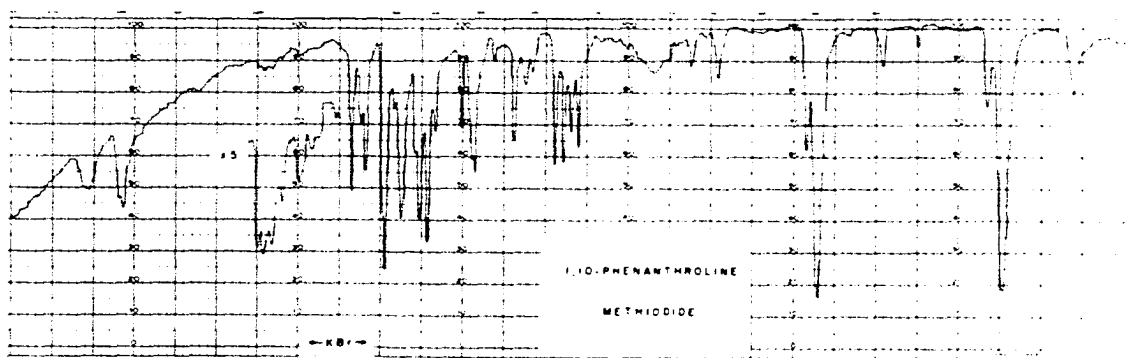
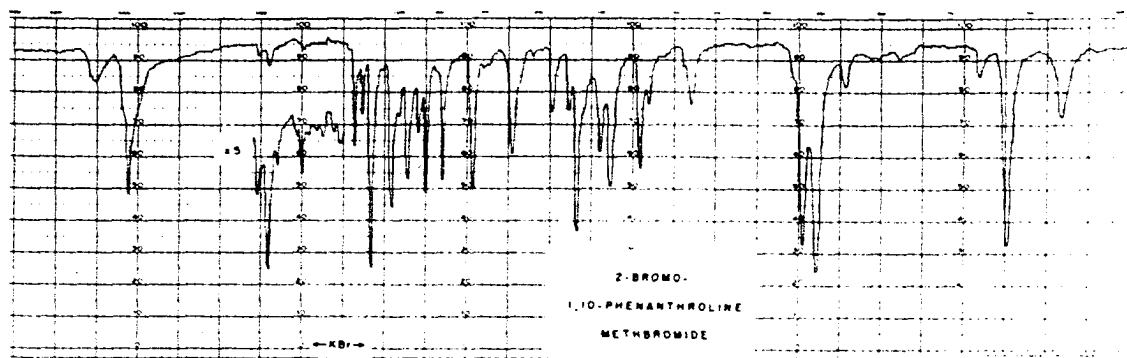
contain any extra peak in this region, and the second ring absorption is shifted to a much lower frequency (1471 cm^{-1}) with this derivative.

An attempt to prepare 2-bromo-1,10-phenanthroline was noted in section II, B. An unidentified dibromo product was obtained, however. Unusual solubility properties are noted for this material in that it does not dissolve readily in chloroform as do the majority of the 1,10-phenanthrolines which were investigated. Instead the solid obtained dissolves easily in water which suggests the possibility of a salt like compound and not a free base derivative of 1,10-phenanthroline. In this respect the material is similar to 1,10-phenanthroline methiodide which is water soluble and only slightly soluble in chloroform. As noted earlier, the elemental analysis of the dibromo material indicated the continued presence of a methyl group bonded to one nitrogen of the 1,10-phenanthroline ring as found in the starting material, 1-methyl-2-(1,10)-phenanthrolone. The investigation of the infrared spectrum of the dibromo material in Figure 65 reveals that shifts to higher frequency, which are recorded in Table 12, of the C=C and C=N ring vibration absorptions occur, and these shifts are comparable to those noted with the acid salts in section III, A (see Table 9). Also the spectrum of the dibromo material is very similar to that of 1,10-phenanthroline methiodide in the $1630\text{-}1400\text{ cm}^{-1}$

Figure 65. Infrared spectrum of 2-bromo-1,10-phenanthroline methbromide

Figure 66. Infrared spectrum of 1,10-phenanthroline methiodide

Figure 67. Infrared spectrum of 1-methyl-2-(1,10)-phenanthrolone



region (see Figure 66 for the spectrum of the latter material). In Table 12 the shifts noted for the methiodide salt are observed to be quite similar to those noted with this dibromo product. Both the unidentified dibromo material and 1,10-phenanthroline methiodide do not form a colored complex with ferrous iron. From these observations, the material synthesized apparently is 2-bromo-1,10-phenanthroline methbromide.

Table 12. Absorptions in the $1630\text{--}1400\text{ cm}^{-1}$ region from spectra of the dibromo product obtained in the attempted synthesis of 2-bromo-1,10-phenanthroline

Compound	Frequency (cm^{-1}) ^a				
	A ^b (triplet)			B	C
1,10-Phenanthroline ^c	1616	1587	1558	1502	1416
Dibromo product	1629	1603	1577	1520	1475
Δv (cm^{-1}) ^d	13	16	29	18	59
1,10-Phenanthroline methiodide	1626	1597	1580	1527	1479
Δv (cm^{-1}) ^d	10	10	22	25	63

^aFrom potassium bromide disk spectra.

^bThe letters A, B, and C designate the three strong absorptions in this region.

^cAnhydrous material.

^dShifts are calculated from frequencies of 1,10-phenanthroline.

If the methyl group is present at the number one position in 1,10-phenanthroline, as assumed with this dibromo product, it is possible that an absorption related to the deformation vibration of the methyl group attached to a nitrogen atom could be located. Bellamy (1) has reported that this absorption in simple molecules is found in the 1460-1430 cm^{-1} region, whereas the C-CH₃ symmetrical deformation is observed at 1375 cm^{-1} . Many complex materials are noted to absorb near 1430 cm^{-1} , but with other compounds the band could not be distinguished from the many C-H deformation vibrations in this region. Also, he has reported that in spectrum of several nitrogen containing compounds, weak absorption in the 1430-1400 cm^{-1} region are found. Bellamy has concluded that the absorption due to the N-CH₃ vibration is too weak and variable to be useful for correlation purposes.

Examination of the spectra of 1,10-phenanthroline compounds with the methyl group at the number one position (see Figures 65, 66, and 67) does not give any conclusive information for the detection of the N-CH₃ vibration band. Since the 1,10-phenanthroline spectrum contains several bands in the region of interest, the correlation noted by Bellamy is rendered even less useful here.

Case (10) reported the synthesis of 3,8-dibromo-1,10-phenanthroline and supplied our laboratory with several

samples of the material in various degrees of purity. The infrared spectra of all the samples are exactly the same. However, close inspection of the $2000\text{--}1667\text{ cm}^{-1}$ region of the chloroform solution spectrum reveals that the material is apparently not a 3,8-disubstituted 1,10-phenanthroline but was a 3,5-disubstituted derivative (see section V, B, for a detailed discussion on the use of this region in the determination of substitution type in 1,10-phenanthrolines). The potassium bromide disk spectra of 3,5-dibromo-1,10-phenanthroline and the above "3,8-dibromo" compound are found to be identical. A mixed melting point also indicated that the two above materials are the same as noted in Table 13.

Table 13. Mixed melting point of the reported 3,5-dibromo- and 3,8-dibromo-1,10-phenanthrolines

Compound	<u>Melting point</u>	
	Reported (10)	Observed
3,5-Dibromo-1,10-phenanthroline	225-226 ^o	228-231 ^o
3,8-Dibromo-1,10-phenanthroline	221-222 ^o	222-226 ^{oa}
Mixture of above materials	---	233-227 ^o

^aSupplied material was recrystallized from benzene.

Other observations indicate that these materials are actually 3,5-dibromo-1,10-phenanthroline and not the 3,8-dibromo derivative. It was noted above that the infrared spectra of the bromo derivatives are in general very similar to correspondingly substituted chloro compounds with the peaks of the bromo-1,10-phenanthrolines appearing at slightly lower frequencies. The potassium bromide spectra of the 3,5-dibromo- and 3,5-dichloro-1,10-phenanthrolines show this close similarity throughout. However, the comparison of spectra of the "3,8-dibromo" and 3,8-dichloro-1,10-phenanthroline compounds does not reveal similar band positions. Before it was observed that with 3,8-substituted derivatives of 1,10-phenanthroline, the second component of the first ring vibration triplet absorption (band A of 1,10-phenanthroline) is missing or is noted only as a weak shoulder, as in the case of 3,8-dichloro-1,10-phenanthroline. Here with both the above materials, the second component is observed as a sharp absorption of medium intensity at 1577 cm^{-1} .

D. Phenyl Derivatives of 1,10-Phenanthroline

The substitution of phenyl groups on the 1,10-phenanthroline rings should in theory (49) give stronger absorptions for those bands which are associated with the aromatic vibrations. These absorptions include the aromatic C-H stretching vibration band, the C=C ring vibration bands, and

C-H deformation bands.

The infrared spectra of ten phenyl-1,10-phenanthrolines are recorded in Figures 68 through 77. Since the 1,10-phenanthroline structure is aromatic itself, the peaks associated with aromatic vibrations are strong in the parent compound originally, and the effect of the substituted phenyl groups on these bands is not too great. The aromatic C-H stretching absorptions in the chloroform spectra of the phenyl derivatives are in general stronger than are found in the 1,10-phenanthroline spectrum. Some phenyl derivatives are not very soluble in chloroform, however, and the C-H stretching peak is correspondingly somewhat weaker as found with the 2,9-diphenyl- and 2,4,7,9-tetraphenyl-1,10-phenanthrolines. The ring vibration absorptions in the 1,10-phenanthroline spectrum are quite strong originally and little change in intensity of these peaks is observed with phenyl substitution. Later in section V, E, phenyl substitution on the 1,10-phenanthroline rings is found to be successfully characterized by the appearance of a strong absorption in the $713\text{-}690\text{ cm}^{-1}$ region.

With most of the phenyl derivatives, the first ring vibration triplet absorption (band A of 1,10-phenanthroline) contains one to two extra bands. The first extra peak appears between the first and second component of the triplet absorption as an inflection, with 4-phenyl-1,10-phenanthroline, and as a

Figure 68. Infrared spectrum of 2-phenyl-1,10-phenanthroline

Figure 69. Infrared spectrum of 3-phenyl-1,10-phenanthroline

Figure 70. Infrared spectrum of 3-phenyl-1,10-phenanthrolium chloride

Figure 71. Infrared spectrum of 4-phenyl-1,10-phenanthroline

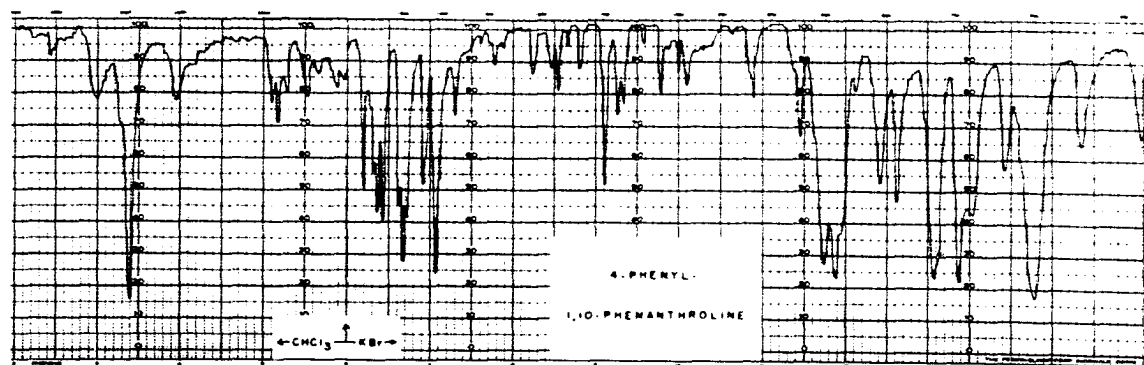
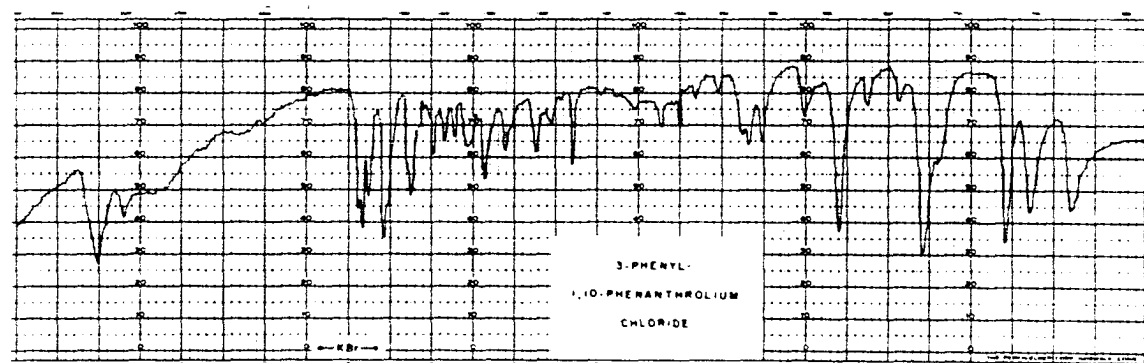
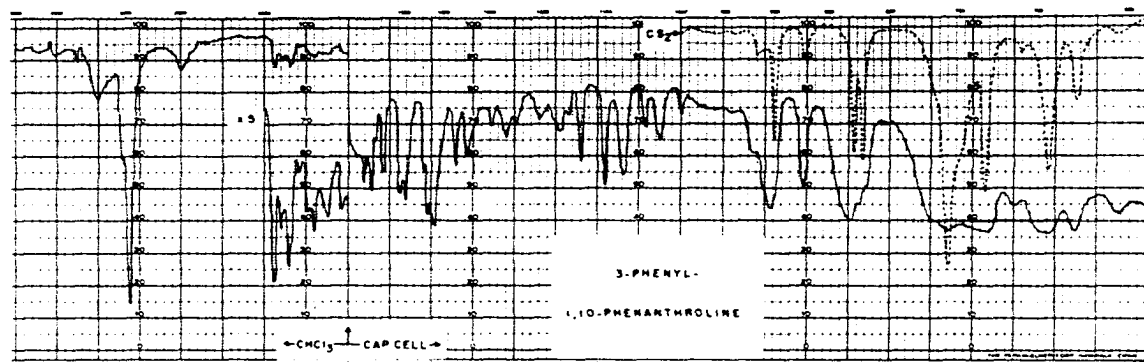
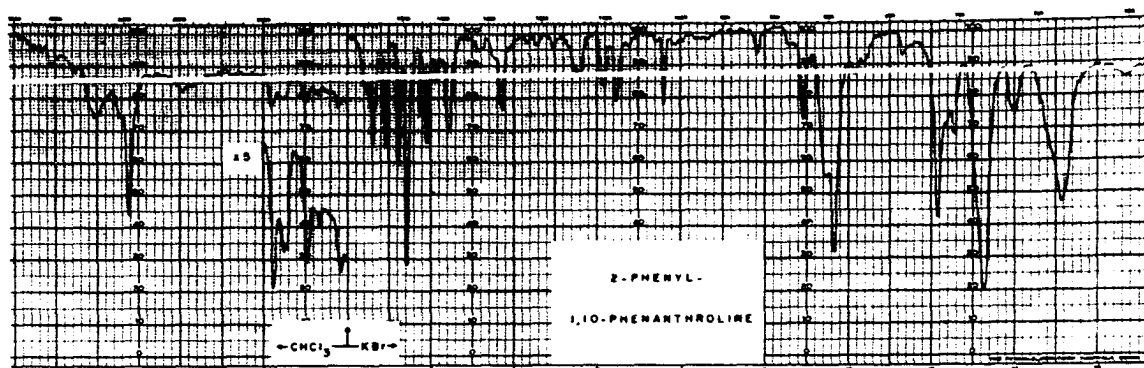


Figure 72. Infrared spectrum of 5-phenyl-1,10-phenanthroline

Figure 73. Infrared spectrum of 2,9-diphenyl-1,10-phenanthroline

Figure 74. Infrared spectrum of 3,8-diphenyl-1,10-phenanthroline

Figure 75. Infrared spectrum of 4,6-diphenyl-1,10-phenanthroline

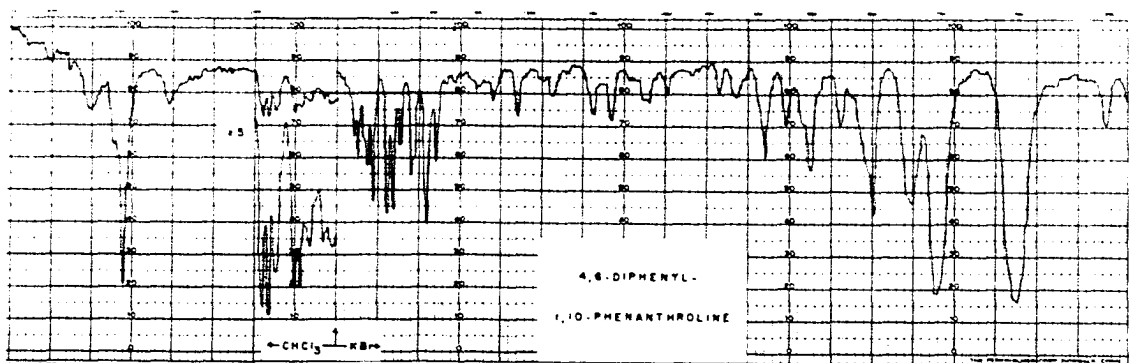
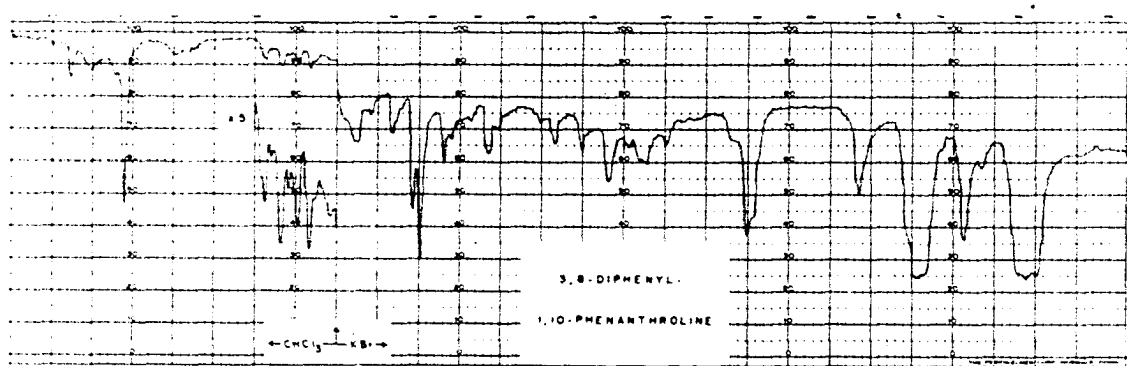
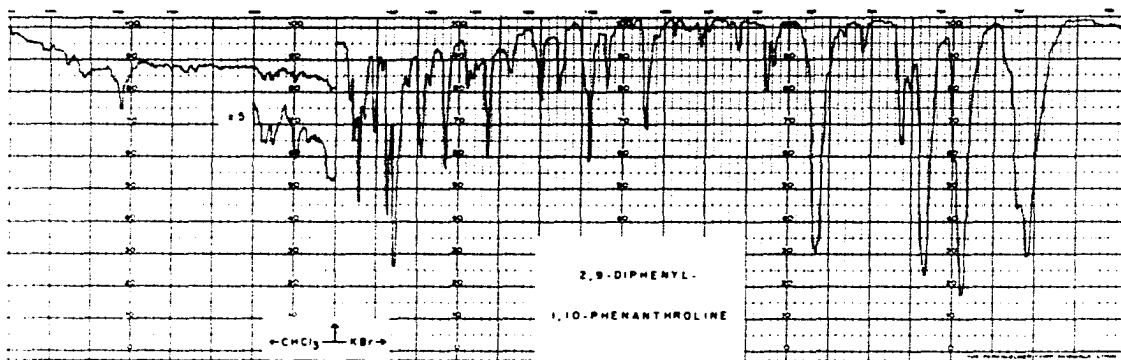
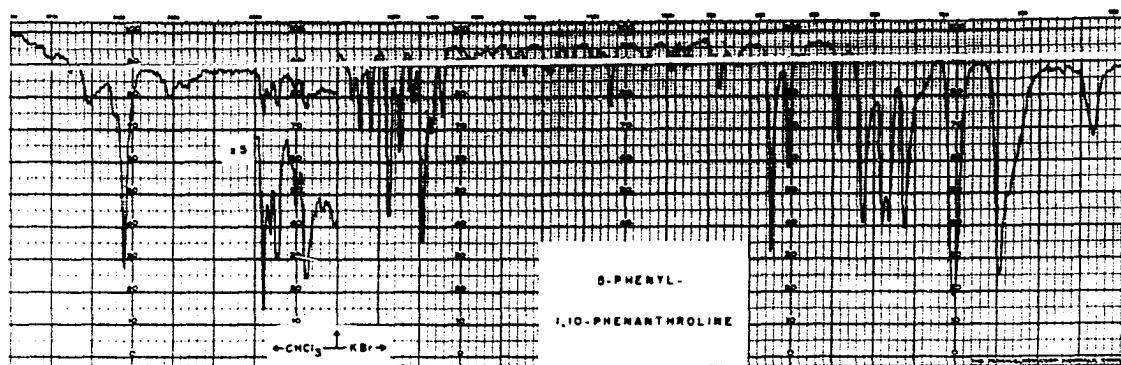
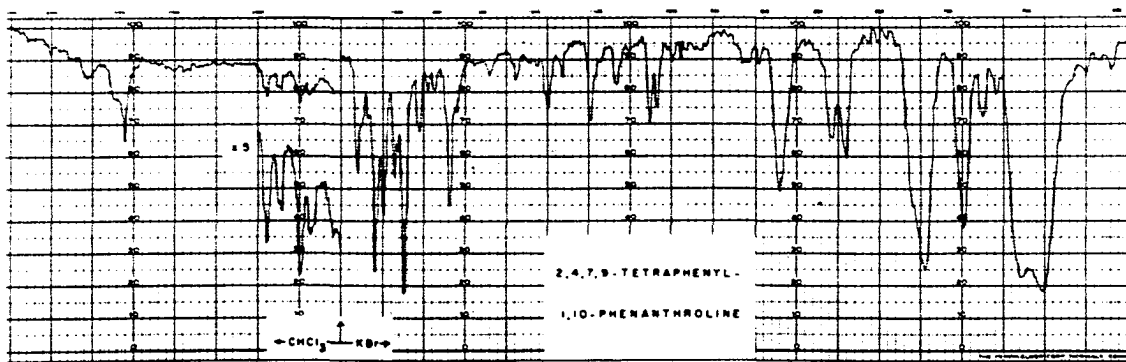
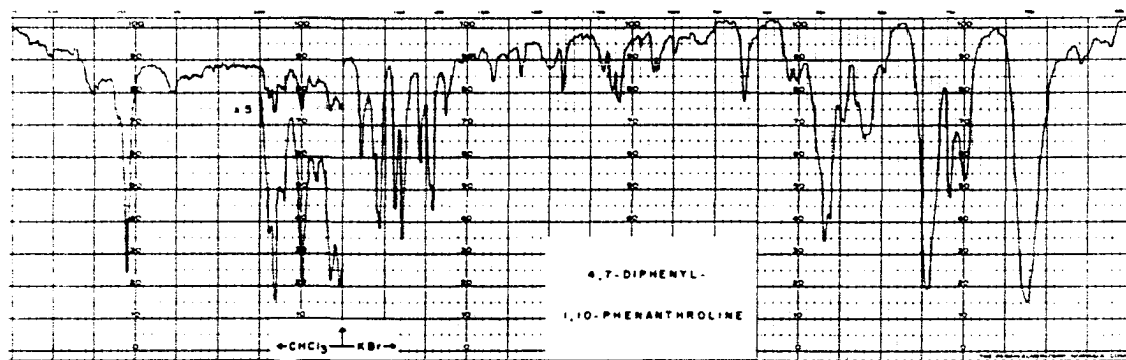


Figure 76. Infrared spectrum of 4,7-diphenyl-1,10-phenanthroline

Figure 77. Infrared spectrum of 2,4,7,9-tetraphenyl-1,10-phenanthroline



medium band in the spectra of 2-phenyl-, 2,9-diphenyl-, and 4,6-diphenyl-1,10-phenanthroline. These absorptions are found in the 1603-1592 cm^{-1} range. The second new peak with phenyl-1,10-phenanthrolines is observed in the 1580-1570 cm^{-1} region as a weak shoulder to a strong absorption for all the phenyl derivatives except 3,8-diphenyl- and 2,4,7,9-tetraphenyl-1,10-phenanthroline. A third new absorption of weak intensity at 1524 cm^{-1} appears in the 2,9-diphenyl-1,10-phenanthroline spectrum. This peak is also found at 1538 cm^{-1} as a doublet with the third component of the original triplet absorption in the 2,4,7,9-tetraphenyl-1,10-phenanthroline spectrum. In the spectra of 3,8-diphenyl-1,10-phenanthroline, the second component of the triplet absorption (band A of 1,10-phenanthroline) is absent as noted before with other types of 3,8-substituted derivatives. Splitting of the second strong ring vibration band (band B of 1,10-phenanthroline) is observed with all the phenyl derivatives. In spectra of some phenyl compounds (4-phenyl-, 4,6-diphenyl-, and 2,4,7,9-tetraphenyl-1,10-phenanthroline), three peaks are noted here rather than two as found earlier with other types of substitution. In several instances the peak on the low frequency side of the original ring vibration band is of stronger intensity.

In the spectrum of 3-phenyl-1,10-phenanthrolium chloride, the shift to higher frequency of the ring vibration bands is observed as before with the 1,10-phenanthroline acid salts in

Table 9. In Table 14 the absorptions found in the spectrum of 3-phenyl-1,10-phenanthroline and its acid chloride salt are recorded together with the resulting shifts to higher frequency.

Table 14. Shifts to higher frequency in the 1635-1400 cm^{-1} region in comparing spectra of 3-phenyl-1,10-phenanthroline and 3-phenyl-1,10-phenanthrolium chloride

Compound	Frequency (cm^{-1}) ^a					
	A ^b (triplet)			B(doublet)		C(doublet)
3-Phenyl-1,10-phenanthroline	1618	1592	1558	1508	1495 (1502) ^c	1437 1429 (1429) ^c
3-Phenyl-1,10-phenanthrolium chloride	1634 ^d	1621	1600	1555		1481
$\Delta\nu(\text{cm}^{-1})$	16	29	42	53 ^e		52 ^e

^aFrom potassium bromide disk spectra.

^bThe letters A, B, and C designate the three strong absorptions in this region.

^cAverage of the doublet absorption frequencies.

^dShoulder.

^eShift from the average of the doublet absorption frequencies of 3-phenyl-1,10-phenanthroline.

The magnitude of the shifts with co-ordination of the proton with 3-phenyl-1,10-phenanthroline is of the same order as that noted earlier with 1,10-phenanthroline in Table 9.

The "immonium bands", which were reported to be in the 2222-1818 cm^{-1} range by Withop (69) and noted earlier for

1,10-phenanthrolium chloride and 1,10-phenanthrolium perchlorate at $2066\text{--}1976\text{ cm}^{-1}$, are observed in the potassium bromide spectrum of 3-phenyl-1,10-phenanthrolium chloride as one, very weak, broad absorption at 2070 cm^{-1} . This band is not as resolved as found with the above acid salts. The Nujol spectrum of the phenyl compound does not reveal any absorption in this region.

E. Miscellaneous Derivatives of 1,10-Phenanthroline

The remaining substituted 1,10-phenanthrolines were divided into several groups and are discussed separately below. The R-O group contained methoxy, phenoxy, and dione derivatives of 1,10-phenanthroline. Any 1,10-phenanthroline compound containing a hydroxy group (except 4-hydroxy-2-aza-1,10-phenanthroline) was placed in one section. This group included many compounds containing other substituents in addition to the hydroxy substitution. Compounds containing a nitrogen atom besides the two present in the 1,10-phenanthroline rings were included in the R-N group. All nitro, amino aza, and dioxime compounds were placed in this category. The group of compounds classed as R-R' contained those derivatives with two different substituents on the 1,10-phenanthroline rings and were not included in the groups above. The cycloalkeno-1,10-phenanthroline derivatives, and derivatives with a substituted six membered unsaturated ring were placed in the last section.

1. Infrared spectra of R-O derivatives of 1,10-phenanthroline

2. Infrared spectra of methoxy-1,10-phenanthrolines Henbest et al. (32) have reported a characteristic band for the methoxy group in the $2832\text{--}2815\text{ cm}^{-1}$ range which appears on the low-frequency side of the strong aromatic C-H stretching absorption. This peak is not observed with compounds containing C-CH₃ or C-OC₂H₅ groups. These authors compared a series of methyl ethers with reference compounds to observe this band. They concluded that the frequency of the symmetrical methyl stretching mode (usually at 2872 cm^{-1}) was lowered approximately 50 cm^{-1} with the bonding of the methyl group through an oxygen atom rather than through a carbon atom. They also reported, as did Bellamy (1), that the symmetric methyl stretching vibration (at 2960 cm^{-1}) was shifted to higher frequency. Page (44) has observed a band at 1100 cm^{-1} which he found useful in methoxy detection in methoxy steroids.

The spectra of four methoxy derivatives of 1,10-phenanthroline are recorded in Figures 78 through 81. A weak shoulder appears in the $2841\text{--}2809\text{ cm}^{-1}$ range in the spectra of the methoxy 1,10-phenanthrolines which corresponds to the absorption reported by Henbest et al. (32). In Table 15 the frequencies observed for this peak are recorded. Neither of the 2-methoxy-1,10-phenanthroline solution spectra contains a peak in this region, and the absorption in the potassium bromide disk spectrum is quite weak. In general the resolution in this region

Figure 78. Infrared spectrum of 2-methoxy-1,10-phenanthroline

Figure 79. Infrared spectrum of 5-methoxy-1,10-phenanthroline

Figure 80. Infrared spectrum of 4,7-dimethoxy-1,10-phenanthroline

Figure 81. Infrared spectrum of 5,6-dimethoxy-1,10-phenanthroline

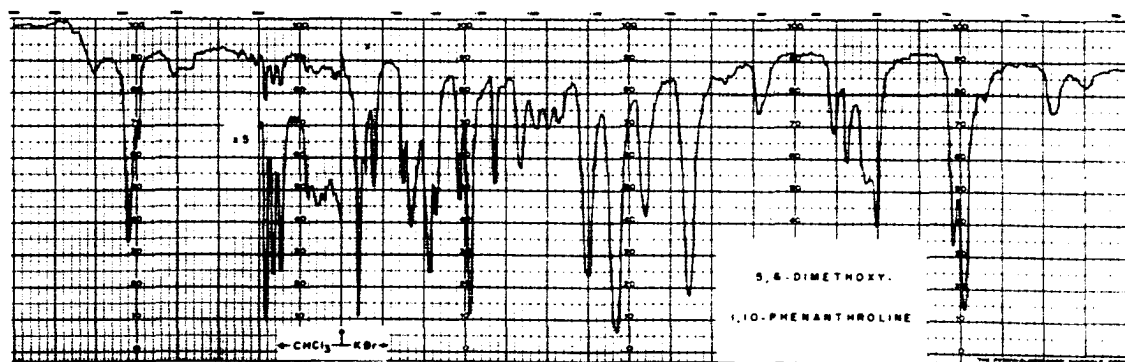
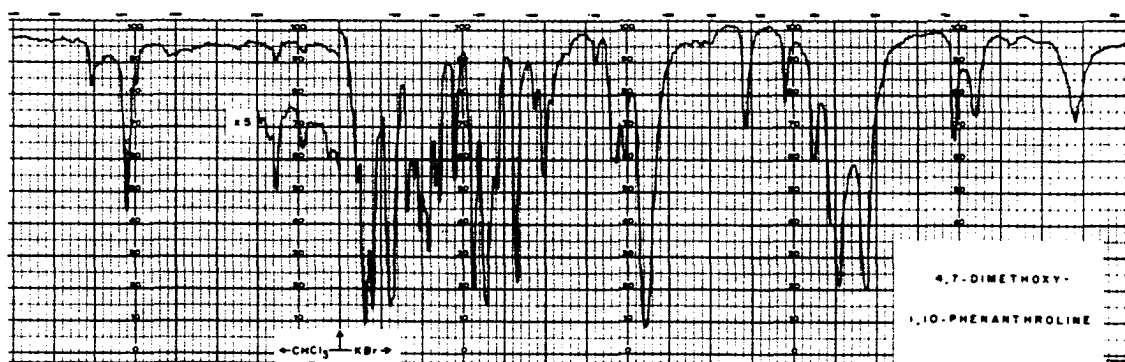
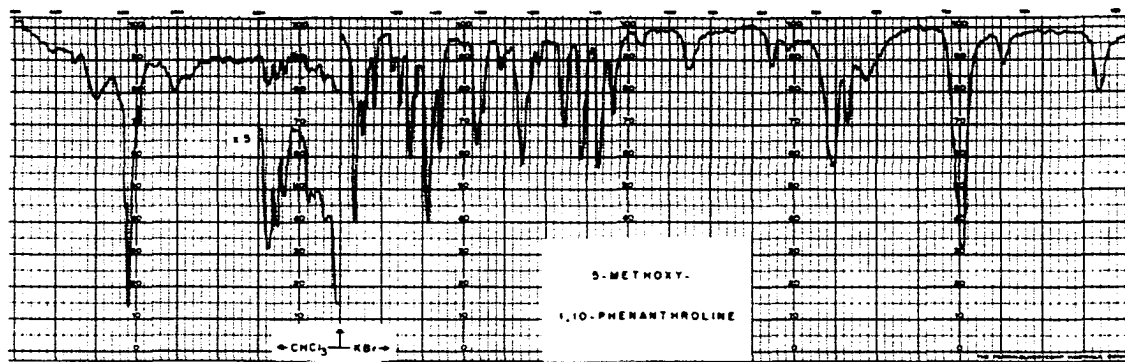
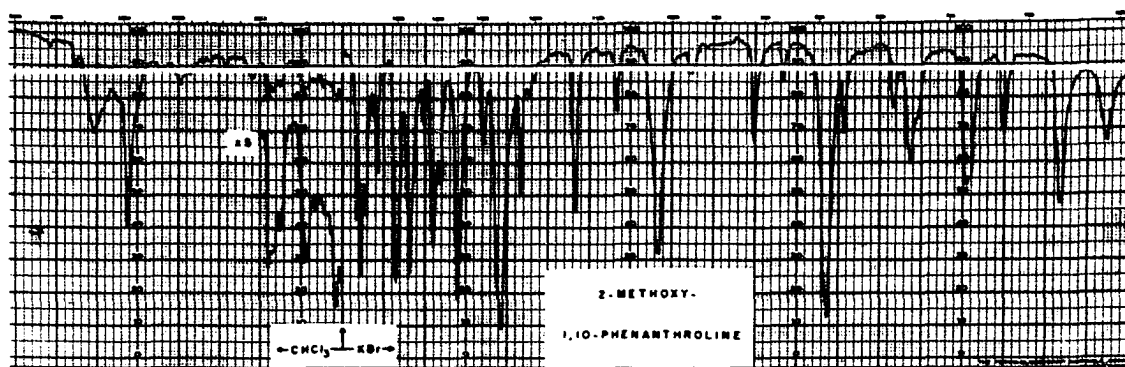


Table 15. Characteristic methoxy absorption in the 2841-2809 cm^{-1} region in spectra of methoxy-1,10-phenanthrolines

Compound	Frequency (cm^{-1}) ^a		
	CHCl_3 solution spectra	CCl_4 solution spectra	KBr disk spectra
2-Methoxy-	--	--	2825 ^b
5-Methoxy-	2825	2825	2809
4,7-Dimethoxy-	2841	-- ^c	2825
5,6-Dimethoxy-	2825	2841	2817

^aAll of these bands were weak shoulders.

