A STUDY OF THE VIBRATIONAL SPECTRA OF
SOME MONOSUBSTITUTED PYRIDINES

BY

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ABSTRACT

Infrared spectra in the range (4000-250 cm^{-1}) and Raman spectra in the range (4000-150 cm^{-1}) of pyridine, 2-, 3- and 4-chloro-, bromo-, and methylpyridines, 2-fluoro-, 2-amino and 4-ethylpyridines have been measured. The spectra, vibration and assignments of the observed frequencies of 2-amino-, and 4-ethylpyridines are presented for the first time. The infrared data for 2-fluoropyridine is combined with the previously reported Raman data of Stephenson and Voelz to allow complete vibrational assignments for this compound for the first time. Frequency assignments for the other molecules are re-examined and where necessary changes and/or additions in frequency assignments are made.

Correlations between related series of pyridine and pyridine derivatives are investigated. The possible correlations between the vibrations of monosubstituted pyridines and the corresponding vibrations of monosubstituted benzene compounds were studied and it was found that they show a few similarities. Also, the location of the substituted on the ring is seen to influence the frequency of some of the vibrations. Further, other than C-H stretching vibrations, 5 vibrational modes are similar for the 1-, 2-, and 3-substituted pyridines (i.e., frequencies are independent of the location of the substituent and analogous to the corresponding vibrations of the monosubstituted benzene compounds. The correlations between a substituted pyridine and a monosubstituted benzene are seen to be useful in making vibrational assignments on other related compounds.

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OF SOME MONOSUBSTITUTED PYRIDINES

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TABLE OF CONTENTS

PAGE

INTRODUCTION 1

EXPERIMENTAL 6

RESULTS 8

DISCUSSION 62

A. 4-Substituted pyridines 63

B. 3-Substituted pyridines 68

C. 2-Substituted pyridines 72

D. General comparison of monosubstituted pyridines and monosubstituted benzenes 78

CONCLUSIONS 87

SUGGESTIONS FOR FURTHER WORK 88

BIBLIOGRAPHY 89

LIST OF TABLES

TABLE PAGE

I. CHEMICALS USED IN THIS INVESTIGATION.......................... 7

II. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR PYRIDINE............ 9

III. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 2-FLUOROPYRIDINE ...12

IV. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 2-CHLOROPYRIDINE ...20

V. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 3-CHLOROPYRIDINE ...24

VI. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 2-BROMOPYRIDINE 27

VII. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 3-BROMOPYRIDINE 31

VIII. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 2-AMINOPYRIDINE.....35

IX. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 2-PICOLINE 38

X. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 3-PICOLINE 41

XI. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 4-PICOLINE 44

XII. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR 4-ETHYLPYRIDINE.....47

XIII. FUNDAMENTAL VIBRATIONAL FREQUENCIES OF PYRIDINE AND 2-SUBSTITUTED PYRIDINES 55

XIV. FUNDAMENTAL VIBRATIONAL FREQUENCIES OF PYRIDINE AND 3-SUBSTITUTED PYRIDINES 57

XV. FUNDAMENTAL VIBRATIONAL FREQUENCIES OF PYRIDINE AND 4-SUBSTITUTED PYRIDINES 59

XVI. NOTATION AND APPROXIMATE DESCRIPTIONS OF VIBRATIONS FOR MONOSUBSTITUTED PYRIDINES 65

XVII. FUNDAMENTAL VIBRATIONAL FREQUENCIES OF 4-ETHYLPYRIDINE AND ETHYLBENZENE 69

TABLE PAGE

XVIII. FUNDAMENTAL VIBRATIONAL FREQUENCIES OF 2-AMINOPYRIDINE AND ANILINE 76

XIX. COMPARISONS OF THE VIBRATIONAL SPECTRA OF THE CHLOROPYRIDINES AND CHLOROBENZENE 79

XX. COMPARISONS OF THE VIBRATIONAL SPECTRA OF THE BROMOPYRIDINES AND BROMOBENZENE 81

XXI. COMPARISONS OF THE VIBRATIONAL SPECTRA OF THE FLUOROPYRIDINES AND FLUOROBENZENE 83

INTRODUCTION

Studies involving the comparison and/or correlation of the properties of series of structurally related molecules are important in understanding the chemistry of the molecules and necessary for the development of predictive tools. Infrared and Raman spectra provide data which could perhaps give insight into molecular structure, the nature of the bonding, and hence the chemistry. e.g., reactivity of the molecules.