^bVery weak absorption.

^cCompound is insoluble in carbon tetrachloride.

is quite poor in these spectra. As noted before, the use of lithium fluoride or calcium fluoride optics in place of the sodium chloride optics would give much better detail in this region (68). The 4,7-diphenoxy-1,10-phenanthroline spectrum does not contain a shoulder in this range. The resolution in this region is too poor to definitely assign any peak to the asymmetrical methyl stretching frequency (which should shift from the normal 2960 cm^{-1} value to higher frequency with the presence of the methoxy group as noted above). Since 1,10-phenanthroline has strong absorption in the 1100 cm^{-1} region, no band could be definitely attributed to the methoxy group as

was observed by Page (44) with steroid compounds.

The position of the methyl symmetrical deformation absorption (usually at $1380\text{--}1370\text{ cm}^{-1}$) was reported by Bellamy (1) to shift when the methyl group was attached to elements other than carbon. Methanol and dimethyl ether were reported (1) to have absorption at 1456 cm^{-1} and 1466 cm^{-1} respectively.

Medium to strong peaks are observed with the four methoxy-1,10-phenanthrolines in the $1466\text{--}1462\text{ cm}^{-1}$ range which appear to be associated with the shifted methyl symmetric deformation mode. In the 2-methoxy- and 5,6-dimethoxy-1,10-phenanthroline spectra, this band is strong and forms a doublet with the second strong ring vibration (band B of 1,10-phenanthroline). There might be some question as to this assignment for these peaks, since in spectra of most 1,10-phenanthroline derivatives, splitting of the second ring absorption has already been observed. However, the second component of the doublet found in other 1,10-phenanthroline spectra, is generally at a somewhat higher frequency than is observed here with these two methoxy compounds. An absorption of medium intensity is found in the spectra of 5-methoxy- and 4,7-methoxy-1,10-phenanthroline and is more separated from the second ring vibration than was noted above. No mention of shifts from the usual position (1460 cm^{-1}) for the methyl asymmetrical deformation mode has been made by Bellamy (1) and no peaks are found which could be assigned to this vibration in the spectra of the methoxy-1,10-phenanthro-

ines.

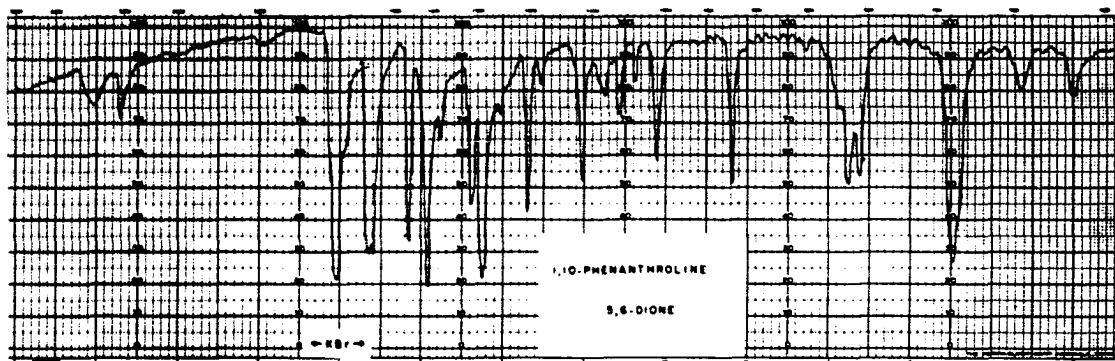
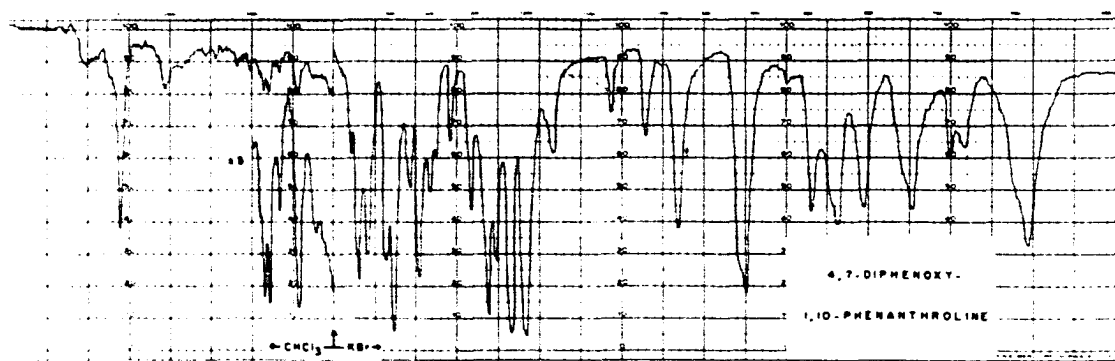
In the spectrum of 5,6-dimethoxy-1,10-phenanthroline, the usual shift of the first component of the triplet ring vibration absorption (band A of 1,10-phenanthroline) to lower frequency is less than usually found (see Table 19 in section V, C). The second ring vibration absorption (band B of 1,10-phenanthroline) is observed at a much lower frequency (1481 cm^{-1}) than found with the other methoxy compounds. Also, this peak has not been observed at such a low frequency with any of the other 1,10-phenanthrolines. Extra peaks are found between the first and second component of the triplet ring vibration absorption in the 2-methoxy- and 5-methoxy-1,10-phenanthroline spectra at 1605 cm^{-1} and 1595 cm^{-1} , respectively. This peak in the 2-methoxy-1,10-phenanthroline spectrum is of very strong intensity; the band in the 5-methoxy-1,10-phenanthroline spectrum is medium shoulder. The usual splitting of the second ring vibration absorption is observed only in the 5-methoxy-1,10-phenanthroline spectrum. Doublet peaks are observed with the 2-methoxy- and 5,6-methoxy-1,10-phenanthrolines, but the second component in each case is related to the symmetrical deformation vibration of the methyl group as was discussed above.

b. Infrared spectrum of 4,7-diphenoxy-1,10-phenanthroline

The spectrum for this derivative is recorded in Figure 82. No characteristic infrared absorptions for the phenoxy group have been reported in the literature. No extra peaks are found in

Figure 82. Infrared spectrum of 4,7-diphenoxy-1,10-phenanthroline

Figure 83. Infrared spectrum of 1,10-phenanthroline-5,6-dione



the first ring vibration triplet absorption. The usual splitting of the second ring vibration absorption occurs, with the second component being of stronger intensity. Strong, unassigned absorptions are noted in the $1350\text{--}1150\text{ cm}^{-1}$ range. These bands are very similar to the strong absorptions in 4,7-dimethoxy-1,10-phenanthroline, except for one extra, intense band at 1199 cm^{-1} in the phenoxy derivative. These peaks are of much greater intensity than generally observed in this region with spectra of other types of 1,10-phenanthrolines. A strong absorption is observed at 692 cm^{-1} , which in Table 33 of section V, E is attributed to the presence of the phenyl ring substituted on 1,10-phenanthroline.

c. Infrared spectrum of 1,10-phenanthroline-5,6-dione The spectrum for this compound is recorded in Figure 83. Bellamy (1) has reported the characteristic carbonyl stretching vibration frequency for quinones with two C=O groups on one ring in the $1690\text{--}1660\text{ cm}^{-1}$ range. Hadzi and Sheppard (29) compared the spectra of polycyclic quinones with related hydrocarbons. They have observed strong absorptions in the $1350\text{--}1200\text{ cm}^{-1}$ region which were not present with similar intensity in hydrocarbon spectra. These authors (29) proposed that these bands were due to some type of motion of the C=O vibration coupled with the rest of the molecule.

A strong absorption at 1678 cm^{-1} which corresponded to

the carbonyl stretching vibration is observed in the 1,10-phenanthroline-5,6-dione spectrum. An intense peak at 1290 cm^{-1} with a strong shoulder on the high frequency side at 1312 cm^{-1} is observed which could correspond to the band reported by Hadzi and Sheppard (29). No absorption in the spectrum of 1,10-phenanthroline is present in this region.

The first component of the ring vibration triplet absorption is absent in the spectrum of this compound. With other types of 5,6-substitution, this first component is generally shifted to lower frequency. It was possible that the carbonyl stretching absorption has masked this band. The second ring vibration absorption (band B of 1,10-phenanthroline) is observed at 1460 cm^{-1} which was at considerably lower frequency than usually noted with 1,10-phenanthroline and other substituted derivatives.

2. Infrared spectra of hydroxy-1,10-phenanthrolines

The spectra of the 1,10-phenanthroline derivatives containing at least one hydroxy group are recorded in Figures 84 through 105. The 4-hydroxy-2-aza-1,10-phenanthroline spectrum (in Figure 115) was included with the other aza-1,10-phenanthrolines in the R-N group below.

Recent infrared studies on the keto and enol tautomerism found with hydroxypyridines and hydroxyquinolines have been

Figure 84. Infrared spectrum of 2-hydroxy-1,10-phenanthroline

Figure 85. Infrared spectrum of 5-hydroxy-1,10-phenanthroline

Figure 86. Infrared spectrum of 2,4-dihydroxy-1,10-phenanthroline

Figure 87. Infrared spectrum of 4,5-dihydroxy-1,10-phenanthroline

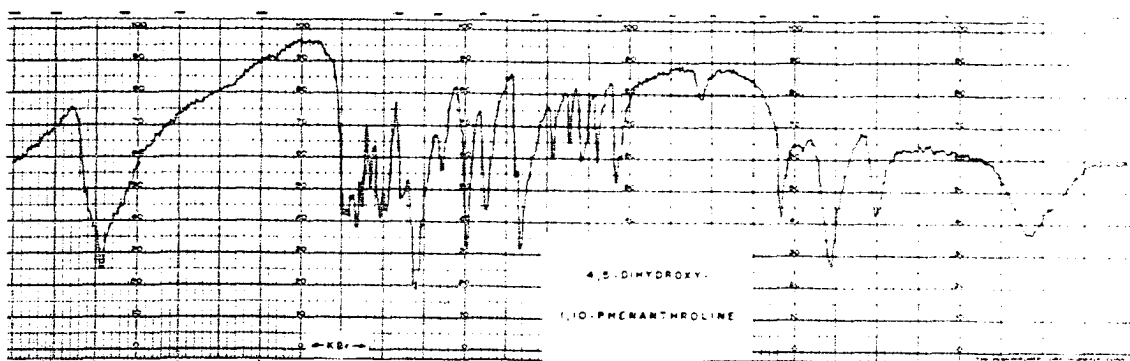
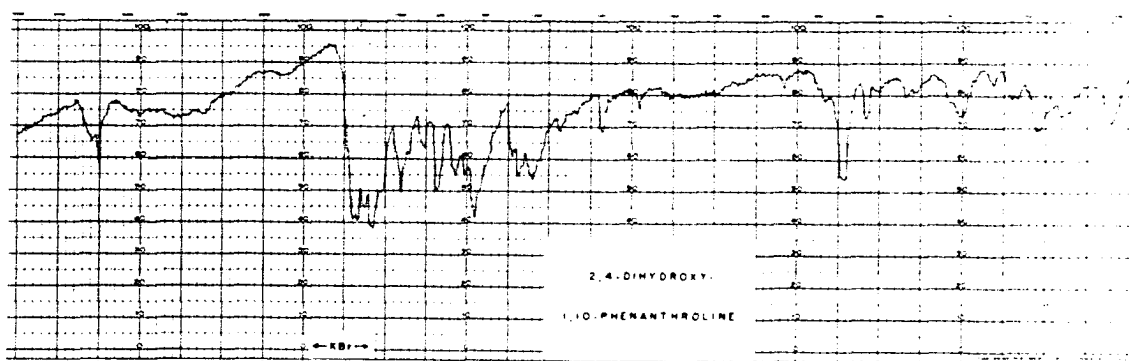
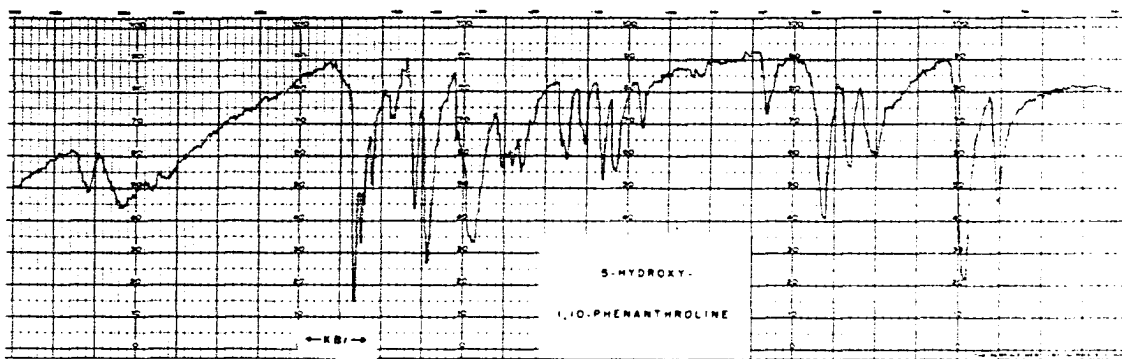
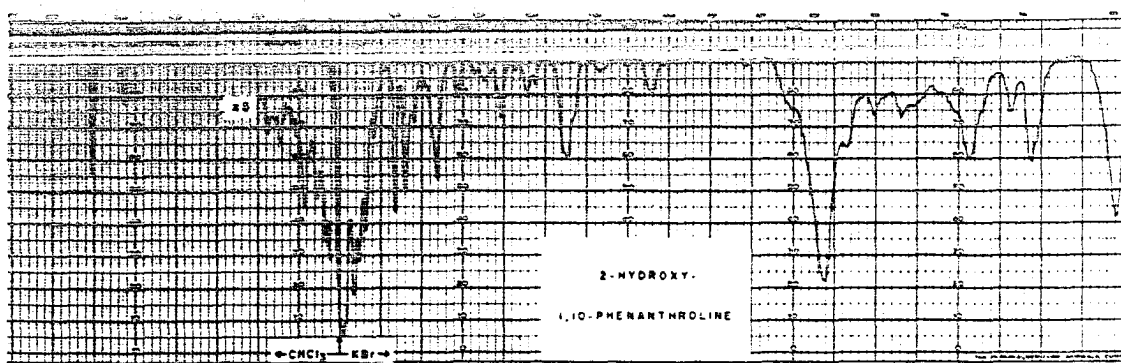


Figure 88. Infrared spectrum of 4,7-dihydroxy-1,10-phenanthroline

Figure 89. Infrared spectrum of 4,7-dihydroxy-1,10-phenanthrolium chloride

Figure 90. Infrared spectrum of 5,6-dihydroxy-1,10-phenanthroline

Figure 91. Infrared spectrum of 2-methyl-4-hydroxy-1,10-phenanthroline

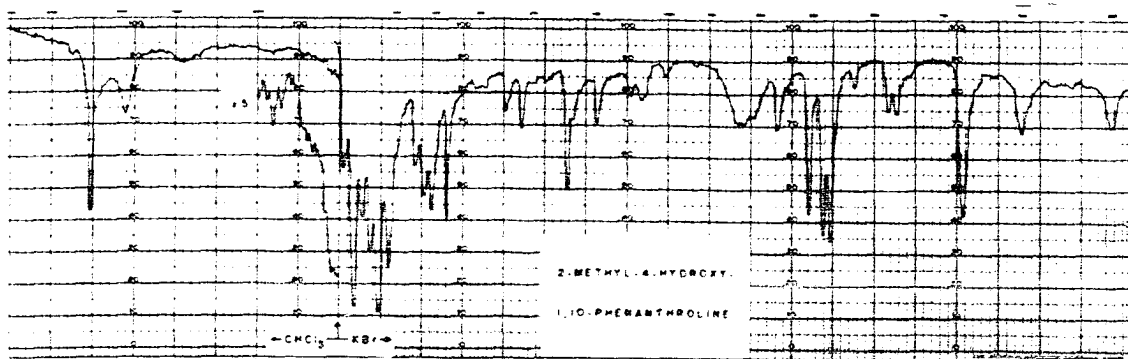
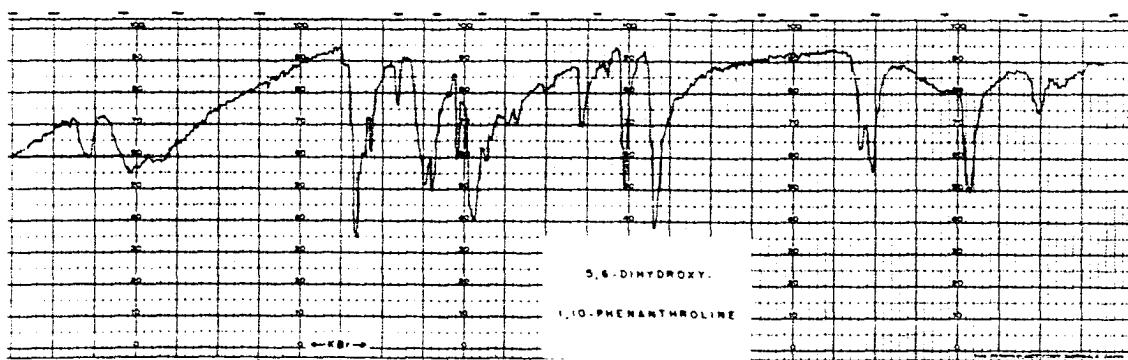
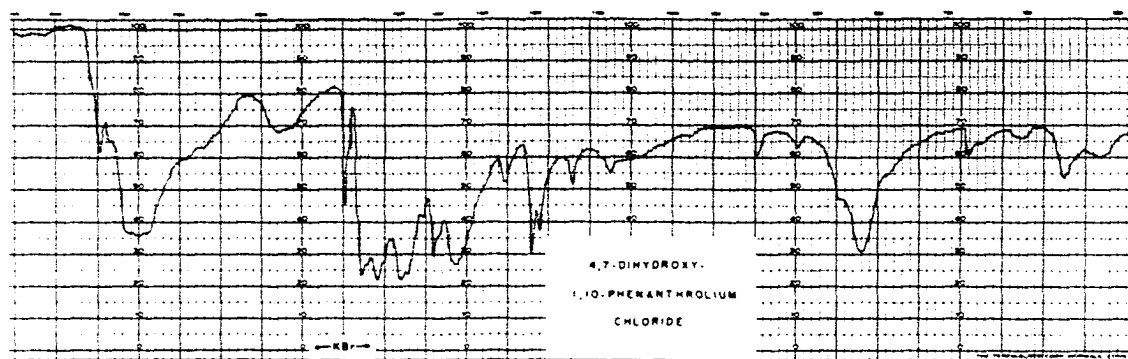
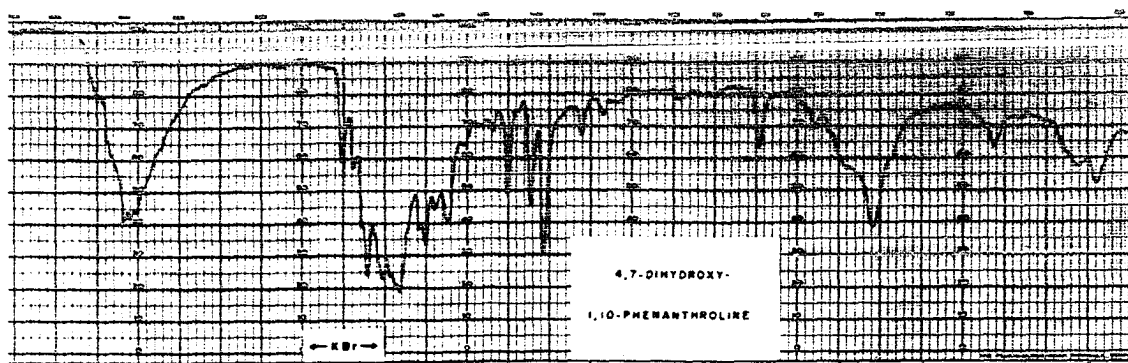


Figure 92. Infrared spectrum of 3-phenyl-4-hydroxy-1,10-phenanthroline

Figure 93. Infrared spectrum of 3-carbethoxy-4-hydroxy-1,10-phenanthroline

Figure 94. Infrared spectrum of 3-carboxy-4-hydroxy-1,10-phenanthroline

Figure 95. Infrared spectrum of 4-hydroxy-5-methoxy-1,10-phenanthroline monopicrate

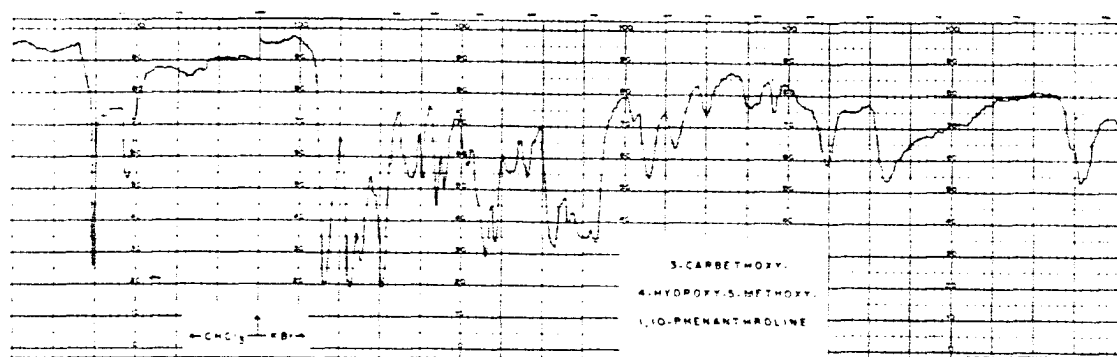
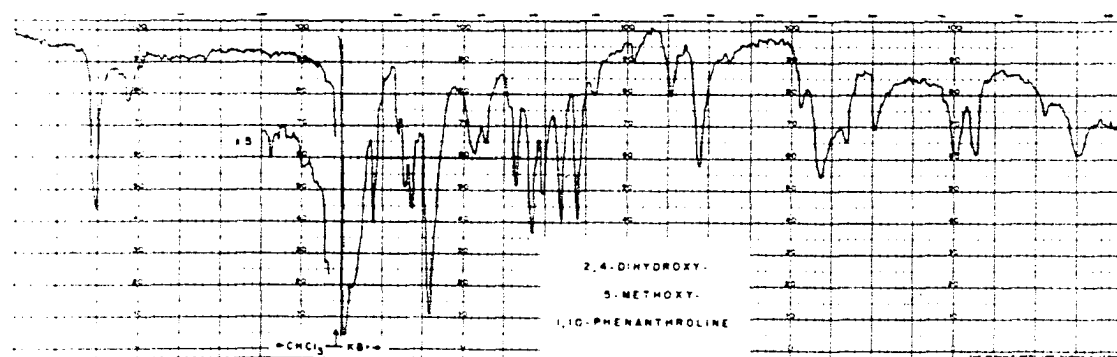
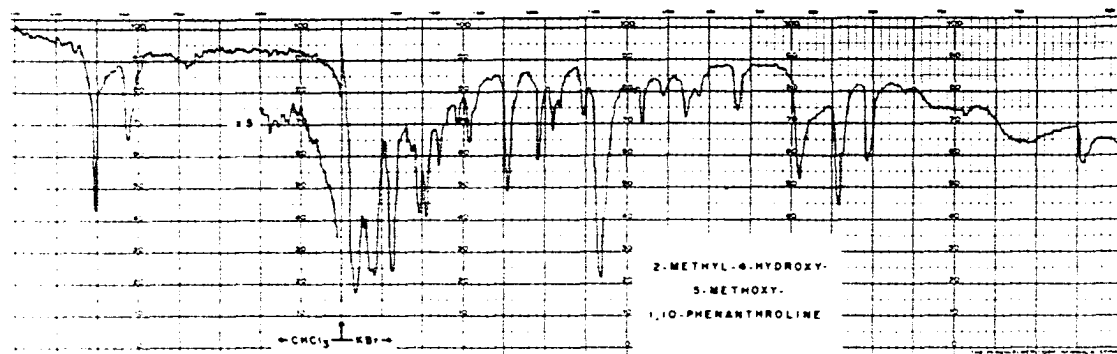
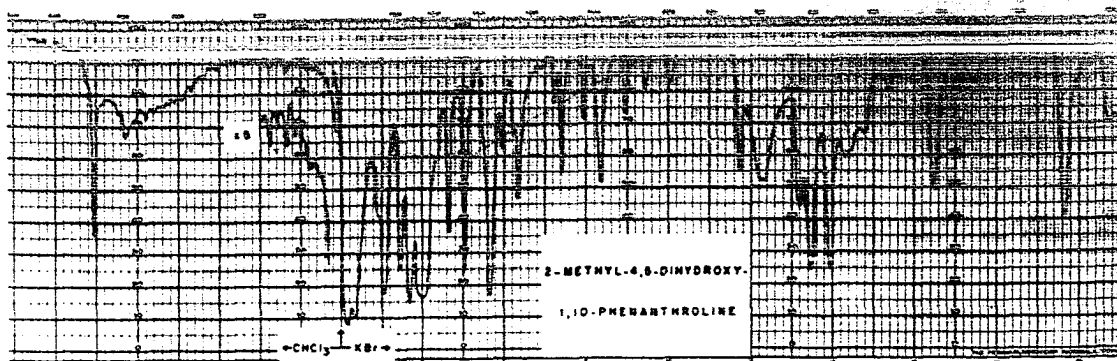


Figure 96. Infrared spectrum of 2-methyl-4,5-dihydroxy-1,10-phenanthroline

Figure 97. Infrared spectrum of 2-methyl-4-hydroxy-5-methoxy-1,10-phenanthroline

Figure 98. Infrared spectrum of 2,4-dihydroxy-5-methoxy-1,10-phenanthroline

Figure 99. Infrared spectrum of 3-carbethoxy-4-hydroxy-5-methoxy-1,10-phenanthroline

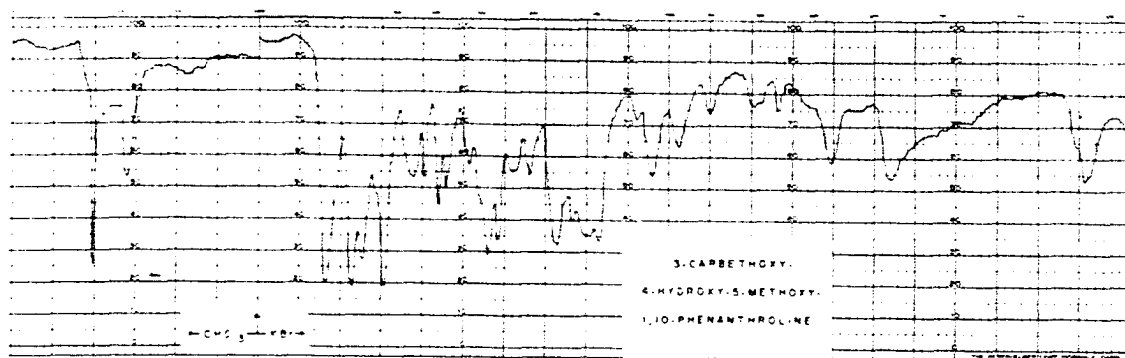
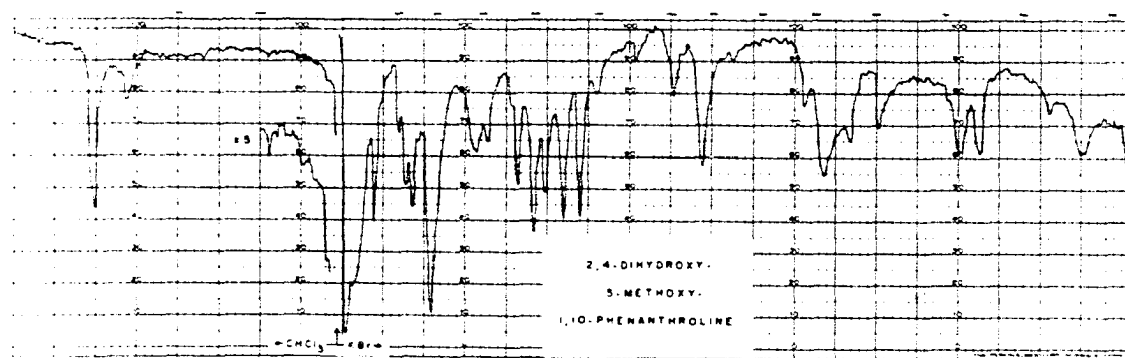
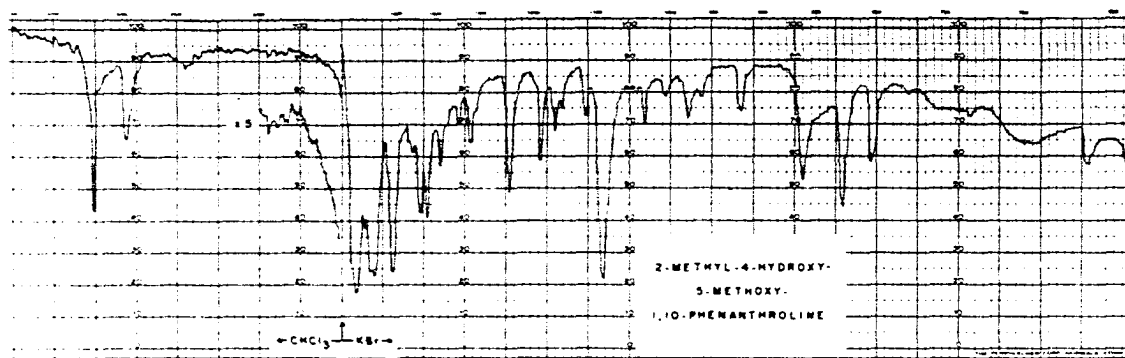
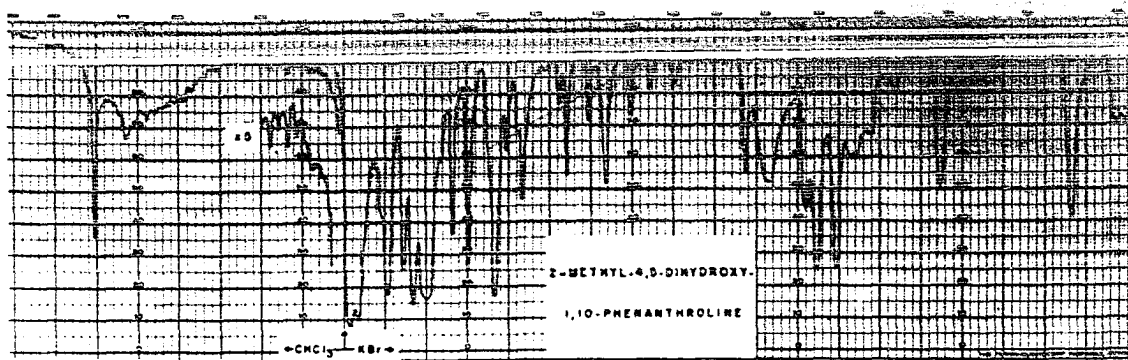


Figure 100. Infrared spectrum of 3-carboxy-4-hydroxy-5-methoxy-1,10-phenanthroline

Figure 101. Infrared spectrum 3-carboxy-4-hydroxy-5,6-dimethoxy-1,10-phenanthroline

Figure 102. Infrared spectrum of 3,8-diphenyl-4,7-dihydroxy-1,10-phenanthroline

Figure 103. Infrared spectrum of 3,8-dicarbethoxy-4,7-dihydroxy-1,10-phenanthroline

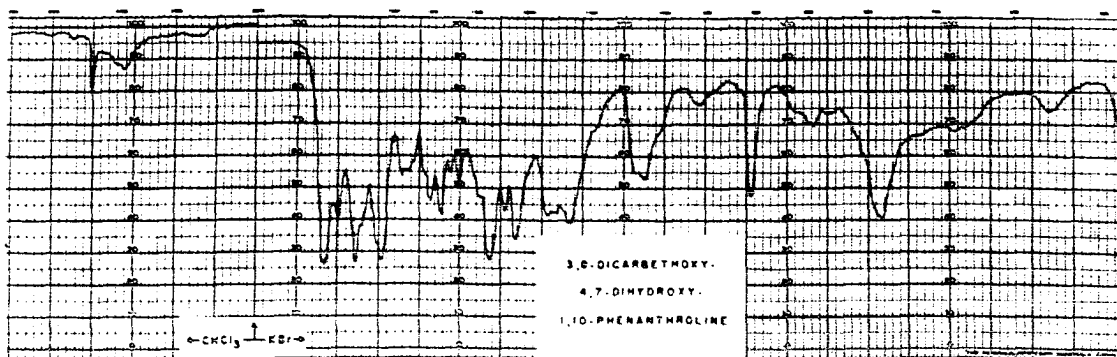
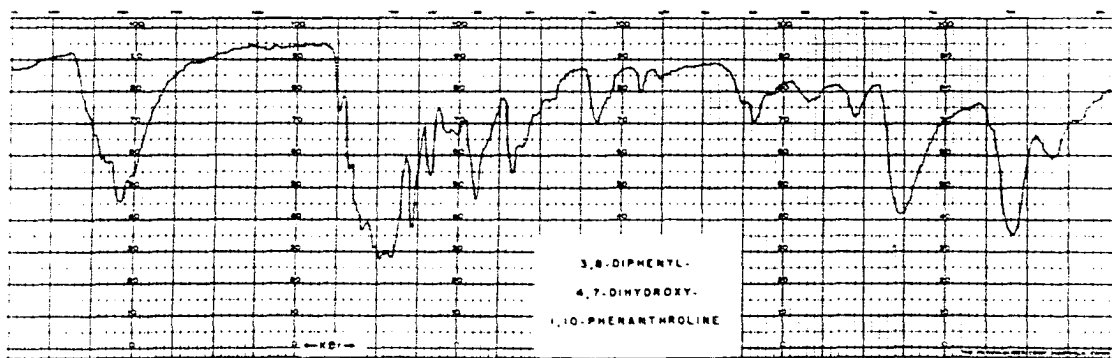
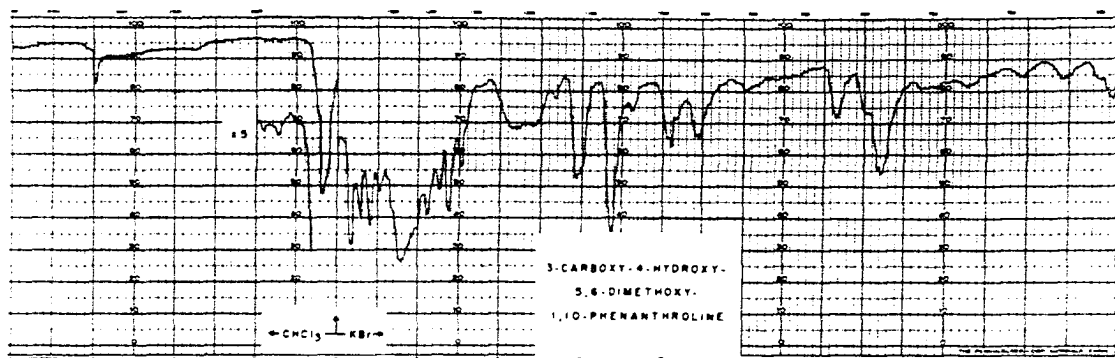
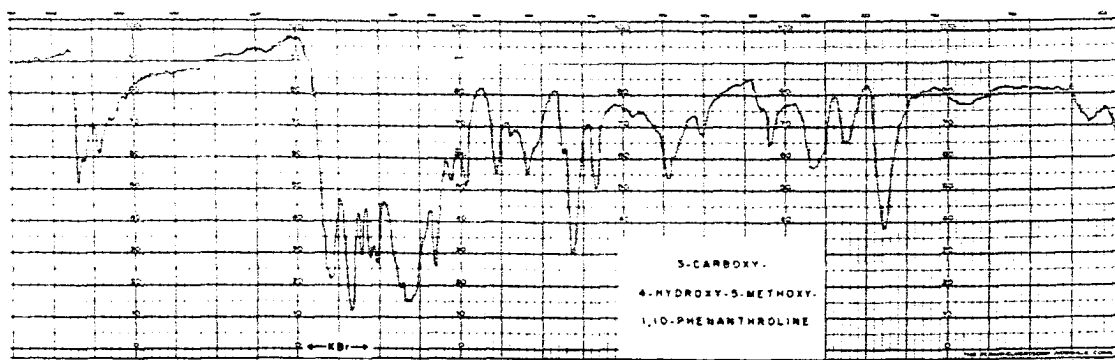
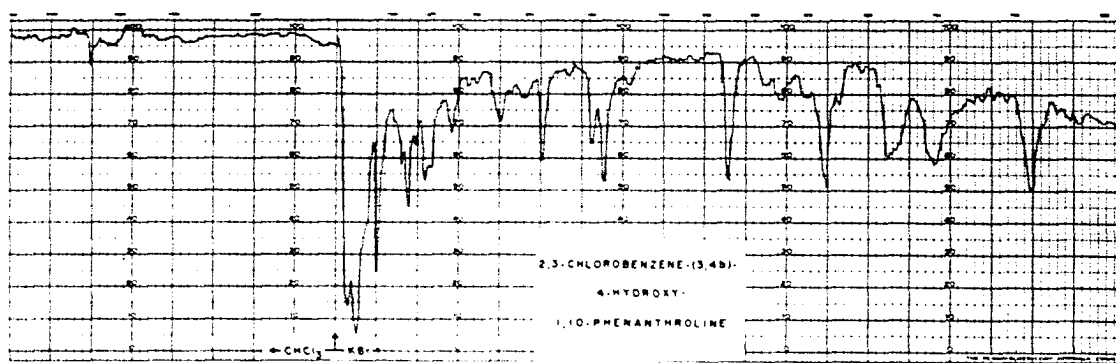
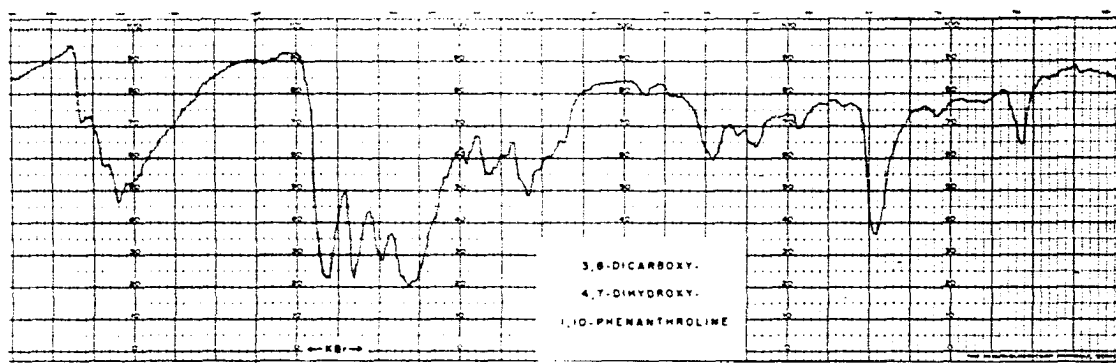
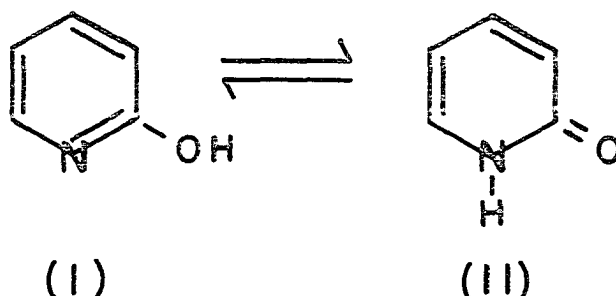


Figure 104. Infrared spectrum of 3,8-dicarboxy-4,7-dihydroxy-1,10-phenanthroline

Figure 105. Infrared spectrum of 2,3-chlorobenzene-(3,4 b)-1,10-phenanthroline

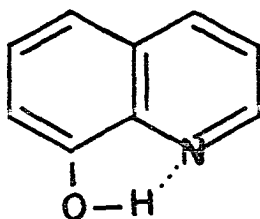


reported (28, 41, 48, 55, 66). These studies support the existence of the amide structure (II) for 2- and 4-hydroxypyridines and 2- and 4-hydroxyquinolines. The secondary amide

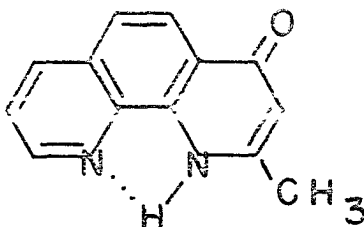


structure is characterized using infrared spectra by the presence of a strong carbonyl absorption near 1650 cm^{-1} in both solid state and in solution spectra and a N-H stretching absorption in the $3420\text{--}3360\text{ cm}^{-1}$ range in dilute solutions (41). This latter absorption is observed near 3200 cm^{-1} in the solid state and was quite broad with several maxima extending down to 2400 cm^{-1} in the case of 2-hydroxypyridine compounds (55). Some question may arise on the assignment of the higher frequency band to the N-H stretching vibration, since it is difficult to distinguish O-H and N-H absorptions in this region. Shindo (55) used a deuteration study to prove the assignment of this absorption to the N-H stretching vibration. With deuteration, the N-H absorption near 3200 cm^{-1} disappeared, and the N-D absorption appeared in the $2300\text{--}2100\text{ cm}^{-1}$ region which was expected for this latter vibration. The 3-hydroxypyridine and 3-hydroxyquinoline spectra do not contain an absorption in the 1650 cm^{-1} region indicating the absence of the amide structure and the existence of the enol form. Also

the O-H stretching vibration absorption was found by Mason (41) near 3600 cm^{-1} in solution spectra (carbon tetrachloride) and in the $2940\text{--}2500\text{ cm}^{-1}$ range in the solid state spectra (potassium bromide disk) for these compounds. Other hydroxyquinolines were also investigated (41). The 5-, 6-, and 7-hydroxyquinoline spectra contain an absorption in the $3601\text{--}3591\text{ cm}^{-1}$ range in solution and $2960\text{--}2500\text{ cm}^{-1}$ region in the solid state. No absorption near 1650 cm^{-1} is found with these compounds. Apparently, these materials exist mainly in the enol form as do 3-hydroxypyridine and 3-hydroxyquinoline. The absorptions found in the 8-hydroxyquinoline spectrum are found at lower frequencies than those above, 3412 cm^{-1} in solution and 3180 cm^{-1} in the solid state. This shift to lower frequency was attributed by Mason (41) to intramolecular hydrogen bonding which occurs with the ring nitrogen of quinoline. Mason (41) observed this tautomerism with



2-methyl-4-hydroxy-1,10-phenanthroline and found absorptions at 3374 cm^{-1} and 1634 cm^{-1} in chloroform solution. He concluded that intramolecular hydrogen bonding is present with this compound, since the absorption observed occurs at lower frequency than found with other diaza compounds of the quasi-



p-quinonoid type.

The majority of the hydroxy-1,10-phenanthrolines investigated in this study are not soluble in carbon tetrachloride or chloroform. Also in several cases the potassium bromide spectra obtained are not resolved too well with many absorptions being quite broad. Most of these derivatives have substitution of a hydroxy group in the 2- or 4-position, and apparently the tautomeric keto form was predominate as is indicated by infrared evidence showing the presence of a secondary amide.

Strong absorptions are found in the 1650 cm^{-1} region with many of these hydroxy derivatives. In several instances the frequency for these absorptions coincide with that expected for the first component of the triplet ring vibration absorption (band A of 1,10-phenanthroline at 1616 cm^{-1}), but the peak in the spectra of hydroxy compounds is much more intense than found with the band noted in spectra 1,10-phenanthroline and other substituted 1,10-phenanthrolines. In Table 16 the absorption frequencies observed in the N-H stretching and carbonyl regions in the spectra of these hydroxy derivatives are

Table 16. Absorptions found in the N-H stretching and carbonyl regions in spectra of hydroxy-1,10-phenanthrolines

Compound	Data ^a source	Frequency (cm ⁻¹)		
		N-H stretch	C=O ^b	C=O ^c
2-Hydroxy-	(1)	3344	--	1650
	(2)	3344	--	1653
	(3)	3367	--	1672
2,4-Dihydroxy-	(1)	3344	--	1634 1621 ^d
4,5-Dihydroxy	(1)	3268	--	1658 1645 ^d
4,7-Dihydroxy-	(1)	2941	--	1699 ^e
2-Methyl-4- hydroxy-	(1)	3322	--	1653 ^e 1618
	(2)	3367 (3374) ^f	--	1634 (1634) ^f
	(3)	3390 (3389) ^f	--	1634
4-Hydroxy-2-aza-	(1)	3175	--	1621
	(2)	3390	--	1645
3-Phenyl-4- hydroxy-	(1)	3003	--	1618
	(2)	3367	--	1634 1621 ^d
3-Carbethoxy-4- hydroxy-	(1)	3185	1704	1631 ^e
	(2)	3378	1724 1686 ^d	1626

^aThe absorption frequencies are taken from (1) potassium bromide spectra; (2) chloroform solution spectra; and (3) carbon tetrachloride spectra.

^bCarbonyl absorption of a carbethoxy or a carboxy group.

^cCarbonyl absorption of a secondary amide.

^dDoublet absorption.

^eShoulder.

^fAbsorptions reported by Mason (41).

Table 16. (Continued)

Compound	Data ^a source	Frequency (cm ⁻¹)		
		N-H stretch	C=O ^b	C=O ^c
3-Carboxy-4-hydroxy-	(1)	3215	1739	1631
4-Hydroxy-5-methoxy- 1,10-phenanthroline monopicrate	(1)	3096	--	1626
2-Methyl-4,5- dihydroxy-	(1)	3155	--	1647
	(2)	3356	--	1661
2,4-Dihydroxy- 5-methoxy-	(1)	3311	--	1661
	(2)	3356	--	1664
3-Carbethoxy-4- hydroxy-5-methoxy-	(1)	3215	1704	1631
	(2)	3356	1724	1686 ^d 1626
3-Carboxy-4-hydroxy- 5-methoxy-	(1)	3257	1692	1623
	(2)	3333 ^g	1718	1631
3-Carboxy-4-hydroxy- 5,6-dimethoxy	(1)	--- ^h	1704	1621
	(2)	3311 ^g	1715	1626
3,8-Diphenyl-4,7-di- hydroxy-	(1)	2994	--	1661 ^e
3,8-Dicarbethoxy- 4,7-dihydroxy-	(1)	3115	1712	1667 ^e
	(2)	3356	1715	1667
3,8-Dicarboxy- 4,7-dihydroxy-	(1)	3030	1704	1616
2,3-Chlorobenzene- (3,4 b)-4-hydroxy-	(1)	3205	--	1626
	(2)	3356 ^g	--	1631

^gWeak absorption; the compound is not very soluble in chloroform.

^hNo peak is resolved in this region.

recorded. Several of these compounds contain a carbethoxy or a carboxy group. Bellamy (1) has reported absorption in the $1750\text{--}1735\text{ cm}^{-1}$ region for the carbonyl vibration with saturated esters, and absorption in the $1700\text{--}1680\text{ cm}^{-1}$ range for the carbonyl mode with aryl acids.

The N-H stretching absorptions in the potassium bromide spectra of these hydroxy-1,10-phenanthrolines are generally broad, medium to strong intensity bands in the $3344\text{--}2940\text{ cm}^{-1}$ range. These absorptions in the solution spectra are quite sharp and are of weak to strong intensity depending upon how soluble the material is in the solvent. These bands are found in the $3390\text{--}3311\text{ cm}^{-1}$ range and are always at slightly higher frequency than observed in the potassium bromide spectra. The carbonyl band related to the carbethoxy group is found in the $1712\text{--}1704\text{ cm}^{-1}$ region in potassium bromide spectra and in the $1724\text{--}1686\text{ cm}^{-1}$ range in chloroform solution spectra. In general with corresponding carboxy compounds, the carbonyl absorption is at lower frequency than noted above (except with 3-carboxy-4-hydroxy-1,10-phenanthroline). The amide carbonyl bands are generally at lower frequency in the potassium bromide disk spectra than found in the solution spectra with a few exceptions.

Two derivatives (5-hydroxy- and 5,6-dihydroxy-1,10-phenanthroline) do not have hydroxy substitution in the 2- or 4-

positions. The infrared spectra of these materials indicate the existence of the enol form in both instances. The first component of the triplet absorption (at 1621 cm^{-1} and 1618 cm^{-1} , respectively in the spectra of 5-hydroxy- and 5,6-hydroxy-1,10-phenanthroline) is stronger than found in general with substituted 1,10-phenanthrolines, but is not as intense as usually found with the other hydroxy derivatives which apparently exist in the amide form. Also a weak absorption at 3425 cm^{-1} is found in the potassium bromide spectra of both of these materials instead of the strong N-H stretching absorption usually found at slightly lower frequency. This weak band at 3425 cm^{-1} is probably due to the O-H stretching vibration.

In the spectrum of 4,7-dihydroxy-1,10-phenanthrolium chloride, Figure 89, a very broad, relatively weak absorption occurs at 1912 cm^{-1} owing to the presence of the "immonium band" (69) discussed before in section IV, A (see Table 10). This absorption distinguishes the acid salt from the free base, 4,7-dihydroxy-1,10-phenanthroline, Figure 88. This peak is not as resolved in the Nujol mull spectrum of 4,7-dihydroxy-1,10-phenanthrolium chloride as found in the potassium bromide spectrum in Figure 89.

3. Infrared spectra of the R-N group of 1,10-phenanthrolines

a. Infrared spectra of nitro-1,10-phenanthrolines Bellamy

(1) has summarized the data from many studies by several in-

investigators on numerous types of compounds containing the nitro group. He has reported two very strong absorptions in the $1570\text{--}1500\text{ cm}^{-1}$ and $1370\text{--}1300\text{ cm}^{-1}$ ranges, which correspond to the asymmetric and symmetric stretching vibrations of the nitro group.

The spectra of two nitro derivatives of 1,10-phenanthroline are recorded in Figures 106 and 107. In Table 17 are tabulated the absorption frequencies of the nitro-1,10-phenanthrolines which correspond to the frequencies reported for nitro groups. The strong absorption related to the asymmetric stretching vibration of the nitro group appears very near to the frequency expected for the second ring vibration (band B of 1,10-phenanthroline). As noted in Table 17, the second ring vibration absorption in the spectrum of 5-nitro-6-methyl-1,10-phenanthroline is absent and is apparently masked by the strong nitro absorption.

Table 17. Absorptions related to the asymmetric and symmetric stretching vibrations of the nitro group in the spectra of nitro-1,10-phenanthrolines

Compound	Frequency (cm^{-1}) ^a		
	Nitro asym. vibration	Ring vibration (band B)	Nitro sym. vibration
5-Nitro-	1520	1502	1342
5-Nitro-6-methyl-	1514	-- ^b	1366

^aFrom potassium bromide disk spectra.

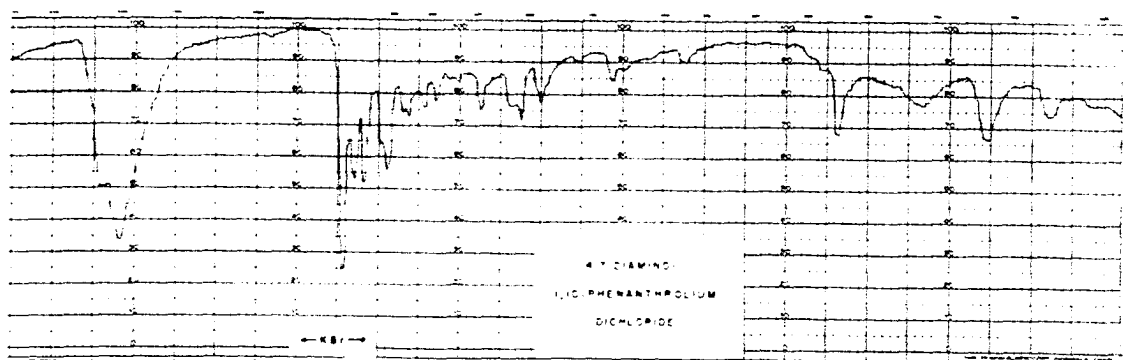
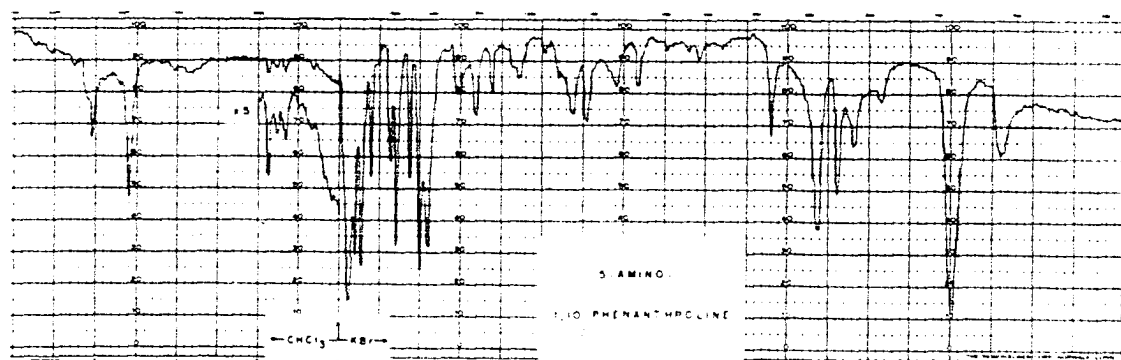
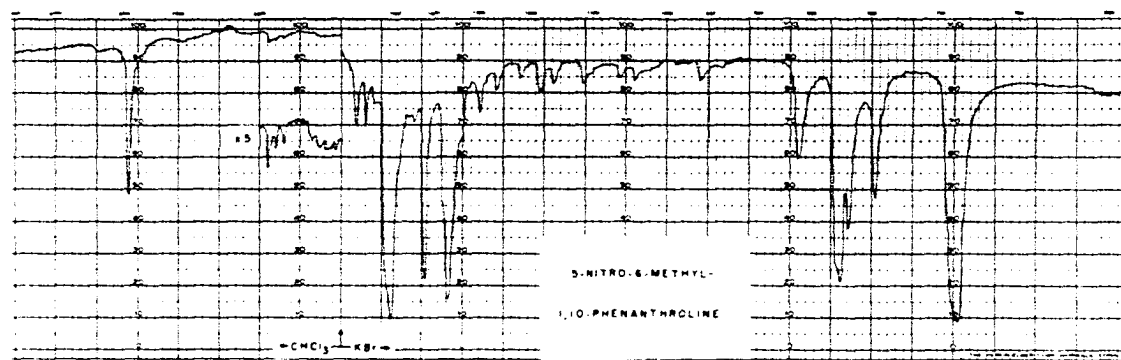
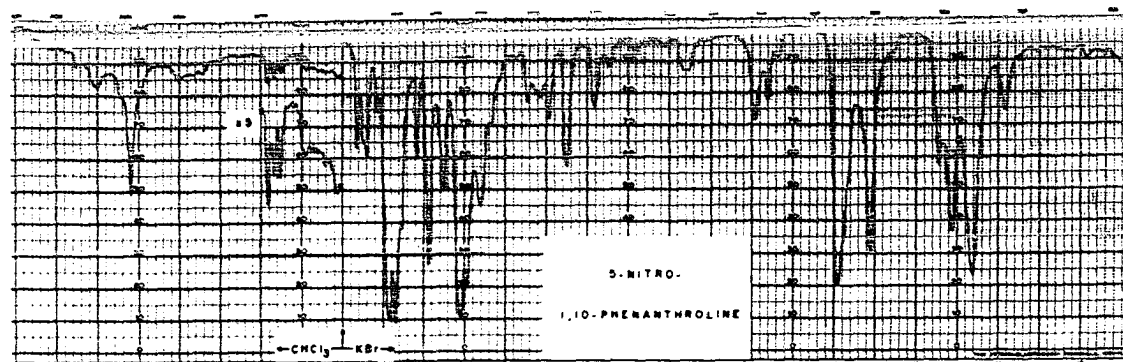
^bRing absorption was apparently masked by the absorption attributed to the asymmetric nitro stretching vibration.

Figure 106. Infrared spectrum of 5-nitro-1,10-phenanthroline

Figure 107. Infrared spectrum of 5-nitro-6-methyl-1,10-phenanthroline

Figure 108. Infrared spectrum of 5-amino-1,10-phenanthroline

Figure 109. Infrared spectrum of 4,7-diamino-1,10-phenanthroline dichloride



b. Infrared spectra of amino-1,10-phenanthrolines The N-H stretching absorptions of primary amines were reported by Bellamy (1) to lie in the 3500-3300 cm^{-1} range. In general, two bands were reported in this region, the first near 3500 cm^{-1} , which was due to the asymmetrical stretching of the hydrogen atoms, and the second near 3400 cm^{-1} , which was related to the symmetrical stretching mode. These frequencies were from spectra obtained in dilute solution in non-polar solvents. With concentrated solutions intermolecular associations occur which give rise to large changes in the above reported frequencies. Small changes were found with the use of polar solvents. In some instances a third band was reported to appear in this region due to hydrogen bonding effects. The hydrogen bonding was noted always to cause displacement of these peaks to lower frequencies. Lowering of these frequencies was also reported with amines in the solid state. Farmer and Thomson (24) has observed three peaks with aniline in pyridine solution. They proposed that possibly only one hydrogen atom of the amino group is hydrogen bonded to the pyridine solvent, and that the overtone of the N-H deformation vibration accounts for the third absorption. Reference was made in this paper (24) to several other authors who have also observed three peaks in this region with various primary amines.

Bellamy (1) has reported that the N-H internal deformation mode occurred in the 1650-1590 cm^{-1} range in nearly all primary amines investigated. He also found that most primary amines

have broad absorptions in the $900\text{--}650\text{ cm}^{-1}$ range which appeared due to the external amino group deformations, but the data for these absorptions was reported to be quite limited. Colthup (20) has reported a strong absorption in the $1340\text{--}1250\text{ cm}^{-1}$ region for aromatic primary amines. Bellamy (1) indicated that this absorption of medium to strong intensity was due to the C-N stretching vibration.

The spectra of two amino derivatives of 1,10-phenanthroline are recorded in Figures 108 and 109. The characteristic absorptions found in the spectrum of 5-amino-1,10-phenanthroline are recorded in Table 18. The N-H stretching absorptions are shifted slightly to lower frequency in the chloroform solution spectrum when compared with the frequencies reported above by Bellamy. This shift is probably caused

Table 18. Characteristic amino absorptions found in the 5-amino-1,10-phenanthroline spectrum

Data source	Frequency (cm^{-1})			
	Asym. N-H stretch	Sym. N-H stretch	Internal N-H deformation	C-N stretch
CHCl_3 solution spectrum	3413 ^a	3356	1631	1295
KBr disk spectrum	3413	3333	3226 1634	1302

^aWeak shoulder.

by the presence of the polar solvent, chloroform. The compound is not soluble in carbon tetrachloride, and no spectrum could be obtained in this solvent. In the potassium bromide spectrum, three N-H stretching absorptions are observed in this region. The shift of the first two peaks to lower frequencies is approximately the same as found in the chloroform solution spectrum. The extra peak at 3226 cm^{-1} found in the potassium bromide disk spectrum is attributed to the overtone of the N-H deformation frequency (which would be expected at 3268 cm^{-1}) as was suggested by Farmer and Thompson (24). The frequency noted in Table 18 for the C-N stretching vibration absorption with 5-amino-1,10-phenanthroline is somewhat questionable since the absorptions in the region are relatively weak. No absorption in the $900\text{-}650\text{ cm}^{-1}$ range could be definitely assigned to the external amino group deformation reported by Bellamy (1). The second and third ring vibration absorptions (band B and band C of 1,10-phenanthroline) appear as doublet bands in both the solution and solid spectra of 5-amino-1,10-phenanthroline.

Bellamy (1), has discussed the absorptions found with primary amine hydrochlorides. Methylamine hydrochloride was reported to absorb at 3075 cm^{-1} and 2972 cm^{-1} , and the N-H deformation absorption was observed at 1617 cm^{-1} .

In the 4,7-diamino-1,10-phenanthrolium dichloride spectrum, a weak shoulder appears at 3226 cm^{-1} which is assigned

to the N-H stretching mode. The N-H deformation band is found at 1647 cm^{-1} which is at a slightly higher frequency than found in the free base of 5-amino-1,10-phenanthroline. A peak of fairly weak intensity at 1289 cm^{-1} is considered as due to the C-N stretching vibration in the diamine derivative. No weak absorption in the 2100 cm^{-1} region is noted in the 4,7-diamino-1,10-phenanthrolium dichloride spectrum as found in section III, A, with the two 1,10-phenanthroline acid salts. It is assumed that the so called "immonium bands" (69) are not present (no hydrogen atoms are bonded to the nitrogen atoms of 1,10-phenanthroline), and the hydrogen atoms are bonded to the amine group giving two NH_3^+ radicals.

c. Infrared spectra of aza-1,10-phenanthroline The spectra of seven aza derivatives of 1,10-phenanthroline were obtained and are recorded in Figures 110 through 116. These compounds contain one or two extra nitrogen atoms within the 1,10-phenanthroline ring system. The 2-aza derivatives present a new vibration (the N=N stretching mode) not encountered earlier in the 1,10-phenanthrolines.