In this laboratory, investingations have been started on the comparisons of vibrational frequencies in several series of related aromatic systems and possible correlations between these frequencies and molecular parameters. The monosubstituted benzene molecules, one of the simpler aromatic systems available, has been studied extensively. The classical studies of WHIFFEN (1,2) give comparisons of all vibrations for the monohalobenzenes. He found that of the thirty fundamental modes of vibration for a monosubstituted phenyl ring, twenty four vibrations are essentially independent of the substituent attached to the ring and the other six are (X) sensitive vibrations; that is the vibrational modes in which the substituent (X) moves with appreciable amplitude and thus the frequencies are sensitive to the nature of (X). Three of these vibrations, denoted as the q-, r-, and t-vibrations, are generally considered to arise from the C-X stretching vibration, or from the coupling of the C-X stretching vibration and a ring mode. VERSANYI (3) has witten an extensive review of the vibrational studies of other substituted benzene compounds which include compilations of vibrational frequencies and force fields.

Some correlations have been observed for the (X) sensitive vibrations and molecular properties. KROSS and FASSEL (4) studied the q-vibration for monosubstituted phenyl derivatives of the type $(\text{phenyl})_nX$, where (n) is the valence of the substituent atom X (n=1, 2, 3 or 4). They found that for each value of n, the frequency of the q-vibration is linearly related to the square of the electronegativity.

The Gordy Rule (5) was used by KIMMEL (6) to study the nature of the t-vibration of monosubstituted phenyl derivatives for the elements of group IVA through VIIA, i.e., molecules with general formula $(\text{phenyl})_nX$, n= 4, 3, 2 or 1. It was found that the general form of the Gordy Rule can be used for a particular value of (n) and that the t-vibration can be considered a pure (phenyl)- X stretching vibration, except for those molecules formed from the first-row elements. Further, the constants of the Gordy Rule varied linearly with (n) and were different from those given by Gordy. The discrepancies for the derivatives of the first-row elements were explained in terms of vibrational coupling.

The purpose of this investigation is to extend the study of the vibrational spectra and structural correlations of related aromatic systems to monosubstituted pyridines. All six positions on an unsubstituted benzene ring are equivalent. Thus for any substituent, there is only one monosubstituted phenyl molecule. However, on an unsubstituted pyridine ring, a substituent can take a position on the ring that is alpha, beta or gamma to the nitrogen atom in the ring. Thus for any substituent, three isomers can exist and it should be possible to correlate molecular parameters with vibrational frequencies for the position of the substituent as well as for substituents in the same group of the Periodic Table; e.g., halopyridines.

Several reports on the Infrared and Raman spectra of different monosubstituted pyridines appear in the literature. The Infrared and Raman spectra of γ-picoline and γ-picoline-d_7 were reported (7) in the range 650-5000 cm^{-1}. An essentially complete assignment of the fundamental vibrations is proposed. It was based on the following considerations:- (i) comparison with pyridine and pyridine-d_5; (ii) investigation of the sensitivity of the pyridine frequencies to the mass of the γ-substituent in pyridine; (iii) calculation of frequencies for the in-plane and out-of-plane wagging modes of the methyl group by the Pitzer and Taylor method.