Bellamy (1) has indicated that very little information is known on the absorptions produced by the N=N vibration. However, this absorption would be expected in the 1600 cm^{-1} vibration region. Bellamy (1) has summarized the work of

Figure 110. Infrared spectrum of 2-aza-1,10-phenanthroline

Figure 111. Infrared spectrum of 3-aza-1,10-phenanthroline

Figure 112. Infrared spectrum of 4-aza-1,10-phenanthroline

Figure 113. Infrared spectrum of 5-aza-1,10-phenanthroline

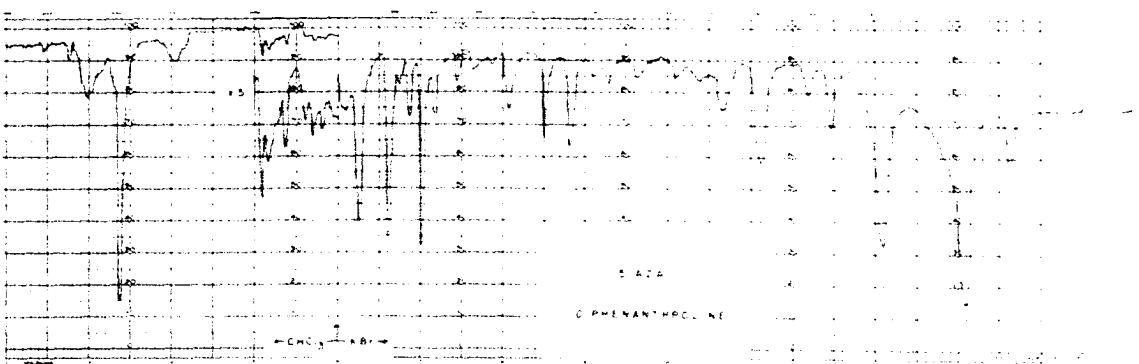
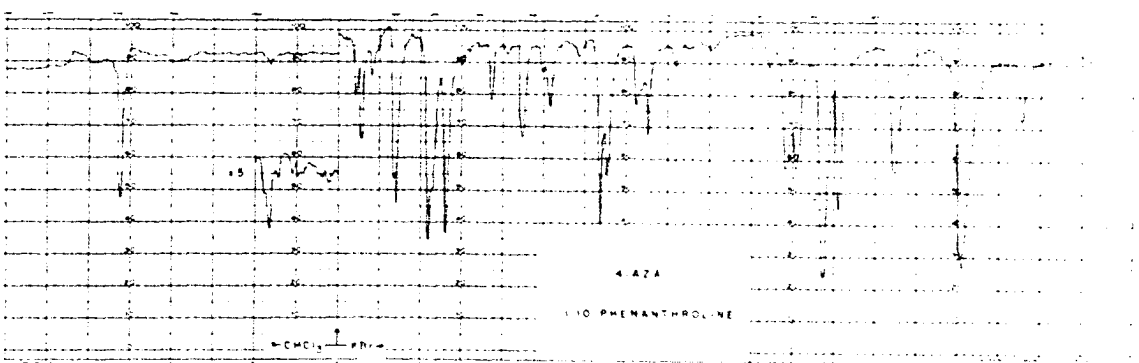
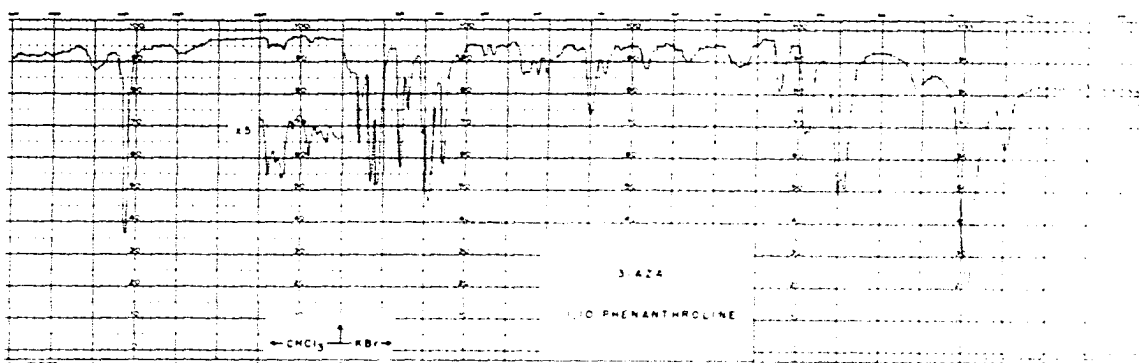
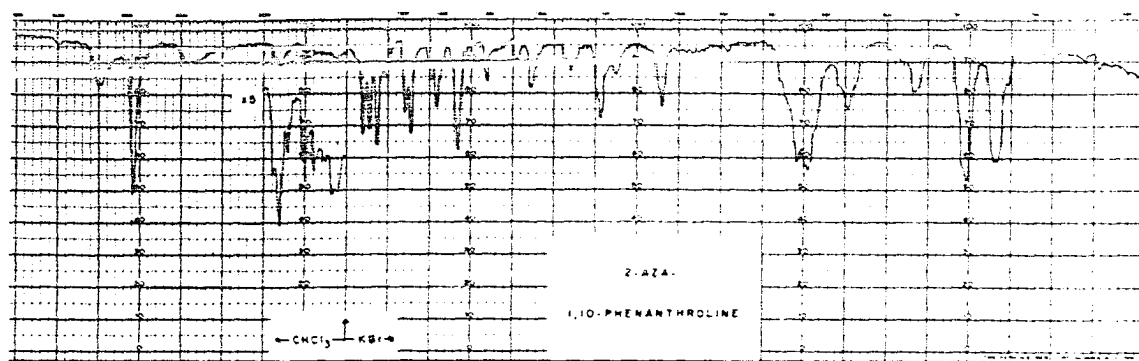
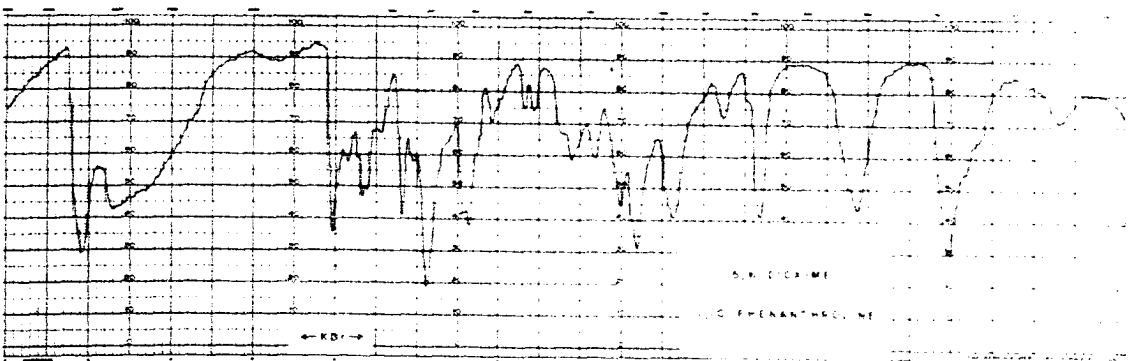
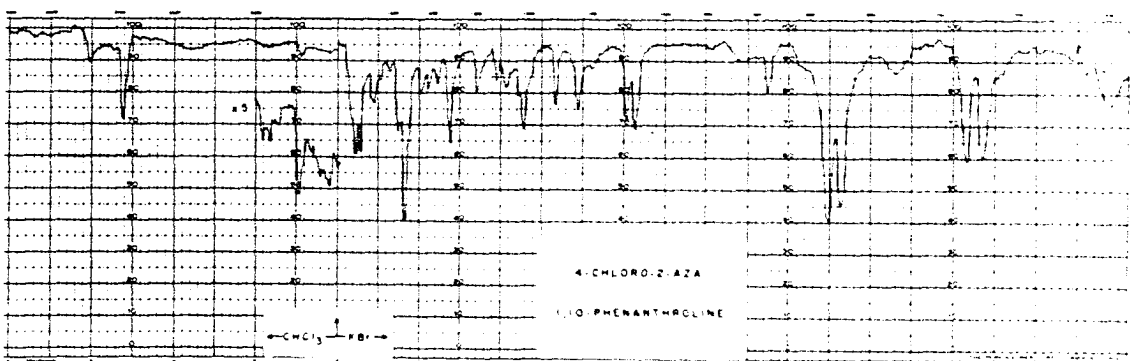
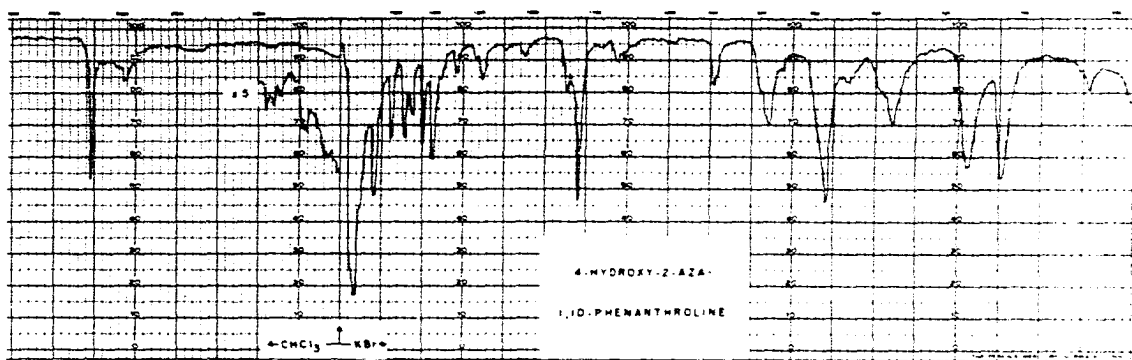
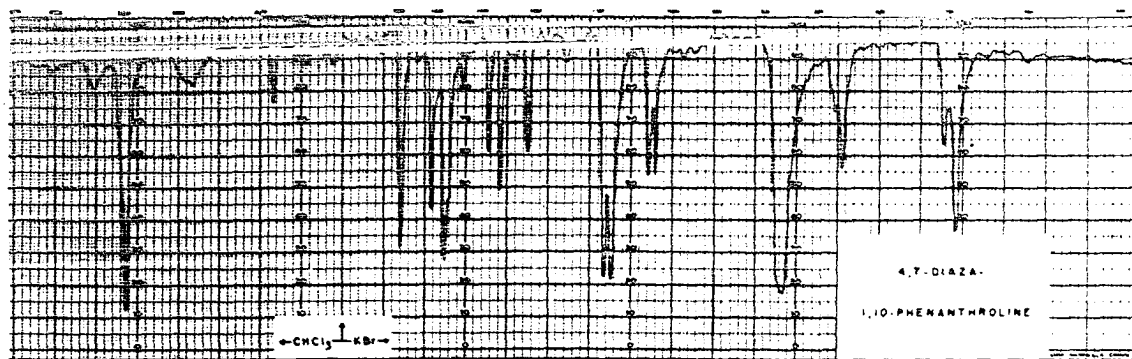


Figure 114. Infrared spectrum of 4,7-diaza-1,10-phenanthroline

Figure 115. Infrared spectrum of 4-hydroxy-2-aza-1,10-phenanthroline

Figure 116. Infrared spectrum of 4-chloro-2-aza-1,10-phenanthroline

Figure 117. Infrared spectrum of 5,6-dioxime-1,10-phenanthroline



several authors who investigated possible N=N absorptions in tetrazole, formazans, and aromatic diazo-compounds. He concluded that the absorption intensity of this N=N band is probably weak and also possibly merges with strong C=C bands. No useful correlations for this group have been noted. Bellamy (1) also has reported that a possible characteristic absorption for the -C-N=N-C- skeleton may exist, and he cites one example where an absorption at 927 cm^{-1} is found which could be attributed to this group.

With C=C and C=N groups in the same molecule in these 2-aza-1,10-phenanthroline compounds, the differentiation of an absorption for the N=N vibration would probably be quite difficult. The investigation of the spectra of the three 2-aza-1,10-phenanthroline derivatives (in Figures 110, 115, and 116) reveals the absence of the usual third strong absorption (band C of 1,10-phenanthroline) in the ring vibration region. Instead, two medium to weak absorptions are observed in the $1429\text{-}1425\text{ cm}^{-1}$ and $1412\text{-}1403\text{ cm}^{-1}$ ranges. The spectra of the four other aza-1,10-phenanthroline compounds contain strong absorption in the $1427\text{-}1408\text{ cm}^{-1}$ range as observed before with the majority of 1,10-phenanthrolines. Apparently the 2-aza-1,10-phenanthrolines could be distinguished from other aza derivatives by the reduced intensity of this third ring vibration absorption.

A strong absorption not usually found in this region in the spectra of 1,10-phenanthrolines is observed at 1361 cm^{-1} and 1355 cm^{-1} in the 2-aza- and 4-chloro-2-aza-1,10-phenanthroline spectra, respectively. This band could not be related to the N=N vibration, however, since a similar strong peak is found in the 4-aza- and 4,7-diaza-1,10-phenanthroline spectra at 1366 cm^{-1} and 1379 cm^{-1} . No absorption appears in this region with 5-aza- and 4-hydroxy-2-aza-1,10-phenanthroline, however. No peak is found near 927 cm^{-1} which could be related to the -C=N=N-C- skeleton as was reported by Bellamy (1).

The shift to lower frequency of the aromatic C-H stretching absorption noted before in spectra of other 1,10-phenanthroline derivatives when using chloroform as the solvent is not so pronounced with the aza-1,10-phenanthroline compounds. The 2-aza-1,10-phenanthroline spectrum is the only exception with a sharp absorption occurring at 2924 cm^{-1} in chloroform. This absorption is observed in the $2976\text{-}2959\text{ cm}^{-1}$ range in the chloroform spectra of the other six aza-1,10-phenanthrolines.

An extra peak of medium to strong intensity at 1570 cm^{-1} appears within the usual triplet ring vibration (band A of 1,10-phenanthroline) in the spectrum of 2-aza-1,10-phenanthroline. Splitting of the second ring vibration (band B of 1,10-phenanthroline) is observed in the spectra of 2-aza-,

3-aza-, 4-aza-, and 4-chloro-2-aza-1,10-phenanthroline.

d. Infrared spectrum of 5,6-dioxime-1,10-phenanthroline

Bellamy (1) has reported the free O-H stretching frequency for the N-O-H group in oximes in the $3650\text{--}3500\text{ cm}^{-1}$ range. The C=N absorption for the oxime group was observed with various oxime compounds near 1667 cm^{-1} . Palm and Werbin (45) gave tentative assignments for the O-H deformation near 1300 cm^{-1} and the N-O-H stretching mode near 920 cm^{-1} , since no similar absorptions were found with corresponding aldehydes.

The spectrum of 5,6-dioxime-1,10-phenanthroline is recorded in Figure 117. This spectrum is not too sharp in most regions. A strong absorption at 3413 cm^{-1} is assigned to the O-H stretching vibration. This frequency is somewhat lower than that reported by Bellamy for the free O-H stretching frequency, but with the oxime as a solid pressed in potassium bromide, hydrogen bonding could occur which would result in a lower frequency absorption for the O-H stretching mode. The C=N absorption is observed at 1675 cm^{-1} as a peak of strong intensity. A strong band at 1307 cm^{-1} appears to correspond to the O-H deformation mode noted Palm and Werbin (45). The strong peak at 895 cm^{-1} could not be definitely attributed to the N-O-H stretching vibration, since many of the other 5,6-disubstituted 1,10-phenanthrolines with other substituents have strong absorption in this region also.

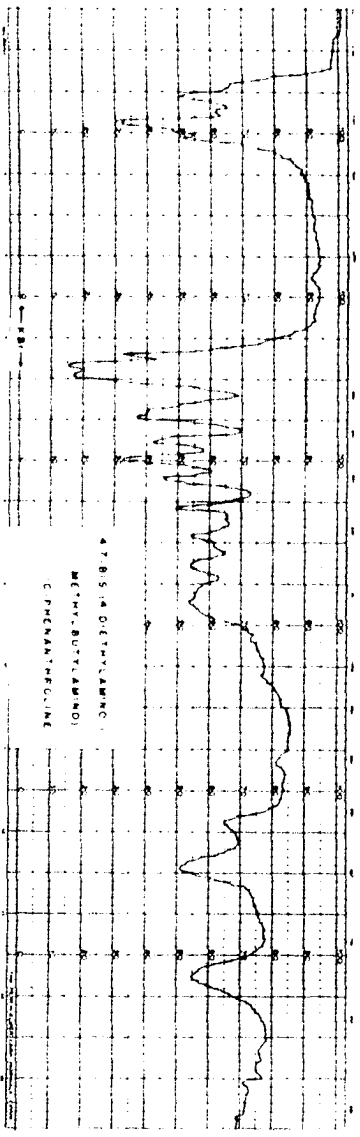
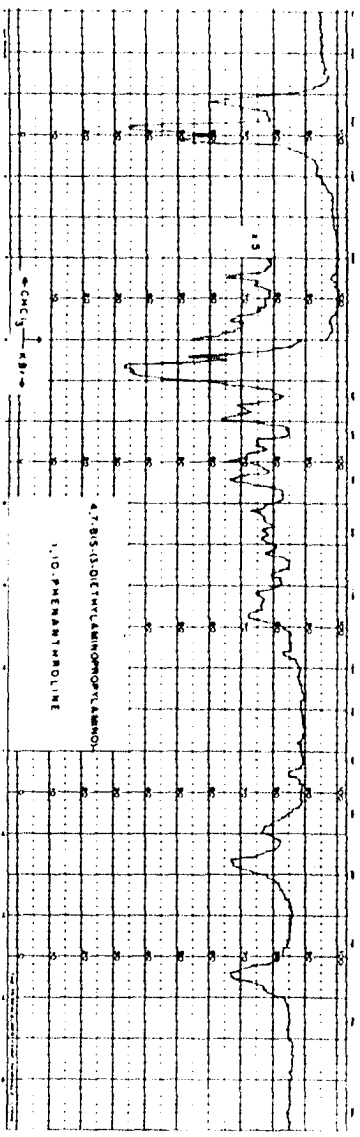
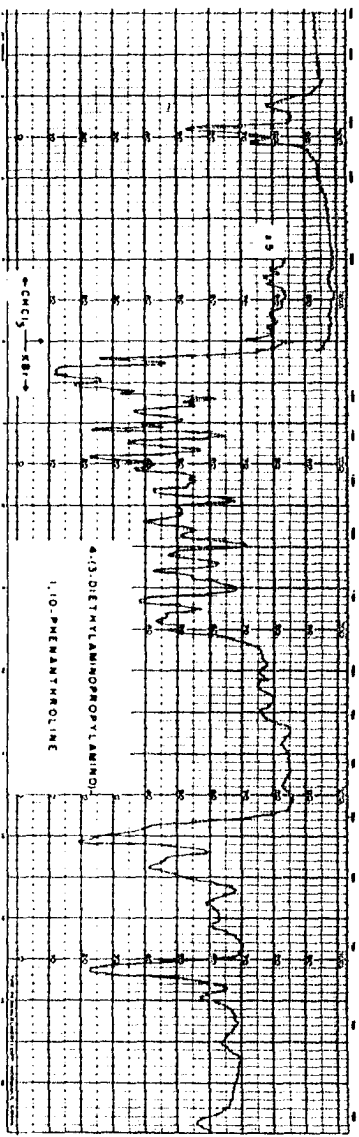
e. Infrared spectra of dialkylaminoalkylamino-1,10-phenanthrolines Bellamy (1) summarized the data appearing in the literature on secondary amines, and the bands associated with the N-H group. He reported a single free N-H stretching absorption of medium intensity in the $3500-3300\text{ cm}^{-1}$ range when using dilute solutions. In concentrated solutions a second band at lower frequencies was sometimes observed. The N-H deformation absorption for secondary aliphatic amines was noted by Bellamy to be of very weak intensity in the $1650-1550\text{ cm}^{-1}$ range. With aromatic secondary amines the distinguishing of this absorption was difficult because of the presence of the aromatic ring C=C absorptions in the same region. Also in some instances the latter absorption was observed to be intensified with a nitrogen atom directly bonded to the ring. Colthup (20) has reported a strong band in the $1350-1280\text{ cm}^{-1}$ range which Bellamy interpreted as corresponding to the C-N stretching vibration for secondary amines. The C-N stretching vibration for tertiary amines was noted in the $1360-1310\text{ cm}^{-1}$ region.

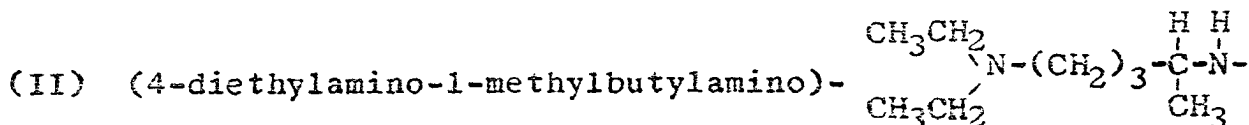
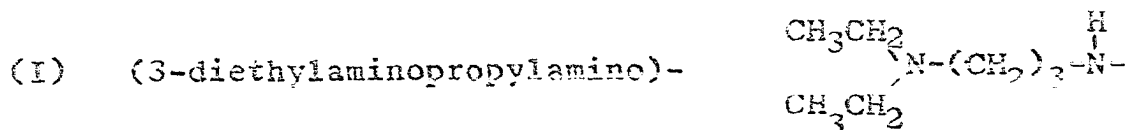
The infrared spectra of three dialkylaminoalkylamino-1,10-phenanthrolines are recorded in Figures 118 through 120. Some of these materials are not very pure, and consequently the spectra obtained are not well defined in some regions. The structures of the two groups substituted in the three 1,10-phenanthrolines in this section are:

Figure 118. Infrared spectrum of 4-(3-diethylaminopropylamino)-1,10-phenanthroline

Figure 119. Infrared spectrum of 4,7-bis-(3-diethylaminopropylamino)-1,10-phenanthroline

Figure 120. Infrared spectrum of 4,7-bis-(4-diethylamino-1-methylbutylamino)-1,10-phenanthroline





In each case both secondary and tertiary amine groups are present. The N-H stretching absorption is observed with these materials as a single peak of medium intensity at 3279-3226 cm^{-1} in the potassium bromide spectra and at 3226-3195 cm^{-1} in the chloroform solution spectra. Both of these frequency ranges found are lower than that noted by Bellamy for the free N-H stretching band. It appears that in both chloroform and potassium bromide, association had occurred causing the shift of this peak to lower frequency. No absorption which could be assigned to the aromatic C-H stretching vibration is observed in either the potassium bromide or chloroform spectra. The second and third absorption in this region are assumed as due to the in-phase CH_2 and the out-of-phase CH_2 vibrational modes of these 1,10-phenanthroline derivatives. Bellamy (1) reported these absorptions at 2926 cm^{-1} and 2853 cm^{-1} , respectively, in other compounds. The methyl bands which Bellamy reported at 2962 cm^{-1} and 2872 cm^{-1} are not resolved in the spectra of these three dialkylaminoalkylamino-1,10-phenanthrolines. The out-of-phase CH_2 absorptions with these compounds are found in the 2809-2793 cm^{-1} range which is at a

lower frequency than generally reported above.

The absorptions found in the ring vibration region are observed to be quite intense, particularly those in the 1580-1531 cm^{-1} range. These peaks are much stronger than generally observed for the ring vibration triplet absorption (band A of 1,10-phenanthroline), thus it appears that the aromatic C=C and C=N ring vibration absorptions may have been intensified (as was suggested above) with a nitrogen atom of the secondary amine bonded to the ring system. In general the appearance of this ring vibration region is much different with these substituents than found with 1,10-phenanthroline and the other substituted 1,10-phenanthrolines. A medium to strong absorption was found in the 1348-1333 cm^{-1} range which is apparently due to the C-N stretching vibration for either the secondary or tertiary amine. An absorption, related to the methylene group deformation which was reported near 1465 cm^{-1} (1), is observed as a weak to medium intensity band in the 1471-1460 cm^{-1} region in spectra of these compounds. This peak is very poorly resolved in the spectrum of 4,7-bis-(4-diethylamino-1-methylbutylamino)-1,10-phenanthroline. The symmetrical deformation mode for the methyl group is found at 1383-1376 cm^{-1} as a weak to medium absorption.

4. Infrared spectra of the R-R' group of 1,10-phenanthrolines

The spectra of these eight of the 1,10-phenanthroline

compounds are recorded in Figures 121 through 128. The characteristic absorptions noted earlier for the methyl group are found in general in the spectra of these derivatives which contained methyl substitution. Extra peaks are observed within the usual triplet (band A of 1,10-phenanthroline) in the spectra of 3-phenyl-4-chloro-, 3-phenyl-4-bromo-, 2,9-dimethyl-4,7-diphenyl-, and 2,9-diphenyl-4,7-dimethyl-1,10-phenanthroline. Splitting of the second ring vibration absorption (band B of 1,10-phenanthroline) is observed in some cases. As found before with phenyl-1,10-phenanthrolines, three peaks are sometimes observed instead of two as generally noted with most derivatives (see the spectra of 3-phenyl-4-chloro-, 3-phenyl-4-bromo-, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). In the 3,8-diphenyl-4,7-dichloro- and 3,8-diphenyl-4,7-dibromo-1,10-phenanthroline spectra, a band of medium intensity is present on the high frequency side of the third ring vibration absorption (band C of 1,10-phenanthroline). As discussed in section IV, C, the chloro and bromo derivatives have very similar spectra with peaks in spectra of the bromo compounds at slightly lower frequencies. This trend is observed also in comparing the spectra of 3-phenyl-4-chloro- with 3-phenyl-4-bromo-1,10-phenanthroline and the spectra of 3,8-diphenyl-4,7-dichloro- with 3,8-diphenyl-4,7-dibromo-1,10-phenanthroline. The major differences occur in the 900-650 cm^{-1} region. As discussed in section V, E, the presence

Figure 121. Infrared spectrum of 3-methyl-7-chloro-1,10-phenanthroline

Figure 122. Infrared spectrum of 3-phenyl-4-chloro-1,10-phenanthroline

Figure 123. Infrared spectrum of 3-phenyl-4-bromo-1,10-phenanthroline

Figure 124. Infrared spectrum of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

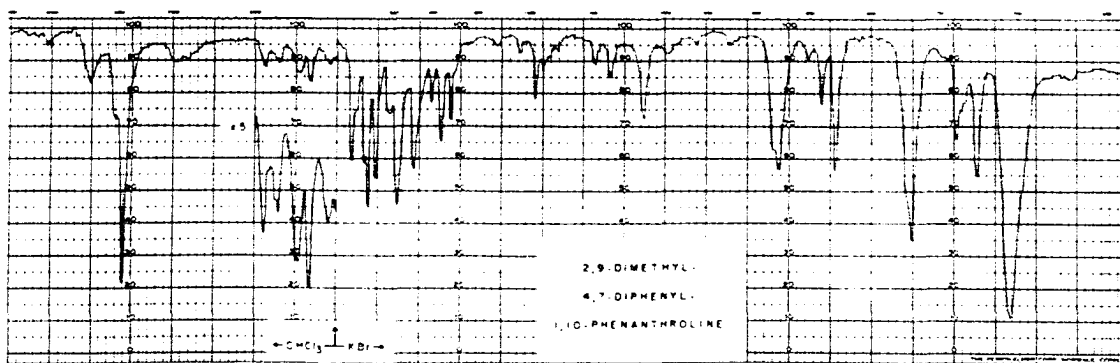
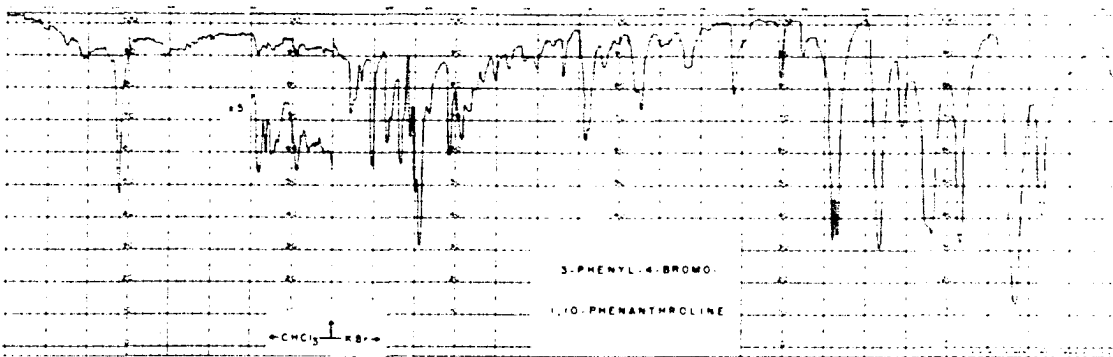
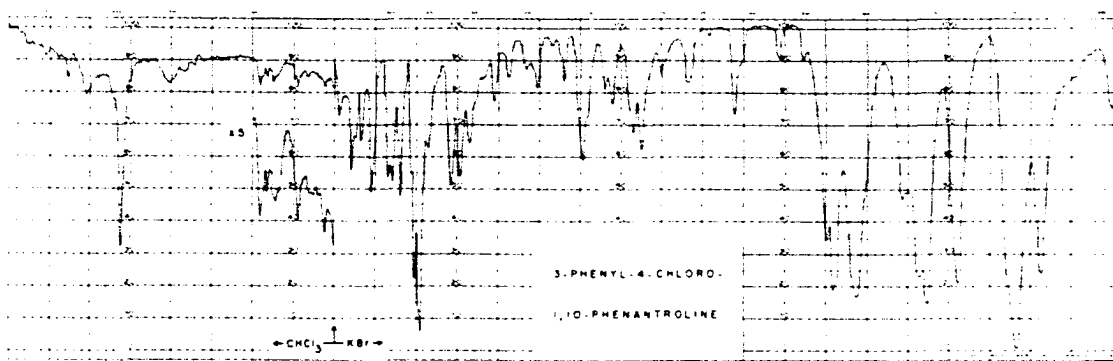
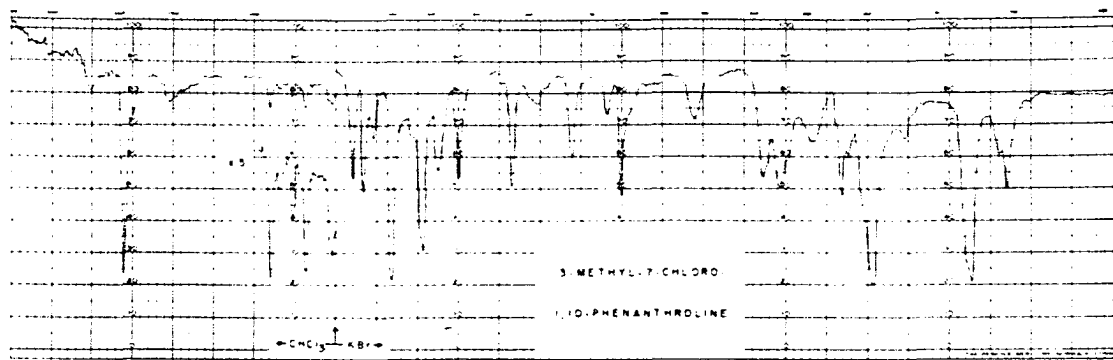
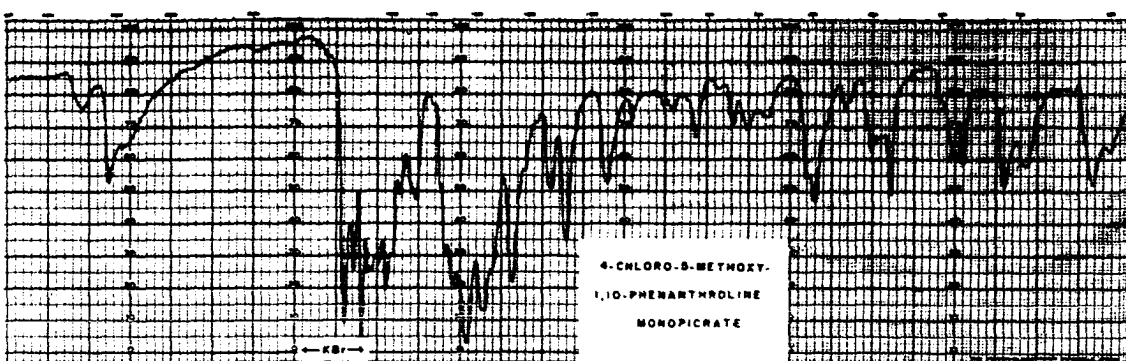
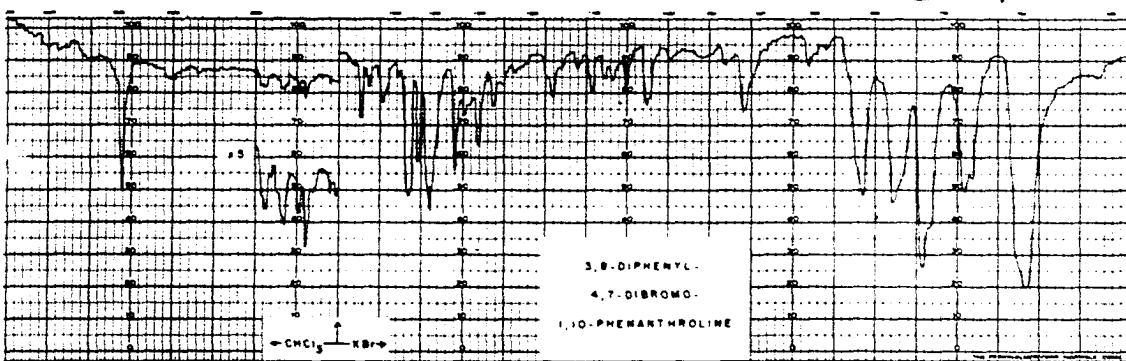
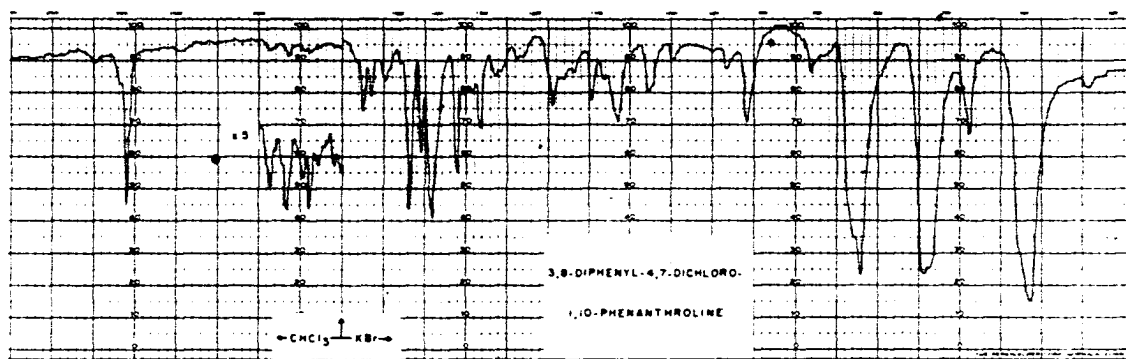
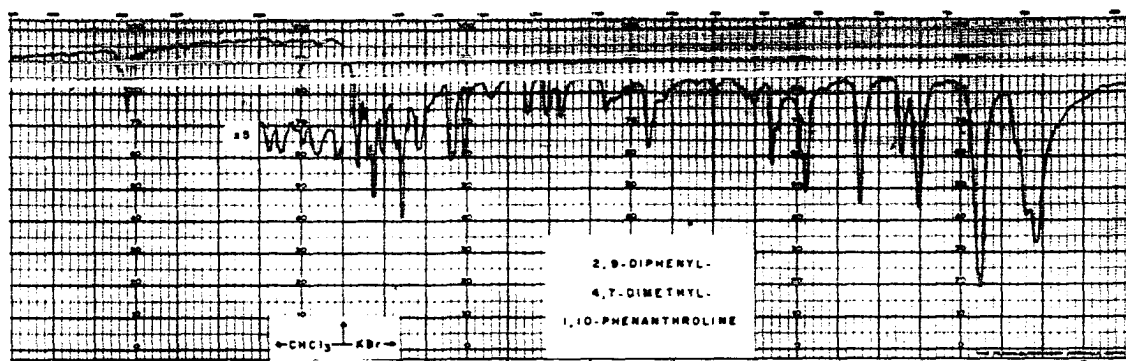


Figure 125. Infrared spectrum of 2,9-diphenyl-4,7-dimethyl-1,10-phenanthroline

Figure 126. Infrared spectrum of 3,8-diphenyl-4,7-dichloro-1,10-phenanthroline

Figure 127. Infrared spectrum of 3,8-diphenyl-4,7-dibromo-1,10-phenanthroline

Figure 128. Infrared spectrum of 4-chloro-5-methoxy-1,10-phenanthroline monopicrate



of phenyl substitution is detected by the presence of strong absorption in the $713\text{-}690\text{ cm}^{-1}$ region.

Kross and Fassel (38) have reported absorption frequencies for the picrate of 1,10-phenanthroline. The asymmetric nitro stretching vibration was observed at 1545 cm^{-1} , and the C-H out-of-plane bending frequency was found at 784.9 cm^{-1} with the above compound. In the spectrum of the picrate of 4-chloro-5-methoxy-1,10-phenanthroline, numerous bands are observed in the $1667\text{-}1200\text{ cm}^{-1}$ region due to vibrations of the nitro groups of the picrate radical. The ring vibration region is more complicated than usual. Still the similar shifts of the ring vibrations to higher frequency observed before with the acid salts of 1,10-phenanthroline and 1,10-phenanthroline methiodide are detected here with the three peaks of the triplet ring vibration (band A of 1,10-phenanthroline). The second and third ring vibration absorptions (bands B and C of 1,10-phenanthroline) could not be distinguished due to the nitro asymmetric absorption in this region (the strongest peak appearing at 1515 cm^{-1}). The symmetric stretching vibration of the nitro group is observed at 1319 cm^{-1} , the strongest absorption among several bands in this region.

5. The infrared spectra of the cycloalkeno and substituted six membered unsaturated ring derivatives of 1,10-phenanthroline

Bellamy (1) reported two characteristic absorptions at

2926 cm^{-1} and 2853 cm^{-1} for the methylene group which corresponded to the in-phase and out-of-phase vibrations of the hydrogen atoms on the CH_2 group. Plyler and Acquista (47) have investigated a number of cyclopentane and cyclohexane compounds, and they did not observe any great shift for these methylene vibrations from the usual frequencies observed. Cyclopentane absorbs at 2959 cm^{-1} and 2853 cm^{-1} , and cyclohexane absorbs at 2934 cm^{-1} and 2845 cm^{-1} . Bellamy noted that with smaller rings, frequency shifts occur for these C-H stretching absorptions due to ring strain. The normal C-H deformation absorption for the methylene group was noted by Bellamy (1) in the $1465 \pm 20 \text{ cm}^{-1}$ range. He also reported that shifts with saturated rings are not large, and with the larger rings the normal values given above are generally found.

The spectra of the cycloalkeno and substituted six membered unsaturated ring derivatives of 1,10-phenanthroline are recorded in Figures 129 through 138. Absorptions assigned to the methylene bands in the cycloalkeno-1,10-phenanthrolines are observed in the 3000-2800 cm^{-1} region. The aromatic C-H stretching absorption is not readily observed in carbon tetrachloride and potassium bromide disk spectra and appears only as a weak shoulder in the 3040-3012 cm^{-1} range. The strong absorptions in the chloroform solution spectra at 2959-2915 cm^{-1} range are probably due to the shifted C-H stretching band and not to the in-phase CH_2 vibration. Strong absorptions are

Figure 129. Infrared spectrum of 2,3-benzo-1,10-phenanthroline

Figure 130. Infrared spectrum of 3,4-cyclopenteno-1,10-phenanthroline

Figure 131. Infrared spectrum of 3,4-cyclohexeno-1,10-phenanthroline

Figure 132. Infrared spectrum of 3,4-cyclohepteno-1,10-phenanthroline

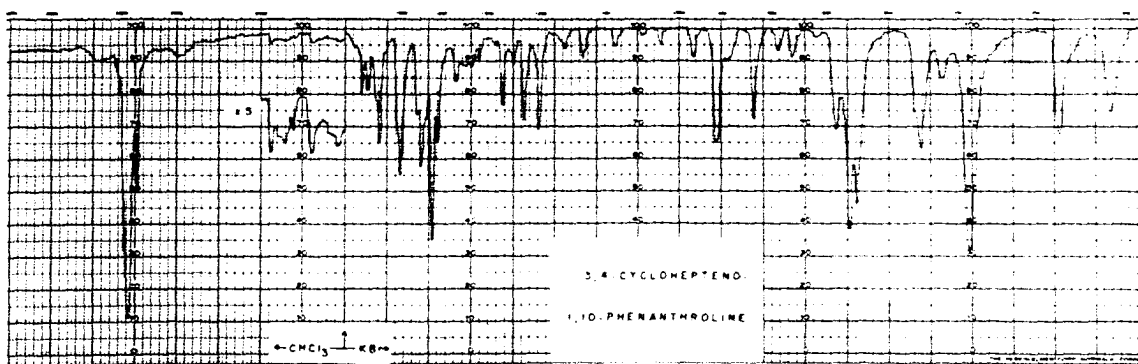
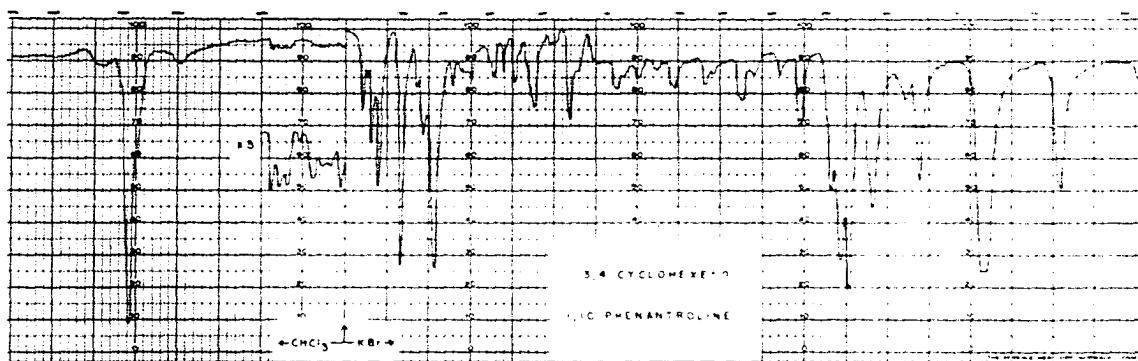
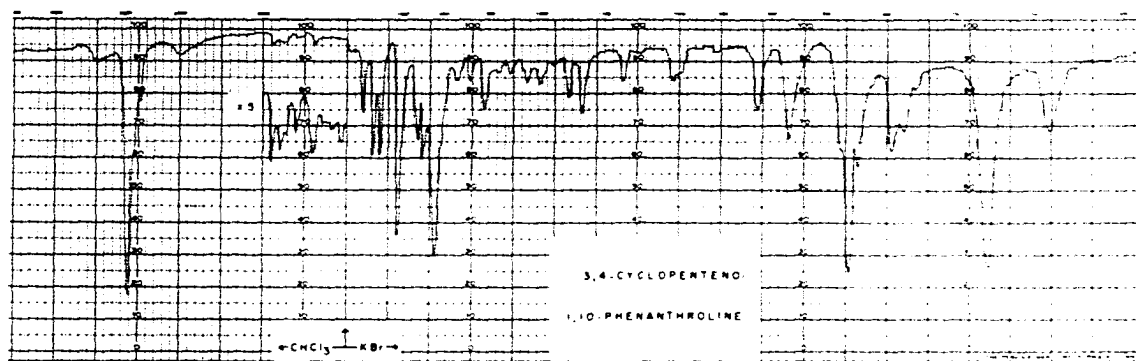
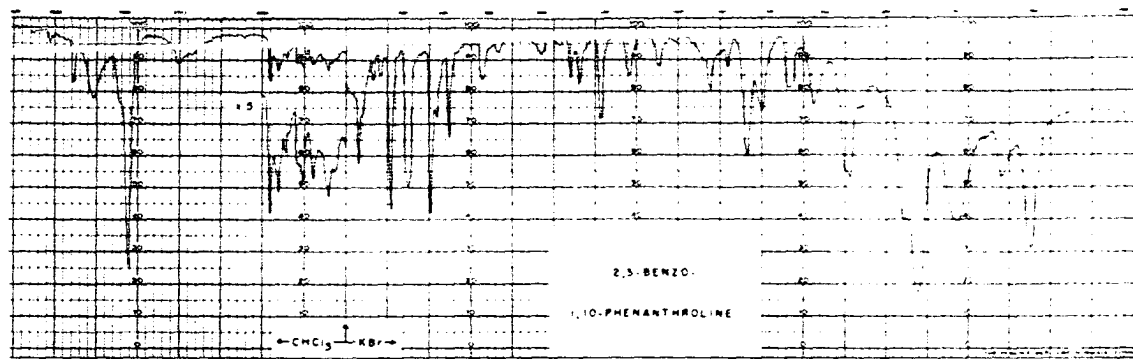


Figure 133. Infrared spectrum of 3,4-cycloocteno-1,10-phenanthroline

Figure 134. Infrared spectrum of 5,6-cyclohexeno-1,10-phenanthroline

Figure 135. Infrared spectrum of 5,6-benzo-1,10-phenanthroline

Figure 136. Infrared spectrum of 5,6-pyrido-(2,3 f)-1,10-phenanthroline

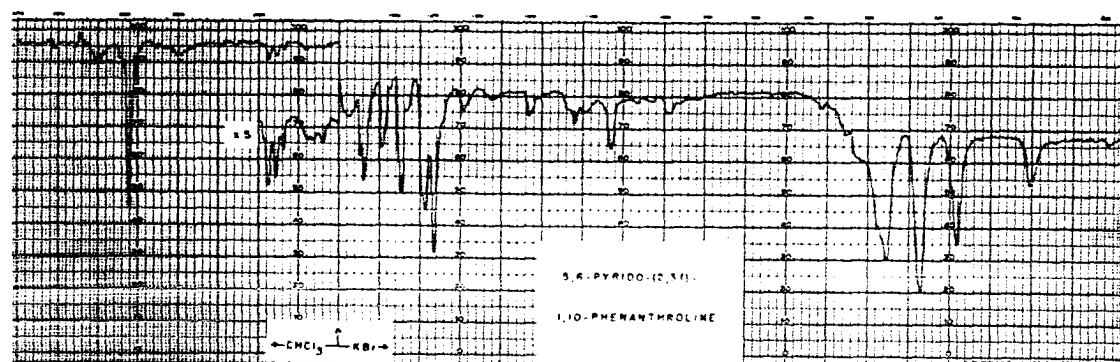
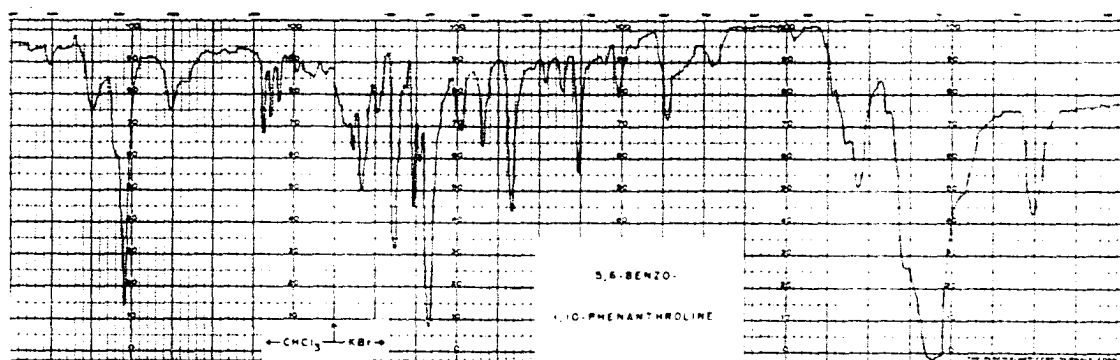
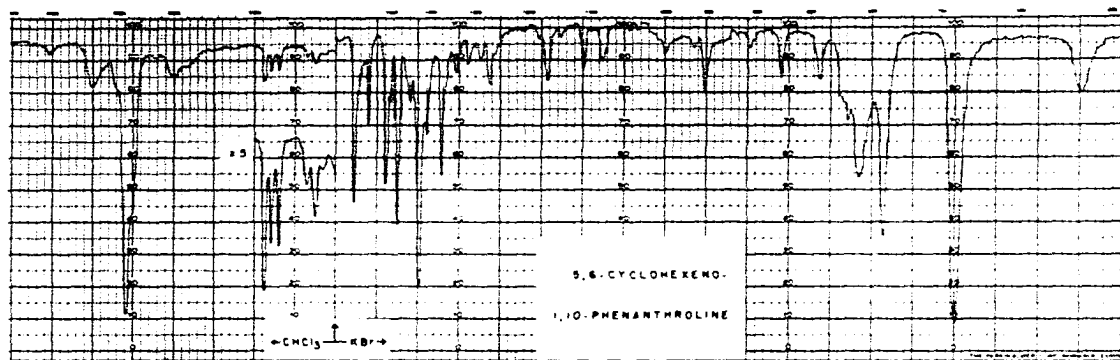
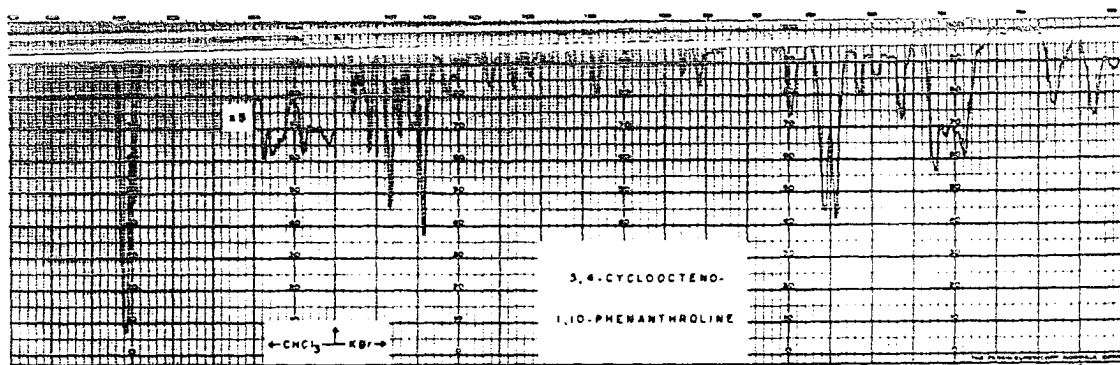
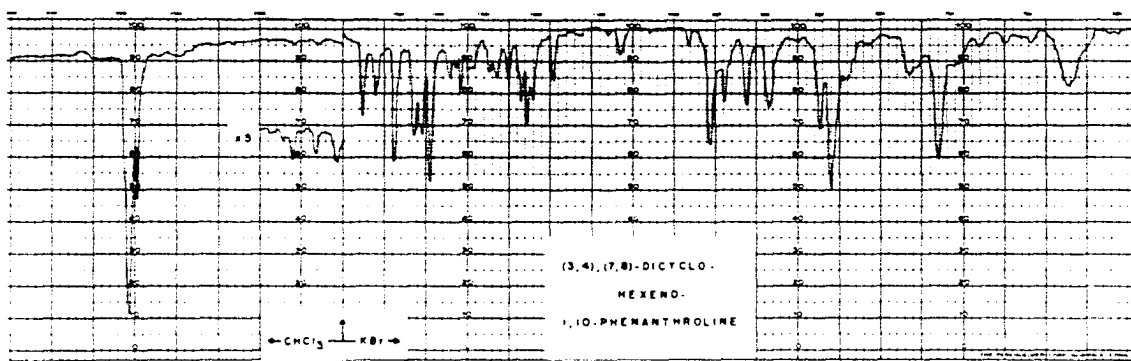
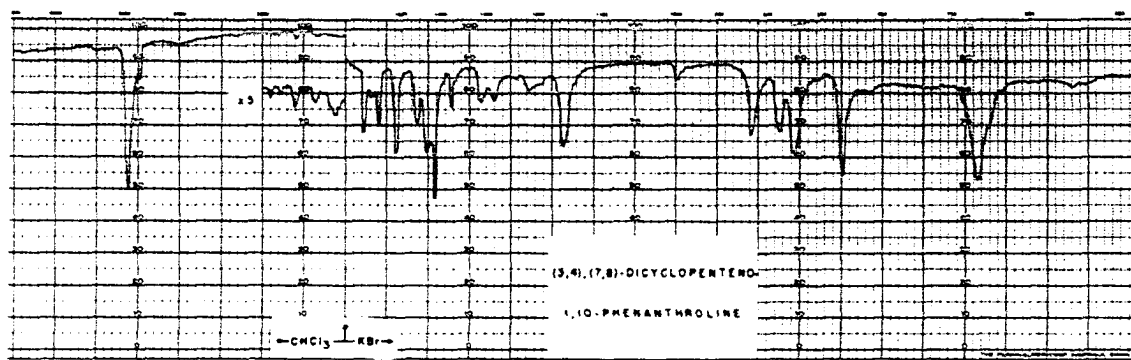


Figure 137. Infrared spectrum of (3,4),(7,8)-dicyclopenteno-1,10-phenanthroline

Figure 138. Infrared spectrum of (3,4),(7,8)-dicyclohexeno-1,10-phenanthroline



observed in the potassium bromide and carbon tetrachloride spectra in the 2959-2907 cm^{-1} and 2857-2825 cm^{-1} regions which are assigned to the in-phase and out-of phase vibrations of the hydrogens of the methylene groups, respectively. Most of these spectra are not very resolved in this region, and the use of lithium fluoride or calcium fluoride optics would be required to obtain better detail. The C-H deformation absorption of the methylene group in the cycloalkeno derivatives of 1,10-phenanthroline are observed in potassium bromide disk spectra in the 1460-1445 cm^{-1} range as a shoulder to a medium peak. The first component of the triplet ring vibration absorption (band A of 1,10-phenanthroline) is observed at lower frequency in spectra of the 5,6-substituted compounds of this group.

Extra peaks or shoulders appear in the first ring vibration triplet absorption in the spectra of 2,3-benzo-, 3,4-cyclohexeno-, and 3,4-cyclohepteno-1,10-phenanthroline. A new medium to strong absorption is found in the 1534-1529 cm^{-1} range with both benzo derivatives and the pyrido compound. Splitting of the second ring vibration absorption does not occur in general with these compounds. However, in the 5,6-cyclohexeno-1,10-phenanthroline spectrum, a weak shoulder at 1499 cm^{-1} and a new, strong band at 1481 cm^{-1} are observed on the low frequency side of the second ring vibration absorption

at 1511 cm^{-1} . With 3,4-cycloocteno-1,10-phenanthroline, a medium absorption at 1473 cm^{-1} also appears on the low frequency side of the second ring vibration absorption at 1499 cm^{-1} .

V. CHARACTERIZATION OF SUBSTITUTION ON

1,10-PHENANTHROLINE

In this section attempts will be made to characterize the position or positions of substituents on the 1,10-phenanthroline rings using infrared spectra. The spectra studied, from 5000 to 650 cm^{-1} , will be divided into several convenient frequency ranges, and each of these ranges will be discussed individually.

A. The 5000-2000 cm^{-1} Region

Sodium chloride optics were used throughout this study. Since the dispersion with the sodium chloride prism in this region is low, the resolution obtained here is not good enough to give detailed information on the absorptions in this range. Lithium fluoride and calcium fluoride prisms have been reported (68) to give much better resolution in this region. In the spectra which were obtained, no trends were observed which could be related with any certainty to the kind of substitution in the 1,10-phenanthroline molecule.

B. The 2000-1667 cm^{-1} Region

Young et al. (70) first reported the use of this region to characterize substitution on the benzene ring. Typical absorption patterns were obtained for various types of substi-

tuted benzene compounds irrespective of the nature of the substituent. As usual in such work some exceptions were noted. Another study of this region was reported by Cook and Church (21) who found typical absorption patterns in the 2080-1667 cm^{-1} region for various mono- and disubstituted pyridines. Again the character of the patterns was different for each arrangement of the substituents and essentially independent of the nature of the substituents. Shindo (54) felt that with the usual conditions of measurement which he used for obtaining spectra (five to six per cent solutions in carbon disulfide with a 0.1 mm cell), the absorptions in this region for pyridines were too weak and too complex to be of any practical use (except for 4-substituted pyridines which gave a weak, but sharp peak at 1950-1920 cm^{-1}). Fuson and Josien (25) investigated this region also in their study of substituted 1,2-benanthracenes. They indicated that the region was not very dependable in identifying substitution position, but did note regularities which were useful. However, only methyl substituted compounds were used in their study.

Bellamy (1) has discussed the use of this region for substitution identification of benzene compounds. Since the bands are relatively weak, he recommended, as did Young et al. (70), the use of fairly thick cells for investigating this region (0.1 mm cell for liquid samples and 1.0 mm cell for ten per cent solutions of solid samples). Consideration of

the intensity and the number of peaks in this region was found to be more important than the frequencies at which the absorptions occurred. Causes of interference with the observed patterns in the 2000-1650 cm^{-1} region were discussed by Bellamy (1). Fundamental frequencies which appeared in this range, such as with carbonyl, were noted to mask a large part of the region and make it less useful. Overtone bands of absorptions at lower frequencies sometime also appeared in this region as an additional peak. As observed by Young et al. (70), certain groups (as fluoride, ether, and nitro) caused great changes in the usual patterns found.

Young et al. (70) attributed these absorptions to overtone and combination bands. Whiffen (65) demonstrated that the absorptions found in spectra of benzene compounds could be assigned to summation bands of the out-of-plane C-H bending vibrations which occurred in the 1000-700 cm^{-1} range. Since the fundamental C-H absorptions depended on substitution type, the summation bands were then also dependent on the substitution type. Young et al. (70) observed that the patterns became simpler with increasing substitution (with fewer ring hydrogens present and correspondingly a smaller number of out-of-plane C-H fundamentals). With the more symmetrical molecules, the patterns were simpler also. These authors (70) indicated that ring skeletal frequencies must also be important in contributing to these patterns.

1. Experimental

The spectra in this region were obtained on the Perkin-Elmer Model 21 Infrared Spectrophotometer using sodium chloride optics. The x5 ordinate expansion on this instrument, as described by Coates and Anacreon (19), was employed to obtain a magnified trace. This expansion was quite convenient in that the two per cent solutions ordinarily used in a 0.5 mm cell for obtaining the complete spectrum were quite satisfactory. More concentrated solutions were not necessary to obtain a reasonably intense and sharp pattern in this region. Spectra of several pyridine derivatives were obtained in this manner, and patterns were compared to those recorded by Cook and Church (21). The agreement was very good, and the absorptions in the patterns obtained using the x5 expansion were more intense and much better resolved than those reported by Cook and Church.

Chloroform was used as the solvent in all cases. Spectra obtained using carbon tetrachloride agreed very well in this region. In many instances the 1,10-phenanthrolines were not soluble in this latter solvent, however, so chloroform was preferred as the general solvent. Expansion of the potassium bromide disk spectra in this region gave sharp patterns in many cases. These patterns were not too useful since in most instances comparison in this region of potassium bromide disk spectra of other compounds with the same

substitution type gave much different patterns. Also these patterns from potassium bromide spectra did not agree generally with the patterns obtained from solution spectra.

2. Spectra obtained in the 5.0-6.0 micron (2000-1667 cm^{-1}) region

The spectra obtained in the 5.0-6.0 micron (2000-1667 cm^{-1}) region are recorded in Figures 139 through 156. In each case, the absorptions reproduced are from the x5 expanded spectra obtained in chloroform solution. The patterns are arranged into substitution position groups in cases where more than one example of a certain substitution type was available. In Figure 156 a group of patterns were recorded from miscellaneous methyl substituted 1,10-phenanthrolines of which there were no other correspondingly substituted compounds which were soluble in chloroform. The units in these traces are linear in wavelength (microns). This magnified region is also reproduced in the spectra given in section IV for all chloroform soluble 1,10-phenanthrolines.

3. Discussion

All absorption positions which are noted in the discussion of this region are given in microns with the corresponding frequency values following in parenthesis. This procedure is followed since the patterns were reproduced on a linear scale in microns and frequency divisions are given

only at the boundaries of this region. In general, the discussions below are centered around observations of exceptions and around noteworthy conformities found in the patterns with the various substitution groups.

The expanded spectrum in the 5.0-6.0 micron (2000-1667 cm^{-1}) region of unsubstituted 1,10-phenanthroline is recorded in Figure 1 together with the entire spectrum. Four major peaks are present which progressively decrease in intensity with increasing wavelength. The first three peaks are grouped in a triplet absorption, and these bands appear in several of the other patterns obtained from the spectra of 1,10-phenanthroline derivatives of various substitution types. This triplet absorption is not reproduced exactly in the spectra of substituted 1,10-phenanthrolines, for slight variations in the intensities and positions of these peaks appear.

a. Monosubstituted derivatives Four types of monosubstituted 1,10-phenanthrolines were investigated. In Figures 139, 140, 141, and 142 are recorded the patterns of 2-, 3-, 4-, and 5-monosubstituted 1,10-phenanthrolines. Each of these monosubstituted pattern groups is quite distinctive. Among the 2-substituted derivatives, 2-hydroxy-1,10-phenanthroline does not resemble those of other 2-monosubstituted derivatives. This probably is the result of tautomerism, a matter which is discussed in section IV, E. Evidence presented before indi-

Figure 139. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 2-monosubstituted-1,10-phenanthrolines

Figure 140. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3-monosubstituted-1,10-phenanthrolines

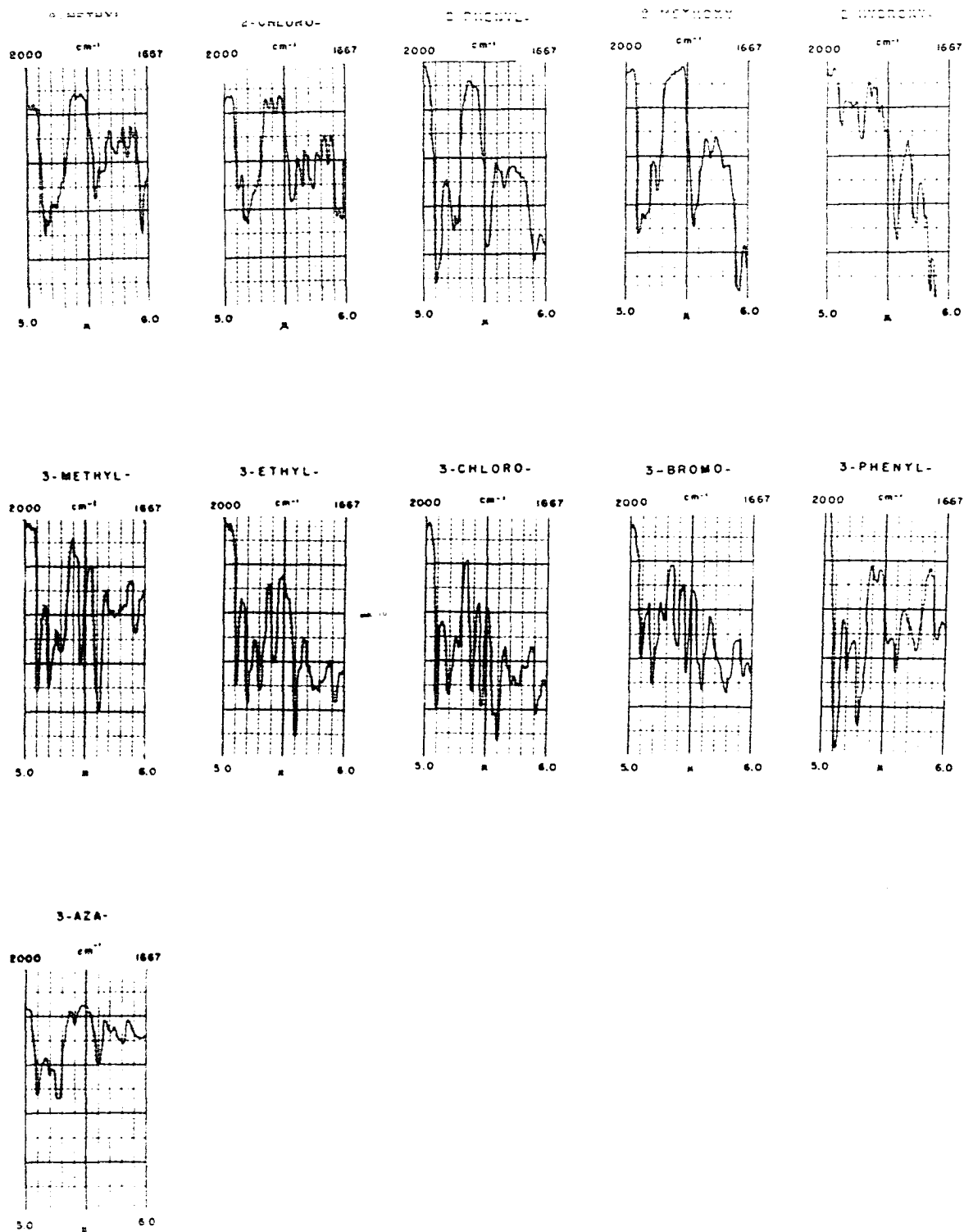


Figure 141. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 4-monosubstituted-1,10-phenanthrolines

Figure 142. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 5-monosubstituted-1,10-phenanthrolines

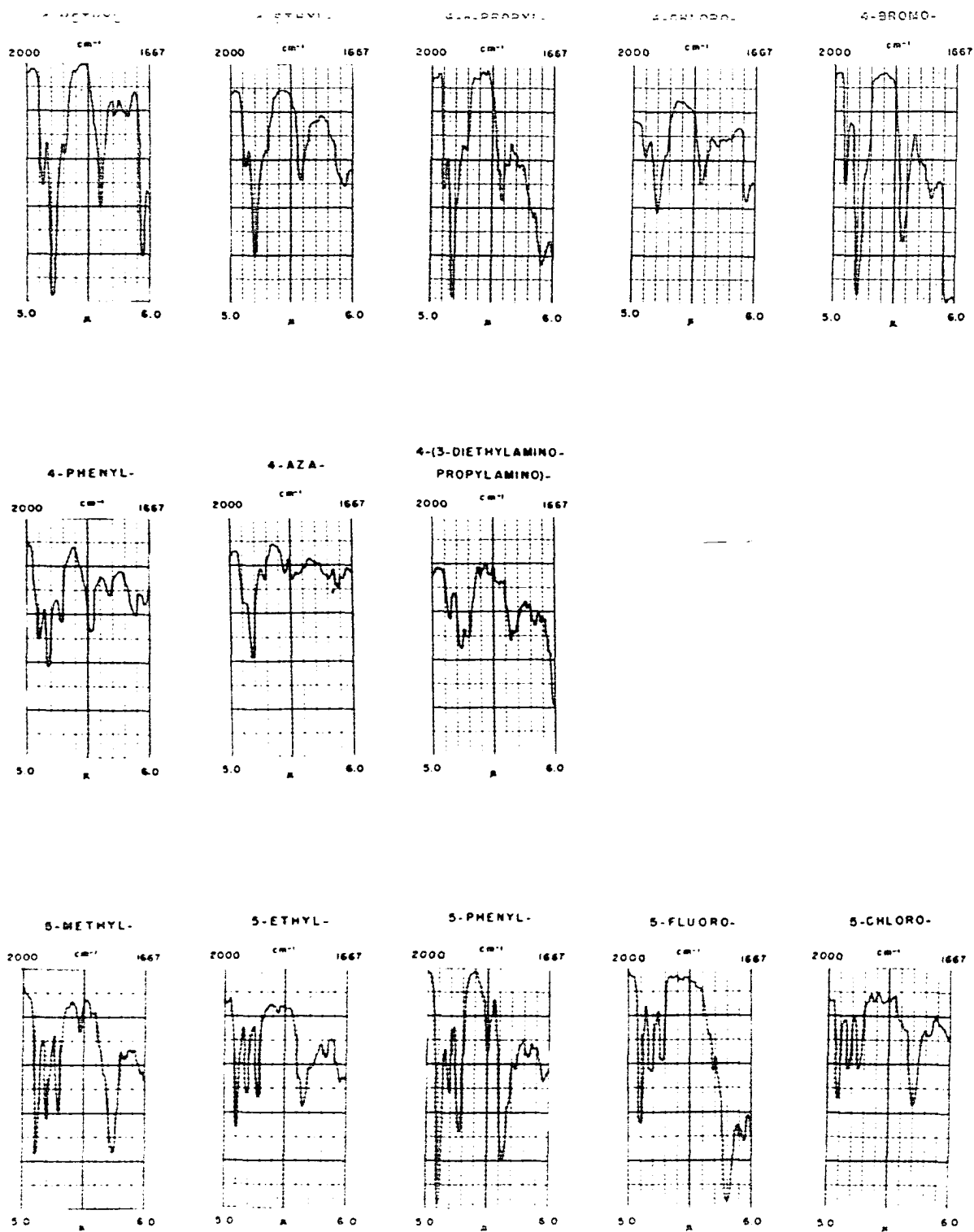
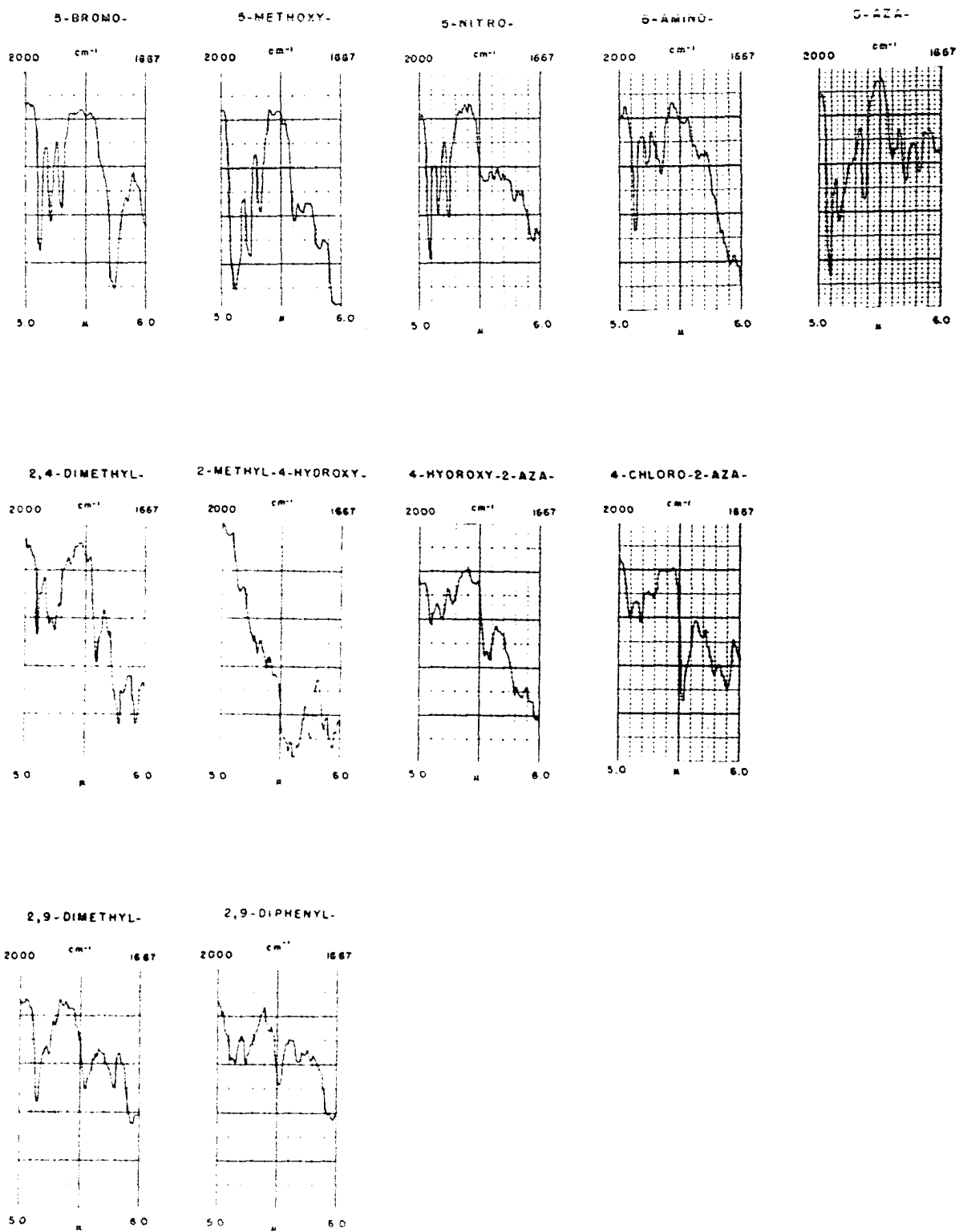


Figure 142. (Continued)

Figure 143. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 2,4-disubstituted-1,10-phenanthrolines

Figure 144. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 2,9-disubstituted-1,10-phenanthrolines



cates that the keto form (a secondary amide in this case) predominates, and the presence of the hydrogen atom bonded to the ring nitrogen atom influences the spectra of this region. In Figure 110 the expanded pattern of 2-aza-1,10-phenanthroline is recorded with the entire spectrum; it agrees fairly well with the spectra of other 2-monosubstituted compounds.