Infrared Spectra of pyridine and of 2-, 3- and 4-methylpyridines were recorded (8) and published together with the Raman displacements. Measurements of both Infrared and Raman spectra of 2-, 3-, and 4-chloro- and bromopyridines had been measured (9). Assignments of the observed frequencies were proposed for these and the corresponding methylpyridines, and for the Raman displacements of 2- and 3-fluoropyridines. The assignments were correlated with one another and with those for the deutero compounds. The calculation and interpretation of the out-of-plane vibrations of 2-, 3- and 4-halopyridines have been considered (10). The frequencies and band intensities in the 900-670 cm^{-1} region of pyridine and its methyl substituted derivatives have been compared with frequencies and band intensities in correspondingly substituted benzenes by CUNLIFF-JONES (11). It was found that the assignment of the umbrella CH and trigonal ØCC modes can be made unambiguously in many cases. CUNLIFF-JONES also indicated that in the assignments published by GREEN, KYNASTON and PAISLEY (9), using the WILSON, WILMSHURST- BERNSTEIN notation (W/W-B) (12, 13), the umbrella mode is incorrectly numbered as $_{10b}$ and the frequency should be changed from 886 to 981 cm^{-1} to fit the thermodynamic data.

The WILMSHURST-BERNSTEIN (W-B) assignment gives both a reasonably close fit of calculated and observed thermodynamic functions (13), and best agreement with the normal co-ordinate calculations of LONG, MURFIN and THOMAS (14). This assignment has been adopted by others as a basis for comparative studies (7, 9, 15). The choice of 886 cm^{-1}, is retained here for pyridine.

In the present work, the Infrared and Raman Spectra of pyridine, 2-, 3- and 4-chloro-, bromo- and methylpyridines, 2-fluoro-, 2-amino-, and 4-ethylpyridines have been measured. Tentative assignments of the observed frequencies of 2-amino-, and 4-ethylpyridines are reported for the first time. The Infrared data for 2-fluoropyridine is combined with previously reported Raman data (20) to allow complete vibrational assignments for this compound for the first time. Frequency assignments for the other molecules are re-examined and where necessary changes and/or additions in frequency assignments are made.

Correlations between related series of pyridine and pyridine derivatives are investigated. Further, possible correlations between the vibrations of monosubstituted pyridines and the corresponding vibrations of monosubstituted benzene compounds were studied.

EXPERIMENTAL

The chemicals used in this study are listed in Table I.

The Infrared spectra were obtained from an IR Perkin-Elmer Model 467 double beam spectrophotometer in the range 4000-250 cm^{-1}. A Jarrel-Ash model 400 Raman spectrometer, using a Spectra-Physics Argon Ion Laser with 2 Watt maximum excitation power, was used to obtain the Raman spectra in the 4000-150 cm^{-1} range.

2-Fluoropyridine was received in a sealed ampule, and was opened in an inert atmosphere. It could not be purified because of excessive decomposition. All the molecules, except for 2-aminopyridine, were studied as capillery films using a cesium iodide cell. The Infrared red spectrum of 2-aminopyridine was obtained as a KI disk. Standard liquid and solid sampling methods were used for obtaining the Raman spectra.

TABLE I CHEMICALS USED IN THIS INVESTIGATION.

Chemicals	Sources
Pyridine	Reilly Tar and Chemical Corp.
2-Picoline	Reilly Tar and Chemical Corp.
3-Picoline	Reilly Tar and Chemical Corp.
4-Picoline	Reilly Tar and Chemical Corp.
2-Bromopyridine	Eastman Kodak Co.
3-Bromopyridine	Aldrich Chemical Comp. Inc., 98% purity.
2-Chloropyridine	Eastman Kodak Co.
3-Chloropyridine	Aldrich Chemical Comp. Inc.
2-Fluoropyridine	Aldrich Chemical Comp. Inc.
2-Aminopyridine	Eastman Kodak Co.
4-Ethylpyridine	Reilly Tar and Chemical Corp.

RESULTS

The Infrared and Raman Spectra of pyridine and 2-fluoro-, 2- and 3-chloro-, 2- and 3-bromo-, 2-amino-, 2-, 3- and 4-methyl, and 4-ethylpyridines and their vibrational assignments are shown in Tables II-XII. The fundamental vibrational frequencies of pyridine, 2-substituted, 3-substituted and 4-substituted pyridines are given in Tables XIII-XV. The symmetry species listed for the 4-substituted pyridines (Tables XI, XII and XV) belong to the C_{2v} symmetry group and refer to the symmetry of the ring where the substituents are assumed to be point groups. The 2- and 3-substituted pyridines belong to the C_s symmetry group and its symmetry species are listed for these molcules in Tables III-X, XIII and XIV. Also the symmetry species are listed (in parenthesis) for the C_{2v} symmetry group in Tables XIII and XIV so that comparisons with the corresponding frequencies of the 4-substituted pyridines are possible.