All the 3-monosubstituted patterns contain a distinctive absorption at 5.40-5.47 microns ($1852\text{-}1828\text{ cm}^{-1}$) which does not appear in the spectra of the other 3-monosubstituted 1,10-phenanthrolines. This extra peak is also found with certain other halogen derivatives (note spectra of the 3,5-, 3,6-, and 3,5,6-substituted derivatives in Figures 146, 147, and 153).

A triplet absorption appears in the spectra of the 4-monosubstituted derivatives with peaks in approximately the same positions as observed in the 1,10-phenanthroline spectrum, however, the intensities differ. Also, a distinguishing strong absorption appears in general near 5.93 microns (1686 cm^{-1}) with the 4-monosubstituted derivatives. The 4-phenyl-, 4-aza-, and 4-(3-diethylaminopropylamino)-1,10-phenanthroline patterns are not too sharp but still agree fairly well with the others in this group.

The pattern observed for the 5-monosubstituted derivatives is similar to that found for unsubstituted 1,10-phenanthroline, particularly in the first triplet absorption. In general, the fourth strong peak is found at lower frequency in these derivatives (especially in the 5-fluoro-1,10-phenanthroline spectrum). The spectra of 5-nitro-, 5-amino-, and 5-aza-1,10-phenanthroline do not correspond exactly with the general pattern for 5-monosubstituted derivatives.

b. Disubstituted derivatives Ten groups of disubstituted 1,10-phenanthrolines were studied in this region; their patterns are recorded in Figures 143 through 152. Each pattern is unique, except in one instance. The pattern found for 4,5-dimethyl-1,10-phenanthroline, Figure 156, is nearly identical with that observed for 4,6-dimethyl-1,10-phenanthroline, Figure 150. The 3,7-dimethyl- and 4,7-dimethyl-1,10-phenanthroline spectra in Figures 148 and 151 are somewhat similar in this region also, with differences appearing in the weaker bands.

Some patterns for disubstituted 1,10-phenanthrolines are very similar in appearance to those found with monosubstituted groups. The 2-monosubstituted and 2,9-disubstituted patterns resembled each other in Figures 139 and 144. The spectra of 5-monosubstituted and the 5,6-disubstituted derivatives re-

semble each other quite closely in Figures 142 and 153, and it would be difficult to distinguish one from the other using this spectral region only. Other mono- and disubstituted patterns are similar in the strong absorptions, but closer examination of the bands reveal important differences (see Figures 140, 145, and 146 to compare spectra of 3-monosubstituted derivatives to those of 3,4- and 3,5-disubstituted compounds; and Figures 141 and 151 to compare spectra of 4-monosubstituted and 4,7-disubstituted compounds).

Some peaks in the spectra of 2,4-disubstituted 1,10-phenanthrolines, Figure 143, are not resolved too well in this region, but the general agreement among these patterns is still found. The spectra obtained in this region with the 3,4-cycloalkeno-1,10-phenanthrolines agrees quite well with the general 3,4-disubstituted pattern, Figure 145. As noted earlier the 3,5-dichloro- and 3,5-dibromo-1,10-phenanthroline spectra contain an extra absorption at 5.38 microns (1859 cm^{-1}) not found with 3,5-dimethyl-1,10-phenanthroline. This same peak appears with 3,6-dibromo-1,10-phenanthroline but not in the 3,5-dimethyl-1,10-phenanthroline spectrum. Two peaks are present in the 4,6-diphenyl-1,10-phenanthroline spectrum in the 5.50 to 5.60 micron ($1818\text{--}1786\text{ cm}^{-1}$) range which are not present in the spectra of the other 4,6-disubstituted derivatives, Figure 150. Of the 4,7-disubstituted

Figure 145. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,4-disubstituted-1,10-phenanthrolines

Figure 146. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,5-disubstituted-1,10-phenanthrolines

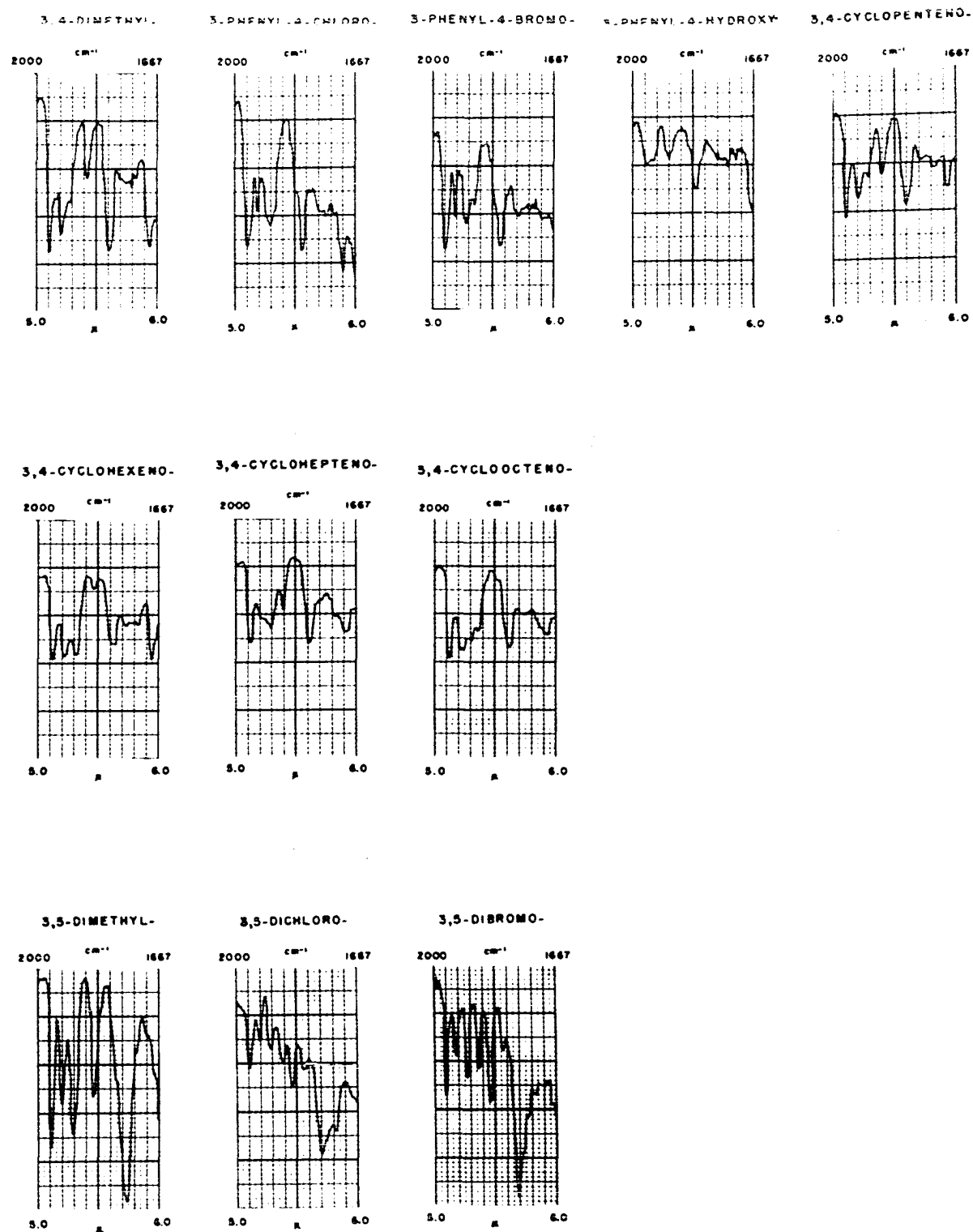


Figure 147. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,6-disubstituted-1,10-phenanthrolines

Figure 148. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,7-disubstituted-1,10-phenanthrolines

Figure 149. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,8-disubstituted-1,10-phenanthrolines

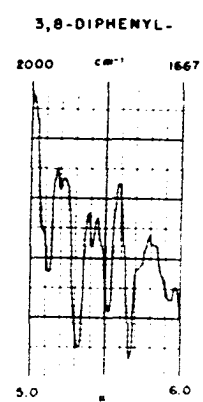
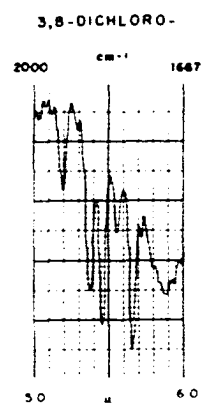
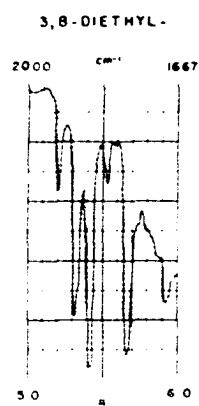
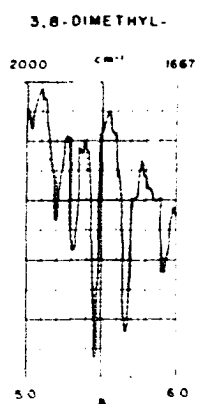
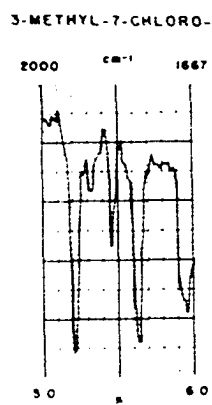
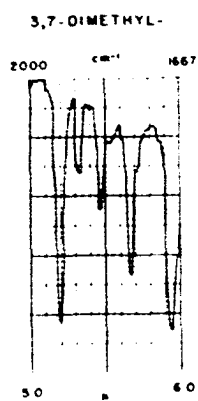
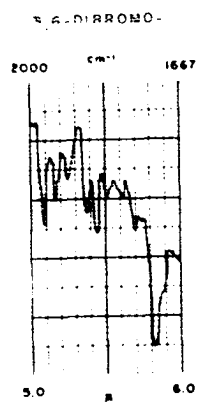
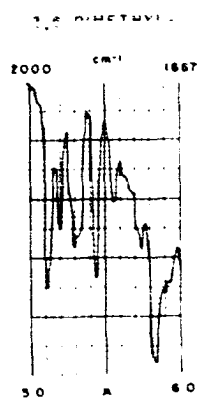


Figure 150. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 4,6-disubstituted-1,10-phenanthrolines

Figure 151. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 4,7-disubstituted-1,10-phenanthrolines

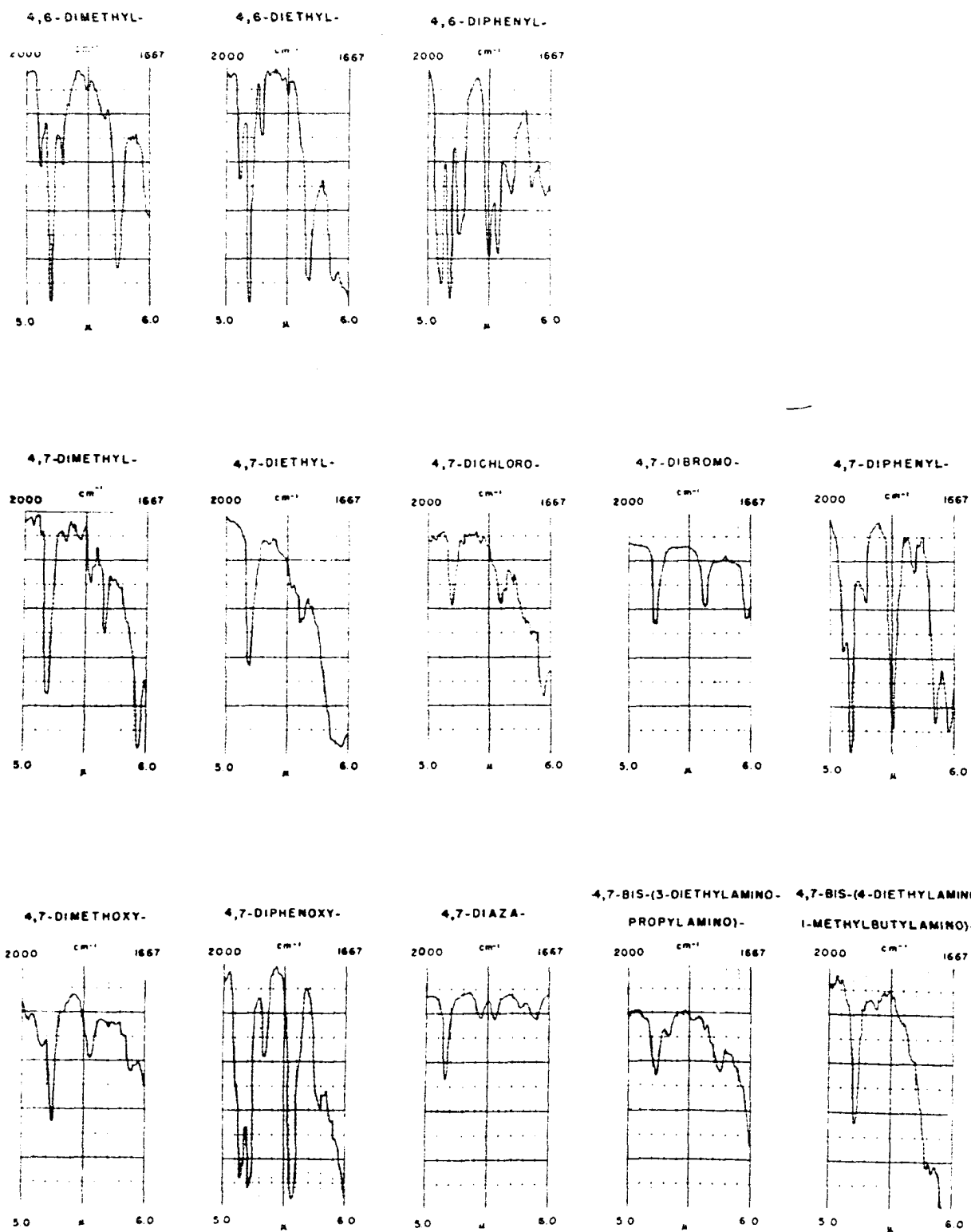
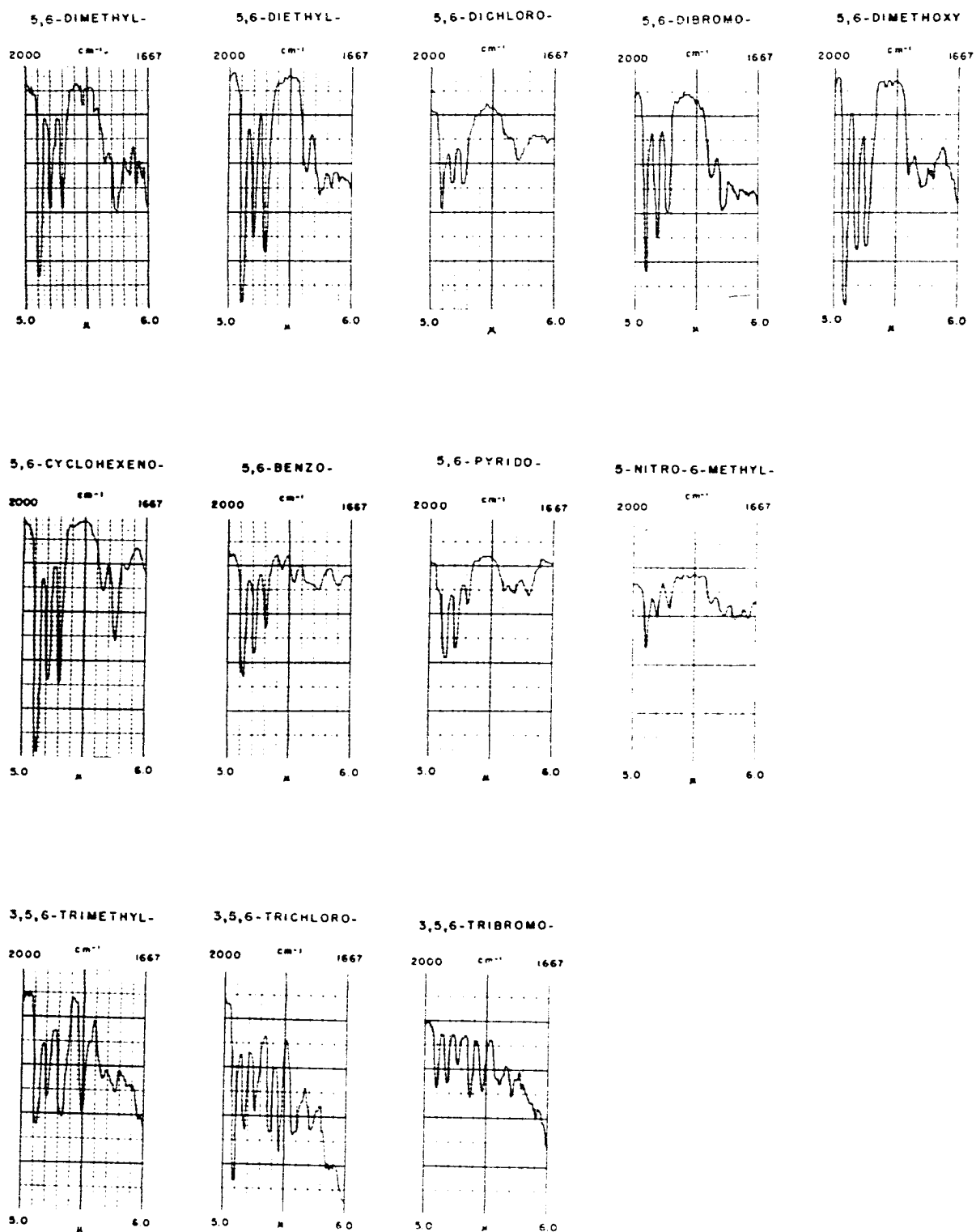


Figure 152. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 5,6-disubstituted-1,10-phenanthrolines

Figure 153. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,5,6-trisubstituted-1,10-phenanthrolines



derivatives, only the 4,7-diphenoxy-1,10-phenanthroline spectrum diverges appreciably from the general pattern.

c. Trisubstituted derivatives The patterns for 3,5,6-trisubstituted 1,10-phenanthrolines are recorded in Figure 153. All other trisubstituted patterns are based on one example only, taken from spectra of methyl-substituted 1,10-phenanthrolines in Figure 156. As observed above, the 3,5,6,-trichloro- and 3,5,6-tribromo-1,10-phenanthroline spectra contains an extra peak at 5.38 microns (1859 cm^{-1}) not found in the 3,5,6-trimethyl-1,10-phenanthroline spectrum. Each of the nine patterns noted in Figures 153 and 156 for trisubstituted derivatives is different.

Some trisubstituted patterns are quite similar to those found with certain disubstituted compounds. Examples where the two types of substitution give nearly identical spectra in this region are: the 3,7-dimethyl- and 3,4,7-trimethyl-1,10-phenanthroline patterns, Figures 148 and 156; and the 3,8-dimethyl- and 3,4,8-trimethyl-1,10-phenanthroline patterns, Figures 150 and 156. A minor difference in the two patterns occurs in the latter case by the presence of a peak of weaker intensity at 5.32 microns (1880 cm^{-1}) in the trisubstituted methyl compound. Examples where the spectra of the dimethyl and trimethyl derivatives are very similar but not identical in this region were found also in these cases: 3,4-dimethyl-

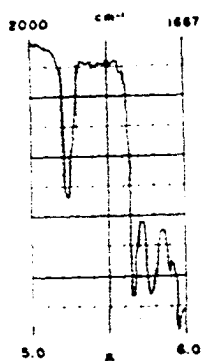
and 2,3,4-trimethyl-1,10-phenanthroline, Figures 145 and 156, with the former containing a distinguishing peak at 5.42 microns (1845 cm^{-1}); 3,6-dimethyl- and 3,4,6-trimethyl-1,10-phenanthroline, Figures 147 and 156, where the minor peaks vary and one intensity difference occurs at 5.29 microns (1890 cm^{-1}); and 4,7-dimethyl- and 3,4,7-trimethyl-1,10-phenanthroline, Figures 151 and 156, where only weak intensity peaks are dissimilar.

d. Tetrasubstituted derivatives Patterns for two types of tetrasubstituted 1,10-phenanthrolines are recorded in Figures 154 and 155. Five other tetrasubstituted patterns are based on the spectra of tetramethyl-1,10-phenanthrolines in Figure 156. The patterns from derivatives containing phenyl groups do not correspond to those from the tetramethyl-1,10-phenanthrolines, Figures 154 and 155. However, within each group the patterns from spectra of phenyl substituted compounds are quite similar. The spectra of the two (3,4),-(7,8)-dialkeno-1,10-phenanthrolines agree very well with the pattern found with 3,4,7,8-tetramethyl-1,10-phenanthroline, Figure 155. All seven of the tetramethyl-1,10-phenanthroline patterns, Figures 154, 155, and 156, are different and can be distinguished from each other. In a few instances the major peaks in trisubstituted patterns are similar to those of tetrasubstituted compounds, but in general can be distinguished with closer examination of the minor absorptions.

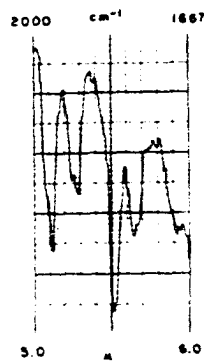
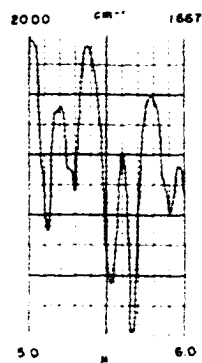
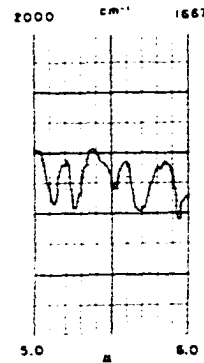
Figure 154. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 2,4,7,9-tetrasubstituted-1,10-phenanthrolines

Figure 155. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of 3,4,7,8-tetrasubstituted-1,10-phenanthrolines

2,4,7,9-TETRAMETHYL-



2,4,7,9-TETRAPHENYL-

2,9-DIMETHYL-
4,7-DIPHENYL-2,9-DIPHENYL-
4,7-DIMETHYL-

3,4,7,8-TETRAMETHYL-

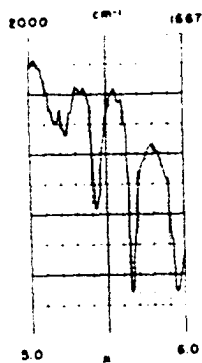
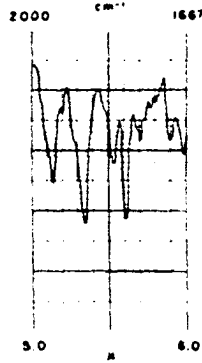
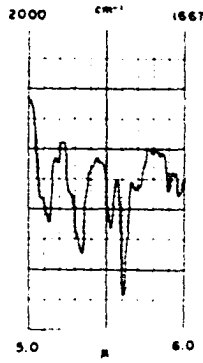
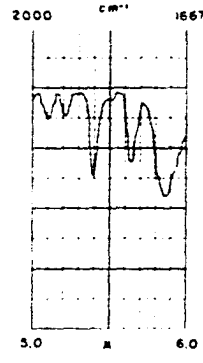
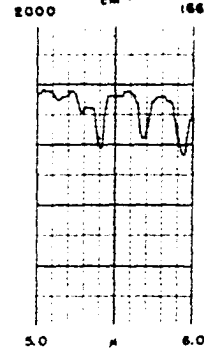
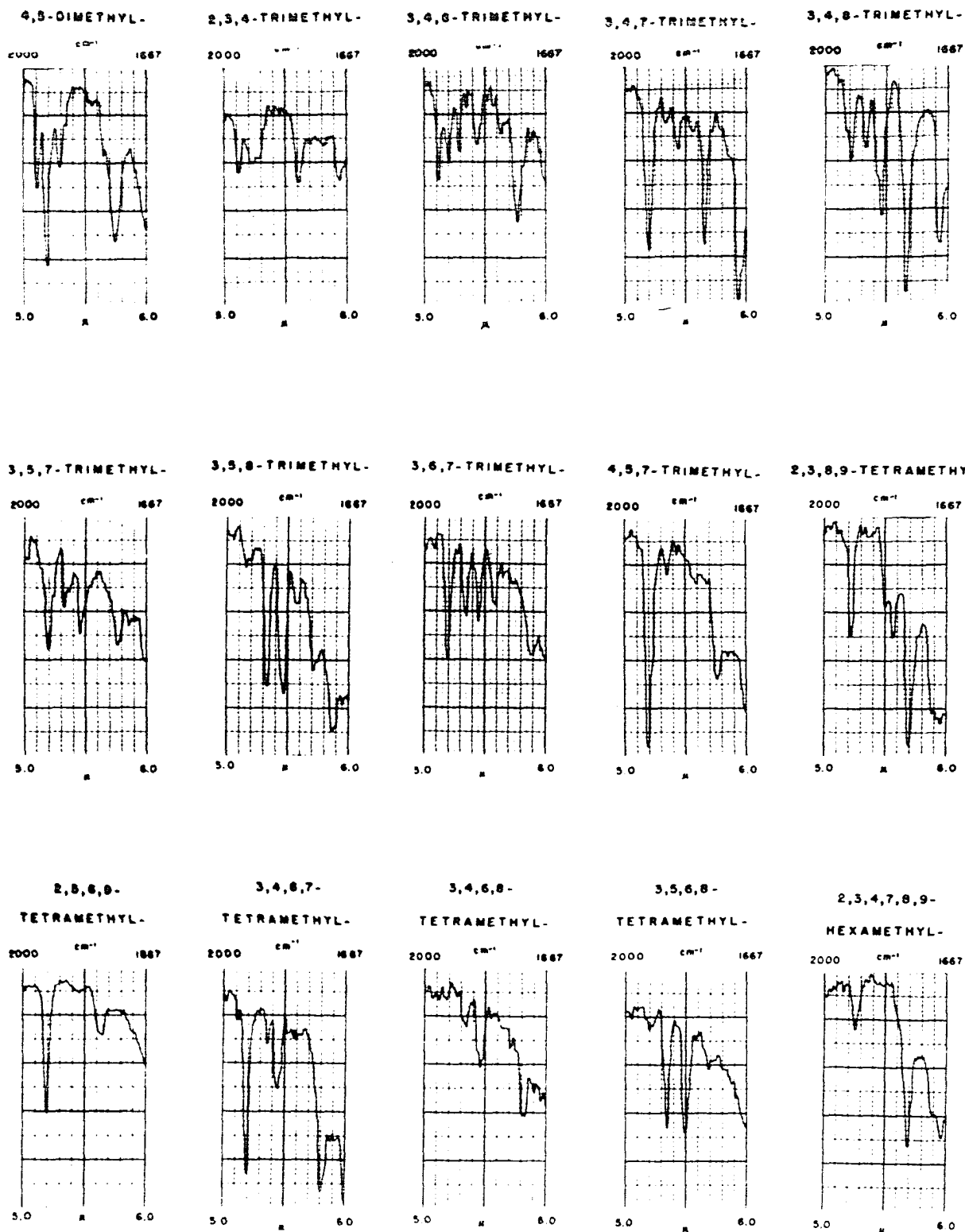
3,8-DIPHENYL-
4,7-DICHLORO-3,8-DIPHENYL-
4,7-DIBROMO-(3,4),(7,8)-
DICYCLOPENTENO-(3,4),(7,8)-
DICYCLOHEXENO-

Figure 156. Expanded 5.0-6.0 micron ($2000-1667\text{ cm}^{-1}$) region of the chloroform spectra of miscellaneous methyl-substituted-1,10-phenanthrolines



The spectra of 3,5,7- and 4,5,7-trimethyl-1,10-phenanthroline are similar to that of 3,4,6,7-tetramethyl-1,10-phenanthroline; the 3,5,8-trimethyl-1,10-phenanthroline spectra in this region resembles that of the 3,4,6,8-tetramethyl derivative, Figure 156. No pattern from spectra of mono- or disubstituted derivatives was found to resemble any of these tetrasubstituted derivative patterns. In general, the first triplet absorption in this region found in the spectra of several mono- and disubstituted compounds is not present in spectra of the tetrasubstituted 1,10-phenanthrolines.

e. Hexasubstituted derivatives One pattern of this type, from the 2,3,4,7,8,9-hexamethyl-1,10-phenanthroline spectrum is recorded in Figure 156. The major peaks in the spectra of one trisubstituted and three tetrasubstituted derivatives are quite similar, but in each case one or two extra peaks are present in these less substituted 1,10-phenanthrolines as noted below. The pattern for this hexasubstituted derivative is still relatively distinctive. Those derivatives with similar patterns and the differences which could be found were: 2,3,4-trimethyl-1,10-phenanthroline, with one additional peak appearing at 5.12 microns (1953 cm^{-1}); 2,3,8,9-tetramethyl-1,10-phenanthroline, with a shoulder at 5.50 microns (1818 cm^{-1}) and an extra peak at 5.57 microns (1795 cm^{-1}); 2,4,7,9-tetramethyl-1,10-phenanthroline, with

one more absorption at 5.77 microns (1733 cm^{-1}); and 3,4,7,8-tetramethyl-1,10-phenanthroline, with one extra peak at 5.43 microns (1842 cm^{-1}).

C. The $1667\text{-}1250\text{ cm}^{-1}$ Region

The characteristic ring vibration absorptions have been reported to fall in this range as was noted earlier. The absorptions found in this region with unsubstituted 1,10-phenanthroline were discussed in section IV, A. In general it would be expected that the substitution of various substituents in place of the ring hydrogen atoms would have comparatively small effect upon the intensity and position of these ring vibration absorptions. Bellamy (1) reported that from spectra of some aromatic compounds it was possible to obtain confirmatory information on the substitution type by observing shifts and intensity changes of the C=C stretching absorptions. Shindo and Ikekawa (56) observed that the relative intensities of the two bands between 1620 cm^{-1} and 1560 cm^{-1} in methylpyridines had a regular correlation with the positions of the methyl groups on the pyridine ring. Cook and Church (21) characterized monosubstituted pyridines by observing the average separation of the two bands in the 1600 cm^{-1} region. With 2- and 3-monosubstituted pyridines, the average separation was 20 cm^{-1} , and with 4-monosubstituted

pyridines the separation was 40 cm^{-1} . Shindo and Tamura (57) observed varying intensity for the band near 1630 cm^{-1} in spectra of quinolines and felt that this intensity change could be correlated to structure. This absorption was of greatest intensity and at highest frequency with 2-methyl- and 7-methylquinoline.

The general characteristics of the spectra of the substituted 1,10-phenanthrolines were reported in section IV. Several shifts, changes in intensity, and the appearances of new peaks in this region were observed. These variations in the spectra with substitution of 1,10-phenanthroline appear to be related in some instances to certain substitution types. The possible correlation of these variations found in the $1667\text{-}1250\text{ cm}^{-1}$ region to substitution types is discussed below.

1. Shift of the 1616 cm^{-1} absorption of 1,10-phenanthroline spectrum correlated to 5,6-substitution

With substitution in the 5,6-positions of 1,10-phenanthroline, the first component (at 1616 cm^{-1} in the 1,10-phenanthroline spectrum) of the triplet ring vibration absorption is generally at a lower frequency than in 1,10-phenanthroline derivatives of other substitution types, Table 19. In some instances this peak is absent or present only as an inflection, as in the halogen derivatives. The shifts which were

observed are tabulated in Table 19. With 5,6-dimethoxy-1,10-phenanthroline, the shift was much less than generally occurs in 5,6-substituted derivatives. Exceptions to this correlation were found. There are a few instances where the shift with 5,6-substituted compounds is not to lower frequency but to slightly higher frequency, for example with 5-nitro-6-methyl-1,10-phenanthroline which absorbs at 1618 cm^{-1} . The 5,6-dihydroxy-1,10-phenanthroline spectrum contains a moderately strong peak at 1618 cm^{-1} also. Shifts of a similar magnitude to lower frequency are found with derivatives other than 5,6-substituted, Table 20. Most of these exceptions are observed in spectra of halogen derivatives. Earlier, in section IV, C, it was observed that the 5-fluoro-1,10-phenanthroline spectrum was unique in that this first peak occurred at a much higher frequency, at 1634 cm^{-1} , in contrast to 1502 cm^{-1} in 1,10-phenanthroline.

Even though exceptions were found, this correlation is still useful in the characterization of 5- and 6-substituted compounds, in particular 5,6-disubstituted derivatives. Earlier, in section V, B, the pattern found in the 5.0-6.0 micron ($2000\text{-}1667\text{ cm}^{-1}$) region of 5,6-disubstituted derivatives was observed to be nearly identical to those found with 5-monosubstituted compounds. With the above correlation the 5-monosubstituted and 5,6-disubstituted derivatives can be distinguished, since with 5-substituted-1,10-phenanthrolines,

Table 19. Shifts to lower frequency of the 1616 cm^{-1} band of 1,10-phenanthroline in spectra of 5,6-substituted derivatives

Compound	Frequency ^a observed for this peak (cm^{-1})	Shift to lower fre- quency ^b (cm^{-1})	Average frequency with derivatives of the same substituent (cm^{-1})
1,10-Phenanthroline ^c	1616	--	--
5,6-Dimethyl-	1597	19	1616
3,5,6-Trimethyl-	1595	21	"
2,5,6,9-Tetramethyl	1605	11	"
3,5,6,8-Tetramethyl-	1595	21	"
5,6-Diethyl-	1592	24	1616
5,6-Dichloro-	-- ^d	--	1616 ^e
3,5,6-Trichloro-	-- ^d	--	"
5,6-Dibromo-	1592 ^f	24	1616 ^g
3,5,6-Tribromo-	1582 ^h	34	"
3,5,6,8-Tetrabromo-	-- ^d	--	"

^aFrom potassium bromide disk spectra in all cases.

^bShift calculated from the 1616 cm^{-1} band found in the spectrum of 1,10-phenanthroline.

^cAnhydrous material.

^dThe peak is absent.

^eExcluding frequencies of the absorptions in the 5-chloro- and 3,5-dichloro-1,10-phenanthroline spectra (see Table 20 for the exceptions to this correlation).

^fInflection only.

^gExcluding frequencies of absorptions in the 5-bromo-, 3,5-dibromo-, and 3,6-dibromo-1,10-phenanthroline spectra (see Table 20 for exceptions to this correlation).

^hShoulder.

Table 19. (Continued)

Compound	Frequency ^a observed for this peak (cm ⁻¹)	Shift to lower fre- quency ^b (cm ⁻¹)	Average frequency with derivatives of the same substituent (cm ⁻¹)
5,6-Dimethoxy-	1610	6 ⁱ	1613
5,6-Dione-	-- ^d	--	-- ^j
5,6-Dioxime-	1590 ^h	26	-- ^j
5,6-Cyclohexeno-	1605	11	1610 ^k
5,6-Benzo-	1605	11	1616 ^l
5,6-Pyrido-	1595 ^h	21	-- ^j

ⁱShift much less than with the other 5,6-substituted derivatives.

^jNo other available derivatives of similar substituent.

^kSingle frequency found with 3,4-cyclohexeno-1,10-phenanthroline.

^lSingle frequency found with 2,3-benzo-1,10-phenanthroline, the only other benzo derivative.

no shift of the 1616 cm⁻¹ peak was generally found. Two exceptions, 5-chloro- and 5-bromo-1,10-phenanthroline are noted in Table 20.

2. Appearance of new absorptions within the first ring vibration triplet band

In the general discussion of the spectra of substituted 1,10-phenanthrolines, Section IV, new peaks were often observed within the usual triple ring vibration absorption

Table 20. Similar shifts of the 1616 cm^{-1} band of 1,10-phenanthroline in spectra of derivatives other than 5,6-substituted

Compound	Frequency observed for this peak (cm^{-1}) ^a	Shift to lower frequency (cm^{-1}) ^b	Average frequency with derivatives of the same substituent (cm^{-1})
1,10-Phenanthroline ^c	1616	--	--
5-Chloro-	1605	11	1616^d
3,5-Dichloro-	1597	19	"
5-Bromo-	1595	21	1616^e
3,5-Dibromo-	1595	21	"
3,6-Dibromo-	1592	24	"
3,8-Diphenyl-4,7-dichloro-	1597^f	19	-- ^g
3,8-Diphenyl-4,7-dibromo-	1595^f	21	-- ^g
(3,4),(7,8)-Dicyclohexeno-	1600	16	1610^h

^aFrom potassium bromide spectra in all cases.

^bShift calculated from the 1616 cm^{-1} band found in the spectrum of 1,10-phenanthroline.

^cAnhydrous material.

^dExcluding frequencies of the absorptions in the 5-chloro- and 3,5-dichloro-1,10-phenanthroline spectra.

^eExcluding frequencies of the absorptions in the 5-bromo-3,5-dibromo-, and 3,6-dibromo-1,10-phenanthroline spectra.

^fAll three peaks of the first ring vibration triplet absorption are shifted to lower frequency.

^gNo other derivative of similar substituents.

^hSingle frequency found with 3,4-cyclohexeno-1,10-phenanthroline spectrum.

(band A of 1,10-phenanthroline). The possibility of correlating the appearance or the absence of the new peak or peaks in the $1608\text{-}1592\text{ cm}^{-1}$ region with certain substitution position types was investigated. Any shifts to lower frequency of the first component of the triplet absorption, such as was observed in most 5,6-substituted compounds, Table 19, and in a few other derivatives noted in Table 20 interfere with the observation of these new absorptions.

No consistent correlations could be made for any substitution type. In some instances, no new peak appears with the methyl derivatives, but a shoulder or medium band appears with other substituents of the same substitution type and vice versa. In general, spectra of most of the halogen and phenyl derivatives contain additional bands within the triplet in the $1608\text{-}1592\text{ cm}^{-1}$ range. As observed in section IV, D, the phenyl derivatives have in addition to the peak in the range above, another shoulder or strong peak in the $1580\text{-}1570\text{ cm}^{-1}$ region.

Two trends were found in this investigation worthy of mention. All spectra of 2-monosubstituted 1,10-phenanthrolines contain a shoulder or medium to strong peak in the $1605\text{-}1559\text{ cm}^{-1}$ range; but this does not distinguish these derivatives from other materials. The spectra of the 4,7-disubstituted derivatives does not in general contain any extra peaks

within the usual triplet absorption (4,7-dibromo-1,10-phenanthroline is the only exception, with a medium band at 1603 cm^{-1}).

3. Absence of the 1587 cm^{-1} band of 1,10-phenanthroline in 3,8-substituted derivatives

In section IV the observation was made that in spectra of many derivatives bearing substituents in the 3,8-positions, the second component of the triplet ring vibration absorption (band A of 1,10-phenanthroline) was found to be absent. The spectra of all the 3,8-substituted-1,10-phenanthrolines were studied to explore the possibility of correlating the absence of this band to 3,8-substitution. In Table 21 are recorded the absorptions found in the triplet ring vibration absorption of 1,10-phenanthroline and all 3,8-substituted derivatives. With all 3,8-methyl substituted derivatives, except 2,3,4,7,8,9-hexamethyl-1,10-phenanthroline, this absorption is found to be absent. However, a shoulder appears at 1582 cm^{-1} in the 3,8-dichloro-1,10-phenanthroline spectrum and a strong peak with 3,5,6,8-tetrabromo-1,10-phenanthroline at 1580 cm^{-1} . This latter peak may have been shifted to this frequency due to the combined effects of the presence of substitution in the 5,6-positions and bromo substitution which has been observed before to give absorptions at a slightly lower frequencies in this region. The absorptions obtained with the hydroxy derivatives are poorly resolved,

and the bands reported in Table 21 for these compounds may not be too reliable. This peak was found to be absent in spectra of a few derivatives which were not substituted in the 3,8-positions. With the 3,5,6-trimethyl-1,10-phenanthroline spectrum, this peak is not present, but it may have been masked by the strong absorption at 1597 cm^{-1} which was shifted to this frequency by the 5,6-substitution. This peak is not resolved in the spectra of 5-aza-, 4,7-diaza-, 4-hydroxy-2-aza-1,10-phenanthroline and in some hydroxy derivatives spectra also.

4. Appearance of a satellite on the low frequency side of the 1502 cm^{-1} ring vibration absorption by substitution in 1,10-phenanthroline

In the spectra of most of the substituted derivatives 1,10-phenanthroline, a new shoulder or peak of medium to strong intensity appears on the low frequency side of the second ring vibration absorption (band B of 1,10-phenanthroline at 1502 cm^{-1}). Schilt and Taylor (53) also found this peak in the spectra of the metal derivatives of 1,10-phenanthroline. They attempted to correlate the splitting of these peaks to the ionic radius of the metal ion in the compound and were able to observe a general trend.

The spectra of the large majority of 1,10-phenanthroline derivatives contains this satellite on the low frequency side of the second ring vibration absorption in the $1497\text{-}1471\text{ cm}^{-1}$

Table 21. Absorptions in the 1620-1540 cm^{-1} region in spectra of 3,8-substituted 1,10-phenanthrolines

Compound	Frequency (cm^{-1}) ^a			
1,10-Phenanthroline ^b	1616	--	1587	1558
3,8-Dimethyl-	1613	--	--	1558
3,4,8-Trimethyl-	1608	--	--	1567
3,5,8-Trimethyl-	1621	1610 ^c	--	1560
2,3,8,9-Tetramethyl-	1618	1603 ^d	--	1543
3,4,6,8-Tetramethyl-	1616	--	--	1565
3,4,7,8-Tetramethyl-	1616 ^d	1608	--	1567
3,5,6,8-Tetramethyl-	--	1595 ^e	--	1563
2,3,4,7,8,9-Hexamethyl-	1613	--	1575	1555
3,8-Diethyl-	1610	1600 ^d	--	1558
3,8-Dichloro-	1618	1595	1582 ^d	1550 ^f
3,5,6,8-Tetrabromo-	--	--	1580	1565
3,8-Diphenyl-	--	1605 ^g	--	1558
3,8-Diphenyl-4,7-dihydroxy- ^h	--	--	1582 ^d	1550 ^d

^aIn all cases from the potassium bromide disk spectra.

^bAnhydrous material.

^cInflection only.

^dShoulder.

^eShifted absorption of a 5,6-substituted derivative as given in Table 19.

^fVery weak absorption.

^gBroad absorption.

^hPoor resolution obtained in this region with this derivative.

Table 21. (Continued)

Compound	Frequency (cm ⁻¹) ^a			
3,8-Dicarbethoxy- 4,7-dihydroxy- ^h	1608	--	1592 ^c	1543
3,8-Dicarboxy- 4,7-dihydroxy- ^h	1616	--	--	--
3,8-Diphenyl-4,7-dichloro-	--	1597 ⁱ	1577 ⁱ	1534 ⁱ
3,8-Diphenyl-4,7-dibromo-	--	1595 ⁱ	1575 ⁱ	1534 ⁱ
(3,4),(7,8)-Dicyclopenteno-	1608	--	1582 ^f	1560
(3,4),(7,8)-Dicyclohexeno-	--	1603 ^j	--	1565

ⁱAll peaks are shifted to lower frequency.

^jShifted absorption as observed in Table 20.

range. Of the monosubstituted derivatives, the spectra of 2-chloro- and 4-chloro-1,10-phenanthroline are the only two which do not contain an extra peak in this region. The spectra of most of the 3,8-substituted and 4,7-disubstituted compounds do not have a band in this region. Two exceptions in the latter case are 4,7-diphenyl- and 4,7-diphenoxy-1,10-phenanthroline. The spectra of the cycloalkeno-1,10-phenanthrolines do not usually have this extra peak in their spectra as was observed in section IV, E. Medium to strong absorptions appear in the 1466-1462 cm⁻¹ region in the spectra of the methoxy derivatives. These bands are associated with the shifted methyl deformation mode where the methyl group is

bonded through an oxygen atom. This absorption is associated with the second ring vibration band, but is differentiated from the usual splitting observed with other derivatives since these peaks are at lower frequency. Other than these general trends, the appearance of the peak due to the splitting of the 1502 cm^{-1} band of 1,10-phenanthroline can not be successfully correlated to any substitution type.

5. Shift of the second ring vibration absorption (band B of 1,10-phenanthroline) to higher frequency with substitution in the 3,7-, 4,5-, and 4,6-positions

In section IV, B, the general shift of the 1502 cm^{-1} band of 1,10-phenanthroline to higher frequency with 3,7-, 4,5-, and 4,6-methyl-substituted-1,10-phenanthrolines was observed. This trend will now be investigated with other derivatives of these substitution types. In Table 22 the shifts to higher frequency with these types of 1,10-phenanthrolines are recorded. With the 4,5-disubstituted derivatives, the greatest displacement of this band is found. The magnitude of these shifts is small in many cases. Other types of derivatives with similar or slightly smaller shifts were found, Table 23. No useful correlation to these substitution types was noted with these general trends. A small shift of this 1502 cm^{-1} band to lower frequencies is observed in spectra of all the 3,8-disubstituted derivatives.

Table 22. Shift of the second ring vibration absorption to higher frequency in spectra of 3,7-, 4,5-, and 4,6-substituted derivatives of 1,10-phenanthroline

Compound	Frequency observed for the second ring vibration (cm ⁻¹)	Shift to higher frequency ^a (cm ⁻¹)
1,10-Phenanthroline ^b	1502	--
3,7-Dimethyl-	1515	13
3,4,7-Trimethyl-	1515	13
3,5,7-Trimethyl-	1506	4
3,6,7-Trimethyl-	1517	15
3,4,6,7-Tetramethyl-	1520	18
3,4,7,8-Tetramethyl	1511	9
3-Methyl-7-chloro-	1497	(5) ^c
4,5-Dimethyl-	1520	18
4,5,7-Trimethyl-	1522	20
4,5-Dihydroxy-	1531	29
2-Methyl-4,5-dihydroxy-	1531	29
2-Methyl-4-hydroxy-5-methoxy-	1511	9
3-Carbethoxy-4-hydroxy-5-methoxy-	1531	29
4,6-Dimethyl-	1515	13
3,4,6-Trimethyl-	1511	9
3,4,6,8-Tetramethyl-	1506	4
4,6-Diethyl-	1511	9
4,6-Diphenyl-	1511	9

^aShift calculated from the 1502 cm⁻¹ band found with 1,10-phenanthroline.

^bAnhydrous material.

^cA shift to lower frequency in this case.

Table 23. Shift of the second ring vibration absorption to higher frequency in the spectra of miscellaneous substituted 1,10-phenanthrolines

Compound	Frequency observed for the second ring vibration (cm ⁻¹)	Shift to higher frequency ^a (cm ⁻¹)
1,10-Phenanthroline ^b	1502	--
2-Phenyl-	1511	9
4-Ethyl-	1511	9
4-n-Propyl-	1511	9
4-Phenyl-	1511	9
5-Methyl-	1513	11
5-Ethyl- ^c	1511	9
5-Phenyl-	1511	9
5-Aza	1511	9
2-Methyl-4-hydroxy-	1517	15
4-Hydroxy-2-aza-	1511	9
3,4-Cyclopenteno-	1511	9
4,7-Dimethyl-	1511	9
4,7-Diethyl-	1511	9
4,7-Diphenyl-	1511	9
4,7-Dimethoxy-	1511	9
5-Nitro-6-methyl-	1511	9
5,6-Cyclohexeno-	1511	9
3,4,8-Trimethyl-	1511	9
(3,4),(7,8)-Dicyclopenteno-	1511	9

^aShift calculated from the 1502 cm⁻¹ band found with 1,10-phenanthroline.

^bAnhydrous material.

^cCap cell spectrum.

D. The 1250-900 cm^{-1} Region

As noted earlier, section IV, A, the absorptions in this region have been related to C-H in plane deformations or to ring vibrations. Bellamy (1) discussed the use of the 1225-950 cm^{-1} region for identification of substitution type with aromatic compounds. Because of the low intensity of the absorptions within this range, the characterizations were not as successful as those using the 1000-650 cm^{-1} region. Generally this spectral region was found to be helpful only as a confirmation of information obtained from other parts of the spectrum. Frequency ranges for absorptions appearing with various mono-, di-, and trisubstitution types were listed. Bellamy did not report any correlations for higher substituted aromatics since the spectra of these materials in this region were very complex. In the spectra of mono-substituted pyridines, Shindo (54) observed a series of weak, sharp absorptions in the 1220-900 cm^{-1} region. The position of these bands was nearly constant irrespective of the nature of the substituent and was found to be characteristic for each of the types of substitution. Cook and Church (21) reported similar characteristic ranges for monosubstituted pyridines and also for di- and trisubstituted derivatives. The trisubstituted pyridines were not successfully characterized using this region, however.

Bellamy (1) indicated that none of the spectra of substituted quinolines which he had examined in his laboratory contained any strong absorption in the $1240\text{-}900\text{ cm}^{-1}$ region. The spectra of several monomethylquinolines were reported by Shindo and Tamura (57), but no discussions of the weak to medium peaks found in the $1250\text{-}900\text{ cm}^{-1}$ range were given. Schilt and Taylor (53) were not able to formulate any correlations with bands in the $1250\text{-}1125\text{ cm}^{-1}$ region with the metal derivatives of 1,10-phenanthroline even though the positions of the peaks varied somewhat with the different metals.

As noted earlier in section IV, A, two sharp bands of medium intensity occur at 1134 cm^{-1} and 1088 cm^{-1} in the spectrum of anhydrous 1,10-phenanthroline, Figure 1. A well defined shoulder appears on the low frequency side of the second band, at 1072 cm^{-1} . Also, the possible methyl rocking absorption, reported to be near 1042 cm^{-1} (50), is found as a weak to medium peak in the $1050\text{-}1036\text{ cm}^{-1}$ range with many methyl-1,10-phenanthrolines.

Even though the absorptions in the $1250\text{-}900\text{ cm}^{-1}$ region in spectra of the 1,10-phenanthrolines vary a great deal with different types of substitution, no trends could be found which would be useful in identifying substitution positions. The numerous absorptions in this region are generally relatively weak, although very strong peaks are present

in halogen, methoxy, phenoxy, and dioxime derivatives. Symmetrically substituted derivatives, such as the 3,8- and 4,7-disubstituted compounds, have somewhat simpler patterns in this region than was generally observed.

E. The 900-650 cm^{-1} Region

Bellamy (1) has reported that strong bands in the 1000-650 cm^{-1} region found in spectra of aromatic compounds were due to the out-of-plane deformation vibrations of ring hydrogen atoms. The frequencies at which these absorptions occur have been related successfully by several authors to the positions of substitutions on the aromatic ring, the frequencies being almost independent of the nature of the substituents. Colthup (20) reported that the out-of-plane bending vibration absorptions observed between 900-650 cm^{-1} were very useful for identification of the substitution type among benzene derivatives, and using an empirical classification he established certain relations. The number of adjacent hydrogen atoms remaining on the benzene ring was correlated to the stronger absorptions observed in the 900-650 cm^{-1} region. In general as the number of adjacent ring hydrogen atoms decreased, the position of the strong absorption in this region was moved to higher frequency. Bellamy (1) has summarized the applications of such empirical classifications as have appeared in the literature. They are quite useful in characterizing di- and trisubstituted aromatic

materials. Such classification has been extended to tetra- and pentasubstituted benzene derivatives, naphthalenes, and polycyclic compounds. Larger deviations occur with the larger molecules, and additional bands were found in many cases which confused the classification scheme. Bellamy (1) has reported that substitution of polar groups as CO, CF₃, and NO₂ caused marked deviations from these correlations. For example, with nitro substitution, shifts to higher frequency were observed. The absorption regions for various substituted types of benzene derivatives as summarized by Bellamy are given in Table 24.

Table 24. The C-H out-of-plane deformation frequency ranges observed in spectra of substituted benzene derivatives correlated to the number of adjacent ring hydrogen atoms^a

Number of adjacent ring hydrogen atoms	Types of substituted benzene derivatives	Frequency ranges and relative intensities ^b (cm ⁻¹)
5	Mono-	770-730(v.s.) and 710-690(s.)
4	1,2-	770-735(v.s.)
3	1,3- and 1,2,3-	810-750(v.s.) and 725-680(m.)
2	1,4-, 1,2,4-, and 1,2,3,4-	860-800(v.s.)
1 ^c	1,3-, 1,2,4-, 1,3,5-, 1,2,3,5-, 1,2,4,5-, and penta-	900-860(m.)

^aAs summarized by Bellamy (1).

^bAbbreviations for intensities are: (v.s.), very strong; (s.), strong; and (m.), medium.

^cOne or more isolated ring hydrogen atoms are present.

The absorptions in this region in substituted pyridines have been reported by several authors (1, 21, 54, 56), and the application of the correlation of above to pyridine compounds investigated (1, 54, 56). Shindo (54) summarized the ranges found with monosubstituted pyridines, and these values are recorded in Table 25.

Table 25. The C-H out-of-plane deformation frequency ranges observed in spectra of monosubstituted pyridines correlated to the number of adjacent ring hydrogen atoms^a

Number of adjacent ring hydrogen atoms	Type of pyridine substitution	Frequency ranges and relative intensities (cm ⁻¹) ^b
4	2-	780-740(v.s.) ^c
3	3-	820-770(m.-s.) and 730-690 (v.s.)
2	4-	850-790(s.)

^aAs summarized by Shindo (54).

^bAbbreviations for intensities are: (v.s.), very strong; (m.-s.), medium to strong; (s.), strong.

^cOnly the nitro derivative absorbs at higher frequency.

^dAn isolated ring hydrogen atom is present with the 3-substituted pyridines, however, no absorption is observed in the 900-860 cm⁻¹ region as expected in Table 24.

The absorptions found in this region with various di-, tri-, and tetrasubstituted pyridines were discussed by Shindo and Ikekawa (56) and related to the correlation proposed by Colthup (20). The frequencies of these absorptions are

recorded in Table 26. Pyridine derivatives which had two or three adjacent ring hydrogen atoms in addition to an isolated ring atom, did not produce any absorption in the 900-860 cm^{-1} region as was also observed above with the 3-mono-substituted pyridines in Table 25. With pyridines containing one or more isolated ring hydrogen atoms and no adjacent ring hydrogens present, absorptions were found in the 905-839 cm^{-1} range. The absorption was in general displaced to a lower frequency with more than one isolated ring hydrogen present (compare the frequencies of tetramethylpyridines to di- and trimethylpyridines in Table 26).

Bellamy (1) briefly discussed the application of the out-of-plane C-H deformation correlation noted above to the spectra of six quinoline compounds. Shindo and Tamura (57) investigated the spectra of quinoline, isoquinoline, and seven monomethylquinolines in the 900-700 cm^{-1} region. By considering each ring separately, these authors correlated the stronger absorptions in this region to the adjacent ring hydrogen atom with some success. The data presented by Shindo and Tamura (57) are summarized in Table 27. They found that additional bands appeared in many instances which could not be interpreted and sometimes caused uncertainty in the assignment to a certain substitution type. For example a strong peak near 780 cm^{-1} was found with 2- and 3-methylquinoline which could not be interpreted. In general the

Table 26. The C-H out-of-plane deformation frequencies observed in spectra of di-, tri-, and tetrasubstituted pyridines^a

Number of adjacent ring hydrogen atoms	Pyridine derivatives	Frequencies observed (cm ⁻¹)
3	2,3-Dimethyl-	784 726
	2,6-Dimethyl-	770
	2-Methyl-6-ethyl-	797
2	3,4-Dimethyl- ^b	819
	3-Methyl-4-methyl- ^b	831
	2,4-Dimethyl- ^b	814
	2-Ethyl-4-methyl- ^b	821
	2-Methyl-4-ethyl- ^b	831
	2,4-Diethyl- ^b	835
	2,5-Dimethyl- ^b	814
	2,3,4-Trimethyl-	821
	2,3,6-Trimethyl-	814
1 ^c	3,5-Dimethyl-	856
	2,3,5-Trimethyl-	877
	2,4,5-Trimethyl-	861
	2,4,6-Trimethyl-	839
	3,4,5-Trimethyl-	878
	2,3,4,5-Tetramethyl-	905
	2,3,4,6-Tetramethyl-	857
	2,3,5,6-Tetramethyl-	893

^aAs reported by Shindo and Ikekawa (56).

^bAn isolated ring hydrogen atom is also present, however, no absorption is observed in the 900-860 cm⁻¹ region as is expected in Table 24.

^cOnly isolated ring hydrogens are present with these pyridines.

attributed to the heterocyclic ring were at higher frequency than observed with corresponding methyl-substituted pyridines. This effect was attributed to the condensation with the benzene ring. With the carbocyclic ring substituted, the bands due to the two rings appeared to be overlapped.

Table 27. The C-H out-of-plane deformation frequencies observed in spectra of quinoline, isoquinoline, and methylquinolines^a

Compound	Absorptions associated with the heterocyclic ring			Absorptions associated with the carbocyclic ring	
	No. of adj. ring hydrogen atoms	Frequency observed (cm ⁻¹)		No. of adj. ring hydrogen atoms	Frequency observed (cm ⁻¹)
Quinoline	3	803	786 ^b	4	734
Isoquinoline	2 1 ^c	859	825	4	739
2-Methyl-	2	816	782 ^b	4	743
3-Methyl-	1 ^d	885	859 ^b 784 ^b	4	749
4-Methyl-	2	860 ^b	838	4	756
5-Methyl-	3	818 ^b	801 ^e	3	801 ^e
6-Methyl-	3	795		2 1 ^c	830 875
7-Methyl-	3	782		2 1 ^c	828 884
8-Methyl-	3	819 ^b	789 ^e	3	789 ^e

^aAs reported by Shindo and Tamura (57).

^bLess intense absorption which was not interpreted.

^cOne isolated ring hydrogen atom is present.

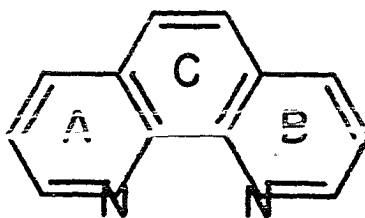
^dTwo isolated ring hydrogen atoms are present.

^eBoth rings contain three adjacent ring hydrogen atoms, and one very strong band is observed.

Schilt and Taylor (53) observed two strong bands in the spectrum of 1,10-phenanthroline at 850 cm^{-1} and 725 cm^{-1} . The 850 cm^{-1} band was assigned to the out-of-plane motion of hydrogen atoms on the carbocyclic ring, and the 725 cm^{-1} band to that of the hydrogen atoms of the two heterocyclic rings. They also observed multiple splittings associated with these peaks which they attributed to out-of-plane hydrogen motions other than those where all atoms move in phase and possibly to overtone of absorptions at lower frequencies. These splittings were sensitive to differences in atoms co-ordinated with 1,10-phenanthroline in the metal derivatives studied. However, the variations were not found to be systematic. Busch and Bailar (5) proposed tentative assignments for the three absorptions at 761 cm^{-1} , 733 cm^{-1} , and 708 cm^{-1} as due to C-H deformations. No attempt to correlate these peaks to any certain ring was made, however.

1. Experimental

The spectra in this region were obtained using the potassium bromide disk technique and are recorded in the Figures 1 to 138 of section IV. In the following discussions, the rings of 1,10-phenanthroline will be considered separately and will be distinguished by use of the letters A, B, and C as indicated below:



Thus, the letters A and B will represent each of the heterocyclic rings, and the letter C will denote the carbocyclic ring. The number of adjacent ring hydrogen atoms which remain on each ring after substitution will be noted. With this information, the above frequency ranges in the correlation summarized in Table 24 will be applied to the 1-10-phenanthrolines to interpret the absorptions found in the spectra and to attempt characterization of substitution types using the 900-650 cm^{-1} region.

2. Discussion

In the spectrum of 1,10-phenanthroline, Figure 1, two strong absorptions appear at 839 cm^{-1} and 733 cm^{-1} . As summarized in Table 28, the absorption at 839 cm^{-1} conforms to the expected 860-800 cm^{-1} range which indicates the presence of two adjacent ring hydrogen atoms. Both heterocyclic rings have three adjacent ring hydrogen atoms, thus absorptions in the 810-750 cm^{-1} and 725-680 cm^{-1} regions would be expected. The second strong absorption at 733 cm^{-1} is at a lower frequency than anticipated above, but is considered here as due

to C-H out-of-plane deformation vibrations of the three adjacent ring hydrogen atoms on both heterocyclic rings as Schilt and Taylor (53) reported. The medium intensity band at 703 cm^{-1} corresponds to the second range quoted for three adjacent ring hydrogens in Table 28.

The spectra of the methyl-1,10-phenanthrolines will be first examined as representative of the majority of the substitution types of available 1,10-phenanthroline compounds. Discussion will follow concerning how well these methyl-1,10-phenanthrolines and derivatives with other substituents conform to the correlation. Phenyl, phenoxy, benzo, and pyrido derivatives will be grouped separately since each introduce adjacent ring hydrogens and other frequency ranges to be considered (the phenyl and phenoxy groups have five adjacent ring hydrogen atoms; the benzo group has four; and the pyrido group has three).

a. Monosubstituted derivatives In Table 28 the absorptions in the $900\text{-}650\text{ cm}^{-1}$ region with monomethyl-1,10-phenanthrolines are correlated to the number of adjacent ring hydrogen atoms. Medium to strong absorptions in the $796\text{-}775\text{ cm}^{-1}$ region and a weak to medium band in the $675\text{-}649\text{ cm}^{-1}$ range could not be interpreted with this correlation scheme. Those methyl derivatives with an isolated ring hydrogen (3-methyl- and 5-methyl-1,10-phenanthroline) are distinguished

Table 28. Absorptions in the 900-650 cm^{-1} region in spectra of 1,10-phenanthroline and monomethyl-1,10-phenanthrolines correlated to the number of adjacent ring hydrogen atoms

Compound	Number of adjacent hydrogen atoms on each ring ^a			Expected absorption regions ^b (cm^{-1})	Absorptions which conformed to the expected regions (cm^{-1})				Major absorptions not interpreted (cm^{-1})
	A	B	C						
1,10-Phenanthroline	3	3	2	(2), (3)	---	839	733	703	765
2-Methyl-	3	2	2	(2), (3)	---	849	734	714	775
3-Methyl-	3	1 ^c	2	(1), (2), (3)	884	829	728	714	779 675
4-Methyl-	3	2	2	(2), (3)	---	842	729	718	
5-Methyl-	3	3	1 ^d	(2), (3)	879	---	740	709	796

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected frequency ranges are: (1) 900-860 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.).

^cTwo isolated ring hydrogen atoms are present.

^dOne isolated ring hydrogen atom is present.

from the other monomethyl compounds by a strong absorption near 880 cm^{-1} . The 5-methyl derivative is differentiated from 3-methyl-1,10-phenanthroline by the absence of a strong absorption in the $849\text{--}829\text{ cm}^{-1}$ range which is related to the two adjacent ring hydrogen atoms of the carbocyclic ring. The peak at 733 cm^{-1} in the 1,10-phenanthroline spectrum, which was earlier related to the C-H out-of-plane deformation vibrations of the three adjacent ring hydrogen atoms on the heterocyclic rings, appears in the $740\text{--}728\text{ cm}^{-1}$ range with monomethyl-1,10-phenanthrolines and in all cases is one of the strongest absorptions in the $900\text{--}650\text{ cm}^{-1}$ region. Apparently the range of $810\text{--}750\text{ cm}^{-1}$ reported by Bellamy (1) for aromatic compounds with three adjacent ring atoms should be expanded to a lower frequency of 725 cm^{-1} in order to include the strong absorption found with the 1,10-phenanthrolines. Using the original ranges noted in Table 24, the apparent presence of four or five adjacent hydrogen atoms would be predicted by the position of this absorption. Examination of Tables 25, 26, and 27 reveals that the absorption related to three adjacent ring hydrogen atoms with pyridines and quinolines conforms to the original ranges summarized in Table 24.

The spectra of monosubstituted derivatives containing other substituents produce similar absorptions in this region with some differences. In Table 29 the bands observed with these compounds are compared to those found above with methyl

Table 29. Absorptions found in the 900-650 cm^{-1} region in spectra of monosubstituted 1,10-phenanthrolines

Compound	Absorptions which conformed to the expected regions ^a (cm^{-1})				Major absorptions not interpreted (cm^{-1})	
1,10-Phenanthroline ^b	---	839	733	703	765	
2-Methyl-	---	849	734	714	775	
2-Chloro-	---	839	729	709	871	766
2-Methoxy-	---	843	739	682		
2-Hydroxy- ^c	---	841	734	700	628	
2-Aza-	---	876 866 ^d	743	723		
3-Methyl-	884	829	728	714	779	675
3-Ethyl-	909	850	741	712	789	673
3-Chloro-	909	830	727	711	871	
3-Bromo-	896	831	726	708	865	753
3-Aza-	888 ^e	834 829 ^d	736	713 ^e	862	
4-Methyl-	---	842	729	718 ^e		

^aAs summarized in Table 24.^bAnhydrous material.^cSee discussion in section IV, E for the probability of this compound being in the keto form.^dDoublet absorption.^eA relatively weak absorption.