The Infrared and Raman spectra and vibrational assignments of 2-amino- and 4-ethylpyridines (Tables VIII and XII) are presented for the first time. The Raman spectrum (20) and partial vibrational assignments based on the Raman spectrum (9) of 2-fluoropyridine have been reported. The Infrared spectrum of 2-fluoropyridine has not been previously discussed. The Infrared and Raman spectra obtained in this study permitted a more extensive assignment of the vibrational modes. Thus all the fundamental vibrational frequencies could now be assigned (Tables II and XIII). The spectra and vibrational assignment of pyridine and the other substituted pyridines studied here are in good

Table II Vibrational Frequencies and Assignment For Pyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3660(W)		
3400(M)		
--	3175(P)	
3140(M)	3145(P)	
3080(S)		ν(CH)
3054(M)	3055(P)	$z_1\nu$(CH), $z_2\nu$(CH)
3036(S)		X-sens., ν(CH)
3020(S)		
3000(M)		
2990(M)	2990(P)	
2950(W)	2955(P)	
2925(W)	2918(dp)	
2900(W)	2875(P)	
2820(W)	2795(P)	
2590(W)		
2500(VW)		
2480(VW)		
2450(W)	2455(P)	
2420(VW)		

Table II (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
2360(W)	2378(P)	
2290(W)		
2260(VW)		
2200(VW)		
2030(VW)		
1985(W)		
1950(W)		
1920(W)		
1890(W)		
1875(W)		
1685(W)		
1640(W)		
1630(W)		
1595(S)		
1583(S)	1581(dp)	ν(CC)
1572(VS)		ν(CC)
1555(sh)		
1482(S)	1478(P)	ν(CC,CN)
1439(VS)		ν(CC,CN)
1375(W)		ν(CC,CN)

Table II (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1350(W)		
1288(VW)		β(CH)
1218(M)	1223(dp)	β(CH)
1205(W)		
1148(M)	1150(dp)	X-sens.
1085(W)		β(CH)
1068(M)	1070(P)	β(CH)
1030(VS)	1032(P)	X-sens.
992(sh)	991(P)	Ring
986(sh)		γ(CH)
940(W)		γ(CH)
890(sh)		γ(CH)
886(VW)	886(P)	γ(CH)
810(VW)		
744(VS)		φ(CC)
700(VS)		φ(CC)
673(M)		
652(W)	655(dp)	α(CCC)
605(S)	606(dp)	X-sens.
405(S)	408(dp)	X-sens. [φ(CC), γ(CH)]
375(VW)		φ(CC)

Table III Vibrational Frequencies and Assignment For 2-Fluoropyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3908(W)		
3680(W)		
3462(W)		
3180(sh)		
3097(sh)		$a_1\nu(CH)$, $b_1\nu(CH)$
3082(M)		
3075(M)		$a_1\nu(CH)$, $b_1\nu(CH)$
3030(M)		
3021(M)		
2938(W)		
2819(W)		
2770(W)		
2725(W)		
2687(W)		
2615(W)		
2558(W)		
2482(W)		
2421(W)		
2339(W)		

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
2297(W)		
2232(W)		
2196(W)		
2062(W)		
2027(W)		
1980(W)		
1950(W)		
1920(VW)		
1823(VW)		
1798(VW)		
1776(VW)		
1750(VW)		
1740(VW)		
1692(W)		
1687(W)		
1679(M)		
1675(M)		
1671(M)		
1657(M)		
1648(M)		

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1619(S)		
1598(VS)		ν(CC)
1582(S)		
1579(VS)		ν(CC)
1573(S)		
1559(M)		
1548(M)		
1539(M)		
1529(M)		
1510(M)		ν(CC,CN)*
1500(M)		
1492(sh)		
1473(VS)		
1466(sh)		
1458(M)		
1434(VS)	1437	ν(CC,CN)*
1424(sh)		
1419(sh)		
1412(sh)		
1405(sh)		