Table 29. (Continued)

Compound	Absorptions which conformed to the expected regions ^a (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)	
4-Ethyl-	---	832	727	718 ^f		
4-n-Propyl-	---	845 835 ^d	746	726		780
4-Chloro-	---	829 820 ^d	727	715 ^e		795
4-Bromo-	---	828 816 ^d	725	716		768
4-Aza-	---	841 830 ^d	738	700	876 867 ^d	786
4-(3-Diethylamino-propylamino)-	---	829	732	717		808
5-Methyl-	879	---	740	709		796
5-Ethyl- ^g	884	---	741	711 ^e		
5-Fluoro-	899 885 ^d	---	736	714		797 647
5-Chloro-	871	---	736	707 ^f		793
5-Bromo-	870	---	734	708 ^h		794
5-Methoxy-	891 ^h	---	739	713 ^h	835 823 ^d	
5-Hydroxy-	896 ^e	---	736	715	841	
5-Nitro-	905 892 ^{d, e}	---	744 730 ^d	710	831 803 ^d	
5-Amino-	884	---	740	709	842 826 ^d	
5-Aza-	899	---	736	708		795

^fOnly a shoulder present.^gFrequencies from a cap cell spectrum.^hA very weak absorption.

derivatives. The 2-chloro-1,10-phenanthroline spectrum has a strong absorption at 871 cm^{-1} which is not observed with the other 2-substituted derivatives. This peak would erroneously indicate the presence of an isolated free hydrogen atom as with the 3- and 5-substituted compounds. Examination of spectra of other chloro derivatives reveals the presence of this peak in many instances, however. The strong absorption at 628 cm^{-1} with 2-hydroxy-1,10-phenanthroline is unique as shown by comparison with spectra of all the other monosubstituted derivatives. All peaks with 2-aza-1,10-phenanthroline are shifted to higher frequencies than are observed with the other 2-substituted derivatives. The strong absorptions at 909 cm^{-1} , 850 cm^{-1} and 741 cm^{-1} in the 3-ethyl-1,10-phenanthroline spectrum are found at higher frequencies than noted with the corresponding peaks in the 3-methyl-1,10-phenanthroline spectrum. As shown in Table 26 similar shifts of absorptions to higher frequency with ethylpyridines occurred. McCaulay *et al.* (42) observed shifts of absorptions in this region with 1,3,5-triethylbenzene contrasted to 1,3,5-trimethylbenzene. This displacement of absorptions to higher frequency is not always observed with the ethyl-1,10-phenanthrolines (note the frequencies recorded in Table 29 for 4-ethyl-1,10-phenanthroline). Similar shifts to higher frequency are found with 4-n-propyl-1,10-phenanthroline. With some 5-substituted derivatives (5-methoxy-, 5-hydroxy-, 5-nitro-, and 5-amino-1,10-phenanthroline), an uninterpreted absorption appears in the 842-803

cm^{-1} range. The presence of these absorptions in this region would mistakenly infer the presence of two adjacent ring hydrogen atoms on the carbocyclic ring.

The absorption frequencies with monophenyl derivatives correlated to the number of adjacent ring hydrogen atoms are presented in Table 30. Two additional frequency ranges ($770\text{--}730\text{ cm}^{-1}$ and $710\text{--}690\text{ cm}^{-1}$) were to be considered in each case owing to the presence of five adjacent ring hydrogen atoms provided by the phenyl group. These ranges overlapped with those reported in Table 24 for three adjacent hydrogen atoms, and the second absorption at $710\text{--}690\text{ cm}^{-1}$ anticipated with five adjacent free hydrogen atoms was reported to be stronger. This greater intensity is indeed observed with the monophenyl derivatives in the $713\text{--}700\text{ cm}^{-1}$ range. This band is, in fact, quite distinctive for phenyl derivatives of 1,10-phenanthroline, in that it is much more intense than observed in spectra of 1,10-phenanthroline and other monosubstituted 1,10-phenanthrolines (note in particular the intensity of this peak with 4- and 5-phenyl-1,10-phenanthroline at 700 cm^{-1} and 713 cm^{-1} respectively in Figures 71 and 72). The absorption at $776\text{--}757\text{ cm}^{-1}$ found with these monophenyl derivatives is associated with the $770\text{--}790\text{ cm}^{-1}$ range quoted above for five adjacent free hydrogen atoms. This peak is not unique for phenyl derivatives since an absorption of similar intensity appears within this region in spectra of 1,10-phenanthroline and other substituted

Table 30. Absorptions in the 900-650 cm^{-1} region in spectra of monophenyl-1,10-phenanthrolines correlated to the number of adjacent free hydrogen atoms

Compound	Number of adjacent free hydrogen atoms on each ring ^a				Expected absorp- tion regions (cm ⁻¹) ^b	Absorptions which conformed to the expected regions (cm ⁻¹)					Major absorp- tions not interpreted (cm ⁻¹)	
	A	B	C	Phenyl								
1,10-Phenan- throline ^c	3	3	2	--	(2), (3)	---	839	---	733	703		765
2-Phenyl-	3	2	2	5	(2), (3), (5)	---	839	765	733	686 ^d		
3-Phenyl- ^e	3	1 ^f	2	5	(1), (2), (3), (5)	899	828 822 ^g	757	732	693		
4-Phenyl-	3	2	2	5	(2), (3), (5)	---	851 841 ^g	765	748	700 ^d	805	792
5-Phenyl-	3	3	1 ^h	5	(1), (3), (5)	888 872 ^g	---	766	742	713 ^d	809	794 788 ^g

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected frequency ranges were: (1) 900-860 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.); (5) 770-730 (v.s.) and 710-690 (s.).

^cAnhydrous material.

^dStronger absorption than usually observed for this band.

^eFrequencies from the carbon disulfide spectrum.

^fTwo isolated ring hydrogen atoms are present.

^gDoublet absorption.

^hOne isolated ring hydrogen atom is present.

derivatives.

b. Disubstituted derivatives In Table 31 the absorptions in the $900\text{-}650\text{ cm}^{-1}$ range with dimethyl-1,10-phenanthrolines are correlated to the number of adjacent ring hydrogen atoms present. The correlation fails in general with substitution on both heterocyclic rings, since strong absorption occurs in the $750\text{-}727\text{ cm}^{-1}$ range with the dimethyl-1,10-phenanthrolines (absorption in this range was related before as due to the presence of three adjacent ring hydrogens on the heterocyclic rings). With 2,9-dimethyl-1,10-phenanthroline, however, the doublet peak in this region is of much less intensity than the one expected absorption which appears at 852 cm^{-1} . In other instances, as with 3,7-dimethyl-, 3,8-dimethyl-, and 4,7-dimethyl-1,10-phenanthroline, the absorptions in this region are quite strong and would cause error in characterization of the substitution position using this region. Even with this above discrepancy, the correlation proved to be useful in detecting the presence of an isolated free hydrogen atom. A medium to strong band is found in the $892\text{-}863\text{ cm}^{-1}$ region in spectra of all the dimethyl-1,10-phenanthrolines which contain an isolated ring hydrogen. Characterization of substitution on the carbocyclic ring is not consistent. The absorption in the $852\text{-}797\text{ cm}^{-1}$ region, which is related to the presence of two adjacent ring hydrogen atoms, is absent in the 3,5-methyl-

Table 31. Absorptions in the 900-650 cm^{-1} region in spectra of dimethyl-1,10-phenanthrolines correlated to the number of adjacent ring hydrogen atoms

Compound	Number of adjacent hydrogen atoms on each ring ^a			Expected absorption regions (cm^{-1}) ^b	Absorptions which conformed to the expected regions (cm^{-1})				Major absorptions not interpreted (cm^{-1})	
	A	B	C							
1,10-Phenanthroline ^c	3	3	2	(2), (3)	---	839	733	703	765	
2,4-Dimethyl-	3	1 ^d	2	(1), (2), (3)	871	834	732	696	768	
2,9-Dimethyl-	2	2	2	(2)	---	852	---	---	750 737 ^{e, f}	
3,4-Dimethyl-	3	1 ^d	2	(1), (2), (3)	863	832	733	684		
3,5-Dimethyl-	3	1 ^g	1 ^d	(1), (3)	882	---	745	699	799	643

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected frequency ranges were: (1) 900-860 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.).

^cAnhydrous material.

^dOne isolated ring hydrogen atom is present.

^eDoublet absorption.

^fAbsorption in this region erroneously infers the presence of three adjacent ring hydrogen atoms.

^gTwo isolated ring hydrogen atoms are present.

Table 31. (Continued)

Compound	Number of adjacent hydrogen atoms on each ring ^a			Expected absorption regions (cm ⁻¹) ^b	Absorptions which conformed to the expected regions (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)	
	A	B	C							
3,6-Dimethyl-	3	1 ^g	1 ^d	(1), (3)	892	---	742	680 ^h	828 820 805 ⁱ	664
3,7-Dimethyl-	2	1 ^g	2	(1), (2)	887	872	---	---	735 709 ^f	
3,8-Dimethyl-	1 ^g	1 ^g	2	(1), (2)	890	825	---	---	736 688 ^f	
4,5-Dimethyl-	3	2	1 ^d	(1), (2), (3)	864	797	751	--- ^j		644
4,6-Dimethyl-	3	2	1 ^d	(1), (2), (3)	866	812	748	705		
4,7-Dimethyl-	2	2	2	(2)	---	848	---	---	727 ^f	
5,6-Dimethyl-	3	3	0	(3)	---	---	738	--- ^j	819 795	

^hRelatively weak absorption.

ⁱTriplet absorption of medium intensity.

^jThe medium absorption usually found with the presence of three adjacent free hydrogen atoms is absent.

1,10-phenanthroline spectrum, however, with 3,6-dimethyl- and 5,6-dimethyl-1,10-phenanthroline medium to strong absorption is found in the $820\text{--}800\text{ cm}^{-1}$ region.

In Table 32 the absorption observed with disubstituted derivatives with other types of substituents (except phenyl, phenoxy, benzo, and pyrido) are compared with those of dimethyl-1,10-phenanthrolines. The spectra of many 3,4-substituted derivatives contain peaks which could not be interpreted using this correlation. With three of the four 3,4-cycloalkeno-1,10-phenanthrolines, a medium intensity absorption is found near 776 cm^{-1} . Also a medium band appears at 659 cm^{-1} with two of these derivatives. The presence of the strong peak at 825 cm^{-1} in the spectrum of 3,5-dichloro-1,10-phenanthroline would incorrectly suggest the presence of two adjacent ring hydrogen atoms. The strong absorption in the $758\text{--}720\text{ cm}^{-1}$ region with many of these derivatives with substitution on the heterocyclic rings could not be accounted for (note the 3,7-, 3,8-, and 4,7-substituted derivatives). Several of the 5,6-substituted derivatives give strong absorption in the $909\text{--}861\text{ cm}^{-1}$ region which would falsely indicate the presence of an isolated ring hydrogen atom. With some of these latter compounds, the medium to weak absorption near 700 cm^{-1} usually found with the presence of three adjacent ring hydrogen atoms is absent. This ob-

Table 32. Absorptions found in the 900-650 cm^{-1} region in spectra of disubstituted 1,10-phenanthrolines

Compound	Absorptions which conformed to the expected regions ^a (cm^{-1})				Major absorptions not interpreted (cm^{-1})	
1,10-Phenanthro- line ^b	---	839	733	703	765	
2,4-Dimethyl-	871	834	732	696	768	
2,4-Dihydroxy-	882 ^c	828	742 ^c	693 ^c		
2-Methyl-4- hydroxy-	884 ^c	853 841 835 ^d	737	700		
4-Hydroxy-2-aza-	891	839	734	713	786	
4-Chloro-2-aza-	889 ^c	834 824 ^e	732	722		
3,4-Dimethyl-	863	832	733	684		
3-Carbethoxy-4- hydroxy-	879 ^c	842	730	691	824	781
3,4-Cyclopenteno-	884	830	728	691		
3-Carboxy-4- hydroxy-	--- ^f	845	--- ^f	--- ^f	792	773
3,4-Cyclohexeno-	873	846 838 831 ^d	733	686	812	776
3,4-Cyclohepteno-	884 ^c	843 832 826 ^d	743	686	776	659
3,4-Cycloocteno-	868	838 829 ^e	753 735 ^e	681	778	659

^aAs summarized in Table 24.^bAnhydrous material.^cRelatively weak absorption.^dTriplet absorption.^eDoublet absorption.^fNo absorption observed in the expected region.

Table 32. (Continued)

Compound	Absorptions which conformed to the expected regions ^a (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)	
3,5-Dimethyl-	882	---	745	699	799	643
3,5-Dichloro-	904 893 884 ^g	---	736	721 ^c	825 794	
3,5-Dibromo-	908 892 877 ^d	---	736	716 ^c	789	
3,6-Dimethyl-	892	---	742	680	828 820 805 ^d	664
3,6-Dibromo-	895	---	734	717	799 768	
3,7-Dimethyl-	887	872	---	---		735 709
3-Methyl-7-chloro-	891 875 ^e	821	---	---	796	726 703
3,8-Dimethyl-	890	825	---	---		736 688
3,8-Diethyl-	919 908 ^e	823	---	---		742 718 684
3,8-Dichloro-	920 912 896 ^d	804 793 ^e	---	---		720 712
4,5-Dimethyl-	864	797	751	--- ^h		644
4,5-Dihydroxy-	882	836	801	697		
4,6-Dimethyl-	866	812	748	705		
4,6-Diethyl-	879	817	741	703	845 791	
4,7-Dimethyl-	---	848	---	---		727
4,7-Diethyl-	---	854	---	---	883 834 826 ^e	739
4,7-Dichloro-	---	834	---	---	873 811 782	719
4,7-Dibromo-	---	832	---	---	775	758

^gPoorly resolved triplet.

^hThe medium absorption usually found with the presence of three adjacent hydrogen atoms is absent.

Table 32. (Continued)

Compound	Absorptions which conformed to the expected regions ^a (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)		
4,7-Dimethoxy-	---	830	---	---			
		809 ^e					
4,7-Dihydroxy-	---	805	---	---			
4,7-Diaza-	---	830	---	---	882		753 745 ^e
4,7-Bis-(3-di- ethyl-amino- propylamino)-	---	810	---	---			728
4,7-Bis-(4-di- ethyl-1-methyl- butylamino)-	---	803	---	---			727
5,6-Dimethyl-	---	---	738	--- ^h	819	795	
5,6-Diethyl-	---	---	745	--- ^h	909 823 804 ^d		
5,6-Dichloro-	---	---	734	--- ^h	903	796	768
5,6-Dibromo-	---	---	732	--- ^h	881	801 794 ^e	
5,6-Dimethoxy-	---	---	745 738 ^e	684 ^c		801	
1,10-Phenanthro- line 5,6-dione	---	---	743	696 ^c	817 808 ^c		
5,6-Dihydroxy-	---	---	733	691 ^c	812 802 ^e		
5-Nitro-6-methyl-	---	---	739	--- ^h	861	825 818 ^e	797
5,6-Dioxime-	---	---	743	--- ^h	896	808	
5,6-Cyclohexeno-	---	---	740	--- ^h		810 791 ^e	

servation would in many instances distinguish the 5,6-disubstituted derivatives from the 5-monosubstituted compounds in which this medium to weak absorption was observed to present in Table 29.

Absorptions found in the $900\text{-}650\text{ cm}^{-1}$ region with diphenyl derivatives, $R\text{-}R'$ compounds containing one phenyl group, benzo derivatives, and pyrido derivatives are recorded in Table 33. As observed before in Table 30 with monophenyl-1,10-phenanthrolines, the band in the $710\text{-}690\text{ cm}^{-1}$ region is of much greater intensity than normally found, and this increased intensity was characteristic of phenyl substitution on 1,10-phenanthrolines. The spectrum of the one phenoxy compound contains a very strong absorption at 690 cm^{-1} also. The spectra of the two benzo derivatives and the one pyrido compound do not have a strong band in this region which is consistent with the correlation. No strong peak was expected here with four and three adjacent hydrogen atoms present with the new rings due to the benzo and pyrido substitution. The absorption at 752 cm^{-1} in the 5,6-benzo-1,10-phenanthroline spectrum is quite intense. The expected region for four adjacent ring hydrogen atoms overlaps with that found with three adjacent ring hydrogens. As observed in Table 33 with 5,6-substitution, two groups of three adjacent ring hydrogens are present on the heterocyclic rings, and together with the four adjacent ring hydrogens of the benzo ring, the strong

Table 33. Absorptions in the 900-650 cm^{-1} region in spectra of disubstituted 1,10-phenanthrolines containing phenyl, phenoxy, benzo, and pyridic groups correlated to the number of adjacent ring hydrogen atoms

Compound	Number of adjacent ring hydrogen atoms on each ring ^a				Expected absorption regions ^b (cm^{-1})	Absorptions which conformed to the expected regions (cm^{-1})	Major absorptions not interpreted (cm^{-1})
	A	B	C	New ^c			
1,10-Phenanthroline ^d	3	3	2	-	(2), (3)	--- 839 --- 733 703	765
2,9-Diphenyl-	2	2	2	5	(2), (5)	--- 845 760 734 693 ^e	
3-Phenyl-4-hydroxy-	3	1 ^f	2	5	(1), (2), (3), (5)	863 842 781 --- 696 ^e 820 769 756 ^g	

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected absorptions ranges were: (1) 900-860 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.); (4) 770-735 (v.s.); (5) 770-730 (v.s.) and 710-690 (s.).

^cThe substitution of a phenyl, phenoxy, benzo, or pyridic group give additional adjacent ring hydrogen atoms.

^dAnhydrous material.

^eStronger absorption than usually observed for this band.

^fOne isolated ring hydrogen atom is present.

^gTriplet absorption.

Table 33. (Continued)

Compound	Number of adjacent ring hydrogen atoms on each ring ^a				Expected absorption regions ^b (cm ⁻¹)	Absorptions which conformed to the expected regions (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)	
	A	B	C	New ^c							
3-Phenyl-4-chloro-	3	1 ^f	2	5	(1), (2), (3), (5)	875 ^h	828	755	734	698	684 ^{e, i}
3-Phenyl-4-bromo-	3	1 ^f	2	5	(1), (2), (3), (5)	872 ^h	826	752	733	698	683 ^{e, i} 789
3,8-Di-phenyl-	1 ^j	1 ^j	2	5	(1), (2), (5)	909	810	763	734	695 ^e	
4,6-Di-phenyl-	3	2	1 ^f	5	(1), (2), (3), (5)	892	850	770	753	703 ^e	799
4,7-Di-phenyl-	2	2	2	5	(2), (5)	---	845	766	750 740 ⁱ	700 ^e	
4,7-Di-phenoxy-	2	2	2	5	(2), (5)	---	847 825 ⁱ	768	741 732 ^{h, i}	692 ^e	804
2,3-Benzo-	3	1 ^f	2	4	(1), (2), (3), (4)	883 ^h	829	776	750	701	
5,6-Benzo-	3	3	0	4	(3), (4)	---	---	---	752 ^e	690	809
5,6-Pyrido-	3	3	0	3	(3)	---	---	---	735	690 ^h	818 761

^hWeak absorption.ⁱDoublet absorption.^jTwo isolated free hydrogen atoms are present on this ring.

absorption at 752 cm^{-1} could be accounted for. This band with 2,3-benzo-1,10-phenanthroline is only of medium intensity. Here only one group of three adjacent ring hydrogen atoms is present in this compound.

c. Trisubstituted derivatives Absorptions found in the $900\text{--}650\text{ cm}^{-1}$ region with trisubstituted-1,10-phenanthrolines are recorded in Table 34. As observed in Table 31 with dimethyl-1,10-phenanthrolines, strong bands appear in the $753\text{--}726\text{ cm}^{-1}$ region which could not be interpreted for derivatives with substitution on both heterocyclic rings. The band in the $900\text{--}860\text{ cm}^{-1}$ range which was associated with the presence of isolated hydrogens on the rings could be detected in all cases where isolated ring hydrogen atoms are found. Absorption is found in the 820 cm^{-1} region with 3,5,6-trimethyl-1,10-phenanthroline as was observed earlier with 5,6-dimethyl-1,10-phenanthroline in Table 31. In each instance this peak would incorrectly predict the presence of two adjacent ring hydrogens. As with the 5,6-dichloro- and 5,6-dibromo-1,10-phenanthrolines, the medium absorption in the $725\text{--}680\text{ cm}^{-1}$ range, generally observed with compounds containing three adjacent ring hydrogen atoms, is absent with 3,5,6-trichloro- and 3,5,6-tribromo-1,10-phenanthroline. A medium band is found in this range with 3,5,6-trimethyl-1,10-phenanthroline, however. With 3,5,8-trimethyl-1,10-phenanthroline, only isolated hydrogen atoms remain on the rings, however other ab-

Table 34. Absorptions in the 900-650 cm^{-1} region in spectra of trisubstituted 1,10-phenanthrolines correlated to the number of adjacent ring hydrogen atoms

Compound	Number of adjacent ring hydrogen atoms on each ring ^a			Expected absorption regions ^b (cm^{-1})	Absorptions which conformed to the expected regions (cm^{-1})				Major absorptions not interpreted (cm^{-1})
	A	B	C						
1,10-Phenanthroline ^c	3	3	2	(2), (3)	---	839	733	703	765
2,3,4-Tri-methyl-	3	0	2	(2), (3)	---	839 ^d 826	734	--- ^e	652
3,4,6-Tri-methyl-	3	1 ^f	1 ^f	(1), (3)	860	---	745	684	795
3,4,7-Tri-methyl-	2	?	1 ^f	(1), (2)	900	879 858 844 ^g	---	---	809 726

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected frequency ranges were: (1) 900-860 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.).

^cAnhydrous material.

^dDoublet absorption.

^eThe medium absorption usually found with the presence of three adjacent ring hydrogen atoms is absent.

^fOne isolated ring hydrogen atom is present.

^gTriplet absorption.

Table 34. (Continued)

Compound	Number of adjacent ring hydrogen atoms on each ring ^a			Expected absorption regions ^b (cm ⁻¹)	Absorptions which conformed to the expected regions (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)		
	A	B	C								
3,4,8-Tri-methyl-	1 ^h	1 ^f	2	(1), (2)	899	861	---	---	825 818 ^d	734	713
3,5,6-Tri-methyl-	3	1 ^h	0	(1), (3)	877	---	745	709	828 821 805 ^g		674
3,5,6-Tri-chloro-	3	1 ^h	0	(1), (3)	897	---	735	--- ⁱ	842	815 ^d 806 ^d	
3,5,6-Tri-bromo-	3	1 ^h	0	(1), (3)	899 893 ^d	---	748 732 ^d	--- ⁱ	817 808 799 ^g		
3,5,7-Tri-methyl-	2	1 ^h	1 ^f	(1), (2)	883	855 ^j	---	---		749	715 698 ^d
3,5,8-Tri-methyl-	1 ^h	1 ^h	1 ^f	(1)	899 883 ^d	---	---	---		744	698 665
3,6,7-Tri-methyl-	2	1 ^h	1 ^f	(1), (2)	891	856	---	---	874	749	667
4,5,7-Tri-methyl-	2	2	1 ^f	(1), (2)	867 849 ^d	828	---	---		753	

^hTwo isolated ring hydrogen atoms are present.

ⁱThe medium absorption usually found with the presence of three adjacent ring hydrogen atoms is absent.

^jRelatively weak absorption.

sorptions are found, which were not interpreted, in addition to the anticipated peak in the expected region of 900-860 cm^{-1} . Those trisubstituted derivatives of the hydroxy group of compounds were not included in Table 34. In general the spectra of these materials are not very intense or resolved in this region.

d. Tetrasubstituted and hexasubstituted derivatives The absorptions in the 900-650 cm^{-1} region of tetra- and hexasubstituted 1,10-phenanthrolines are recorded in Table 35. None of these compounds contain three adjacent hydrogen atoms on the heterocyclic ring, yet strong absorption occur in the 758-729 cm^{-1} region in spectra of each of these derivatives. Also in some instances medium to weak absorption is found in the 725-688 cm^{-1} region. Most of these materials contain one or more isolated ring hydrogen atoms, and in every case absorption in the 900-860 cm^{-1} region is observed. Only isolated hydrogens are present with 3,4,6,8-tetramethyl-1,10-phenanthroline, however, the strong peak appeared at 849 cm^{-1} which would incorrectly imply the presence of two adjacent ring hydrogen atoms.

The absorptions found in the 900-650 cm^{-1} region with tetrasubstituted 1,10-phenanthrolines containing phenyl groups are recorded in Table 36. Very strong bands are found in the 705-693 cm^{-1} range which are characteristic of phenyl substitution as observed earlier, Tables 30 and 33.

Table 35. Absorptions in the 900-650 cm^{-1} region in spectra of tetra- and hexa-substituted 1,10-phenanthrolines correlated to the number of adjacent ring hydrogen atoms

Compound	Number of adjacent ring hydrogen atoms on each ring ^a			Expected absorption regions ^b (cm^{-1})	Absorptions which conformed to the expected regions (cm^{-1})				Major absorptions not interpreted (cm^{-1})	
	A	B	C							
1,10-Phenanthroline ^c	3	3	2	(2), (3)	---	839	733	703	765	
2,3,8,9-Tetra-methyl-	1 ^d	1 ^d	2	(1), (2)	904	818	---	---	737	718 ^e 667
2,4,7,9-Tetra-methyl-	1 ^d	1 ^d	2	(1), (2)	880 873 861 ^f	812	---	---	750	725 679
2,5,6,9-Tetra-methyl-	2	2	0	(2)	---	834 823 815 ^f	---	---	745	649

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected frequency ranges were: (1) 900-860 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.).

^cAnhydrous material.

^dOne isolated ring hydrogen atom is present.

^eRelatively weak absorption.

^fTriplet absorption.

Table 35. (Continued)

Compound	Number of adjacent ring hydrogen atoms on each ring ^a			Expected absorption regions ^b (cm ⁻¹)	Absorptions which conformed to the expected regions (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)		
	A	B	C								
3,4,6,7-Tetra-methyl-	2	1 ^d	1 ^d	(1), (2)	887	867 849 ^g	---	---		754	
3,4,6,8-Tetra-methyl-	1 ^h	1 ^d	1 ^d	(1)	882	---	---	---	849	748	701 688 ^g
3,4,7,8-Tetra-methyl-	1 ^d	1 ^d	2	(1), (2)	864 850 ^g	825	---	---		732	709
(3,4),(7,8)-Dicyclopenteno-	1 ^d	1 ^d	2	(1), (2)	889 874 ^g	832	---	---		732	
(3,4),(7,8)-Dicyclohexeno-	1 ^d	1 ^d	2	(1), (2)	896	850 840 ^g	---	---		758	
3,5,6,8-Tetra-methyl-	1 ^h	1 ^h	0	(1)	879	---	---	---		744	724 690
3,5,6,8-Tetra-bromo-	1 ^h	1 ^h	0	(1)	897 887 ^g	---	---	---		730	
2,3,4,7,8,9-	0	0	2	(2)	---	818 805 796 ^f	---	---		729	720 ⁱ

^gDoublet absorption.^hTwo isolated ring hydrogen atoms are present.ⁱShoulder.

Table 36. Absorptions in the 900-650 cm^{-1} region in spectra of tetrasubstituted 1,10-phenanthrolines containing a phenyl group correlated to the number of adjacent ring hydrogen atoms

Compound	Number of adjacent hydrogen atoms on each ring ^a				Expected absorption regions ^b (cm^{-1})		Absorptions which conformed to the expected regions (cm^{-1})				Major absorptions not interpreted (cm^{-1})	
	A	B	C	Phenyl								
1,10-Phenanthroline ^c	3	3	2	-	(2), (3)	---	839	766	733	703		765
2,4,7,9-Tetraphenyl-	1 ^d	1 ^d	2	5	(1), (2), (5)	886	839 ^e 828	766	740	691 ^f		
2,9-Dimethyl-4,7-diphenyl-	1 ^d	1 ^d	2	5	(1), (2), (5)	880	840 830 ^e	769	740 726 ^e	705 ^f		

^aThe designation of A, B, and C for the three rings in 1,10-phenanthroline was made above.

^bAs summarized in Table 24, the expected frequency ranges were: (1) 900-850 (m.); (2) 860-800 (v.s.); (3) 810-750 (v.s.) and 725-680 (m.); (5) 770-730 (v.s.) and 710-690 (s.).

^cAnhydrous material.

^dOne isolated ring hydrogen atom is present.

^eDoublet absorption.

^fMuch stronger absorption than usually observed for this band.

Table 36. (Continued)

Compound	Number of adjacent hydrogen atoms on each ring ^a				Expected absorption regions ^b (cm ⁻¹)	Absorptions which conformed to the expected regions (cm ⁻¹)				Major absorptions not interpreted (cm ⁻¹)	
	A	B	C	Phenyl							
2,9-Diphenyl-4,7-dimethyl-	1 ^d	1 ^d	2	5	(1), (2), (5)	894	815	783 770 ^e	728	693	867
3,8-Diphenyl-4,7-dihydroxy-	1 ^d	1 ^d	2	5	(1), (2), (5)	899 ^g	808 ^g	772	---	698	
3,8-Diphenyl-4,7-dichloro-	1 ^d	1 ^d	2	5	(1), (2), (5)	856 ^g	814	767	734 ^g	697 ^f	
3,8-Diphenyl-	1 ^d	1 ^d	2	5	(1), (2), (5)	855 ^g	810	765	736 731 ^e	697 ^f	786

^gRelatively weak absorption.

VI. SUMMARY

The infrared spectra of 1,10-phenanthroline and of one hundred and thirty-six 1,10-phenanthroline derivatives have been obtained and studied in detail.

The purity of the available 1,10-phenanthrolines has been carefully checked and impure materials recrystallized and analyzed. Sixteen 1,10-phenanthroline derivatives, not otherwise available, have been synthesized and purified following procedures previously described. In a few instances new structures have been assigned to previously reported compounds and to one new derivative.

The spectrum of 1,10-phenanthroline has four regions of strong absorption. Assignments of the absorption bands in these regions to specific modes of vibration in the molecules which have been previously reported have been critically examined, and certain new assignments have been proposed.

A large shift to lower frequency of the C-H stretching absorption has been found in the spectra of the 1,10-phenanthrolines in chloroform solution; this has been attributed to the interaction of the solvent with the 1,10-phenanthroline ring nitrogen atoms.

The acid salts of 1,10-phenanthroline have also been studied, and the alterations in the spectra from that of the

parent, free base have been attributed to shifts of the ring vibration bands to higher frequencies. In some instances the "immonium bands" found in the 2066-1912 cm^{-1} range as very weak and broad absorptions have been used as aids in identification of these salts.

The absorption bands which appear or are altered by the introduction in the 1,10-phenanthroline molecule of various substituents, as methyl, ethyl, propyl, halogen, phenyl, methoxy, phenoxy, dione, hydroxy, nitro, amino, aza, dioxime, dialkylaminoalkylamino, R-R', cycloalkeno, benzo, and pyrido, have been identified. The general characteristics of spectra of the 1,10-phenanthroline derivatives have been established.

Examination of the infrared spectra of these numerous 1,10-phenanthroline derivatives has shown that in certain regions, patterns exist which are characteristic of the number and position of the substituents in the molecule but are essentially independent of the nature of the substituent. Three regions have been found to be useful in this respect.

The absorption patterns in the 5.0-6.0 micron (2000-1667 cm^{-1}) region in the spectra of the 1,10-phenanthrolines have been related to the substitution type. This region has provided the most useful and versatile information for characterization of position of substituents on 1,10-phenanthroline. Typical expanded patterns have been recorded for all 1,10-phen-

anthrolines which are soluble in chloroform. The exceptions to the usual patterns have been noted in spectra of some derivatives. Similar patterns are found in some instances with derivatives of different substitution type, and examination of other regions of spectra are required for positive identification of the position of substitution.

Confirmatory information on the substitution type present has been found in the $1667\text{--}1250\text{ cm}^{-1}$ and $900\text{--}650\text{ cm}^{-1}$ regions. The 5,6-substituted derivatives have been generally distinguished in the first of the above ranges by the shift of the 1616 cm^{-1} band of 1,10-phenanthroline to lower frequency. Also 3,8-substitution has been detected by the absence of the 1587 cm^{-1} band of 1,10-phenanthroline. The stronger absorptions appearing in the $900\text{--}650\text{ cm}^{-1}$ region in spectra of the 1,10-phenanthrolines have been correlated to the number of adjacent ring hydrogen atoms present on each ring of the 1,10-phenanthroline structure. In general, those derivatives with one or more isolated ring hydrogen atoms have been distinguished by the appearance of a medium band in the $900\text{--}860\text{ cm}^{-1}$ range. Substitution on the carbocyclic ring has been detected in many instances by the absence of an absorption in the $860\text{--}800\text{ cm}^{-1}$ range, but several exceptions to this correlation have been observed. The strong absorption in the $810\text{--}725\text{ cm}^{-1}$ has been found not to be completely charac-

teristic for the presence of three adjacent ring hydrogens, since with substitution on both heterocyclic rings strong absorption is consistently present in this region. Phenyl substitution on 1,10-phenanthroline has been characterized by the appearance of a strong absorption in the $713\text{-}690\text{ cm}^{-1}$ region.

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