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1400(sh)		
1390(W)		
1375(W)	1376	ν(CC,CN)*
1370(W)		
1354(W)		
1342 (W)		
1327(W)		
1320(sh)		
1302(sh)	1303	β(CH)
1291(M)		
1259(sh)		
1247(VS)	1250	X-sens.
1240(sh)		
1226(sh)		
1219(sh)		
1200(W)		
1193(W)		
1181(W)		
1173(W)		
1168(W)		

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1153(sh)		
1143(S)	1155	β(CH)
1136(sh)		
1128(sh)		
1113(W)		
1106(sh)		
1098(M)	1102	β(CH)
1090(sh)		
1070(W)		
1062(sh)		
1054(sh)		
1047(M)	1050	β(CH)
1037(M)		
1022(M)		
1008(sh)		
995(S)	997	Ring
972(sh)		
962(W)	965	γ(CH)*
947(W)		
937(W)	935	γ(CH)*

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
872(M)	875	γ(CH)*
856(sh)		
840(VS)		
828(VS)	832	X-sens.
813(sh)		
809(M)		
791(sh)		
787(VS)	792	γ(CH)*
779(VS)		
769(sh)		
760(sh)		
753(M)		
747(M)		
732(S)		Φ(CC)*
720(S)		
700(sh)		
669(M)		
662(W)		
620(S)	630	α (CCC)
584(W)		

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
566(sh)		
558(S)	555	X-sens.
529(sh)		
520(M)		ν(C-F) mode*
504(W)		
495(W)		
486(sh)		
477(M)	479	ϕ(CC)*
470(sh)		
460(W)		
454(W)		
449(W)		
439(sh)		
433(M)		
428(sh)		
418(M)	420	ϕ(CC)*
400(W)		
388(W)		X-sens.*
378(W)		
371(W)		

Table III (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
359(W)	363	
342(W)		
338(W)		
329(W)		
317(W)		
303(M)		
291(W)		
280(W)		
269(W)		
254(W)		
230(W)		X-sens.

* An additional bands.

Table IV Vibrational Frequencies and Assignment For

2-Chloropyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3800(W)		
3660(W)		
3460(W)		
3130(W)	3130(P)	
3090(sh)		
3075(W)	3079(P)	$a_1 \nu(CH)$, $b_1 \nu(CH)$
3060(M)	3055(P)	$a_1 \nu(CH)$, $b_1 \nu(CH)$
3000(W)	2995(P)	
2900(W)	2900(P)	
--	2860(P)	
2800(VW)		
2740(VW)		
2680(VW)		
2650(VW)		
2520(VW)		
--	2475(P)	
2440(VW)		
--	2390(P)	
2320(VW)		

Table IV (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
2298(VW)	2300(P)	
2220(VW)		
2200(VW)		
1985(VW)		
1953(W)		
1920(VW)		
1875(VW)		
1840(W)		
1808(VW)		
1763(VW)		
1725(VW)		
1660(W)		
1610(W)		
1580(VS)	1575(P)	ν(CC)
1568(S)		ν(CC)
1560(S)		
1548(M)		
1470(M)		
1452(VS)	1456(P)	ν(CC,CN)
1420(VS)	1422(dp)	ν(CC,CN)

Table IV (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1366(W)	1362	ν(CC,CN)
1360(W)		
1288(M)	1289(dp)	β(CH)
1280(sh)		
1275(sh)		
1250(VW)		
1236(VW)	1240(P)	
1153(sh)		
1150(S)	1152(P)	β(CH)
1120(VS)	1119(P)	X-sens.
1085(VS)	1084(P)	β(CH)
1045(S)	1045(P)	β(CH)
1038(W)		
1005(W)		
994(S)	994(P)	Ring
983(W)		
960(W)	965(P)	γ(CH)
935(W)		γ(CH)
910(VW)		
881(VW)	885(dp)	γ(CH)
830(VW)		
763(S)	767	γ(CH)

Table IV (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
727(S)	726(P)	X-sens.
724(S)		ϕ(CC)
700(W)		
690(W)		
618(M)	618(P)	α(CCC)
610(VW)		
480(M)	480(dp)	ϕ(CC)
428(M)	429(P)	X-sens.
410(M)		ϕ(CC), γ(C-Cl)mode
310(VW)	310(dp)	X-sens.
--	188(dp)	X-sens.

Table V Vibrational Frequencies and Assignment For 3-Chloropyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3800(W)		
3660(W)		
3420(W)		
3130(W)	3128(P)	
3079(W)		$a_1\nu(CH)$, $b_1\nu(CH)$
3050(S)	3050(P)	$a_1\nu(CH)$, $b_1\nu(CH)$
2970(W)	2968(P)	
--	2920(P)	
2870(W)		
2780(W)		
2600(W)		
2425(W)		
2405(W)		
2230(W)		
1955(W)		
1920(W)		
1890(W)		
1850(W)		
1825(W)		
1735(W)		

Table V (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1710(W)		
1573(sh)		ν(CC)
1569(S)	1570(dp)	ν(CC)
1463(VS)		ν(CC,CN)
1415(VS)	1415(P)	ν(CC,CN)
1385(sh)		
1345(W)		
1320(M)		ν(CC,CN)
1260(W)		
1225(W)		β (CH)
1190(M)	1190(dp)	β (CH)
1155(M)	1155(P)	
1118(sh)		
1107(VS)	1101(P)	β (CH)
1093(VS)		X-sens.
1040(sh)	1037(P)	β (CH)
1015(VS)		Ring
980(W)		γ(CH)
943(W)		γ(CH)
915(W)		γ(CH)
795(W)		γ (CH)

Table V (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
728(VS)	730(P)	X-sens.
698(VS)		φ(CC)
668(W)		
612(S)	615(dp)	α(CCC)
460(W)	462	φ(CC)
428(M)	425(P)	X-sens.
420(M)		
404(M)		φ(CC)
294(M)	290(dp)	X-sens.
--	199(dp)	X-sens.

Table VI Vibrational Frequencies and Assignment For

2-Bromopyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3780(W)		
3660(W)		
3460(W)		
3150(W)		
3130(W)	3124(P)	
3070(M)	3065(P)	$a_1\nu(CH)$, $b_1\nu(CH)$
3050(W)	3049(P)	$a_1\nu(CH)$, $b_1\nu(CH)$
2990(M)		
2980(W)		
2890(W)		
2840(VW)		
2790(W)		
2725(VW)		
2660(VW)		
2642(VW)		
2630(VW)		
2590(VW)		
2550(W)		
2520(W)		
2460(VW)		

Table VI (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
2430(W)		
2400(W)		
2300(W)		
2270(VW)		
2210(VW)		
2180(W)		
2110(VW)		
2090(VW)		
2055(VW)		
2020(VW)		
1980(W)		
1950(W)		
1915(W)		
1875(W)		
1845(W)		
1808(VW)		
1728(VW)		
1760(W)		
1720(W)		
1688(W)		
1657(W)		

Table VI (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1640(W)		
1602(M)		
1573(VS)		ν(CC)
1563(VS)	1567(dp)	ν(CC)
1464(VS)		
1450(VS)	1450(P)	ν(CC,CN)
1422(VS)		ν(CC,CN)
1416(VS)		
1350(W)		ν (CC,CN)
1282(M)	1282(dp)	β (CH)
1253(W)		
1240(M)	1236(dp)	
1150(S)	1150(dp)	β (CH)
1112(VS)		
1105(VS)	1110(P)	X-sens.
1079(VS)	1078(P)	β (CH)
1043(VS)	1041(P)	β (CH)
1013(M)		
989(VS)	992(P)	Ring
976(W)		
960(W)		γ(CH)

Table VI (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
932(W)		γ(CH)
900(W)		
880(W)		γ(CH)
760(VS)		γ(CH)
725(W)		φ(CC)
702(VS)	700(P)	X-sens.
698(sh)		
650(W)		
615(S)	612(dp)	α(CCC)
470(S)		φ(CC)
405(S)		φ(CC),ν(C-Br)sym.
312(M)	312(P)	X-sens., (C-Br) assym.
260(W)	264(dp)	X-sens.
--	174(dp)	X-sens.

Table VII Vibrational Frequencies and Assignment For 3-Bromopyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3780(W)		
3670(W)		
3440(W)		
3120(W)	3117(P)	
3075(sh)		$a_1\nu(CH)$, $b_1\nu(CH)$
3052(S)	3050(P)	$a_1\nu(CH)$, $b_1\nu(CH)$
3020(M)		
3000(M)		
2970(W)	2970(P)	
2920(W)	2920(P)	
2870(W)	2875(dp)	
2820(W)		
2780(W)	2779(P)	
2750(W)		
2650(W)	2645(P)	
2600(W)		
--	2540(P)	
2500(VW)		
2440(VW)	2442(P)	
2400(VW)	2410(P)	

Table VII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
2377(VW)	2380(P)	
2220(VW)		
2160(VW)		
1965(W)		
1922(W)		
1895(W)		
1860(W)		
1830(W)		
1730(W)		
1712(W)		
1645(W)		
1574(VS)		ν(CC)
1557(M)	1567(dp)	ν(CC)
1463(VS)	1470(dp)	ν(CC, CN)
1434(sh)		
1417(VS)	1415(P)	ν(CC, CN)
1410(VS)		
1392(M)		
1365(M)		
1342(W)		
1320(M)	1322(dp)	ν(CC, CN)
1282(VW)		

Table VII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1245(VW)		
1220(W)	1222(dp)	β (CH)
1190(W)	1192(dp)	β (CH)
1150(VW)		
1118(M)	1120(P)	
1095(VS)		β (CH)
1087(VS)	1088(P)	x-sens.
1035(M)	1035(P)	
1025(S)		β (CH)
1008(VS)		Ring
980(sh)		γ(CH)
945(W)	946(?)	γ(CH)
915(W)		γ(CH)
895(W)		
872(VW)		
792(VS)	795(dp)	γ(CH)
760(W)		
705(VS)	705(P)	x-sens.
699(VS)		φ(CC)
635(W)		
614(VS)	612(dp)	α (CCC)

Table VII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
580(VW)		
530(VW)		
--	506	
447(W)	445(P)	φ(CC)
400(M)	402(P)	φ(CC)
358(M)	365(P)	
319(M)	326(P)	X-sens.
246(M)	255(dp)	X-sens.
--	190(dp)	X-sens.

Table VIII Vibrational Frequencies and Assignment For 2-Aminopyridine

Frequency		Interpretation
IR (cm^{-1}) in KBr	Raman (cm^{-1})	
--	3502	
3445(VS)	3450	ν(NH) assym. (of NH_2 group)
3300(S)	3300	ν(NH) sym.(of NH_2 group)
3238(M)	3250	γ(HH) intermolecular (H) bonding (of NH_2 group).
3165(S)	3150	
4072(M)	3072	$a_1\nu$(CH), $b_1\nu$(CH)
3050(M)	3057	$a_1\nu$(CH).
3020(M)	3033	$b_1\nu$(CH)
2950(M)		
2910(M)		
2750(M)		
2670(M)		
2590(M)		
1954(W)		
1915(W)		
1850(W)		
1705(W)		
1655(sh)		

Table VIII (continued)

Frequency		Interpretation
IR (cm^{-1}) in KBr	Raman (cm^{-1})	
1650(sh)		
1635(sh)		
1625(VS)	1635	β(NH)
1615(sh)		
1598(VS)	1600	ν(CC)
1560(S)	1560	ν(CC)
1540(sh)		
1535(M)		
1510(W)		
1488(VS)	1494	ν(CC,CN)
1472(sh)		
1440(VS)	1445	ν(CC,CN)
1340(M)	1345	ν(CC,CN)
1325(M)	1330	β (CH)
1278(M)	1282	X-sens., ν(CN) of NH_2 group.
1255(W)		
1158(M)	1165	β(CH)
1140(S)	1133	
1120(W)		β (CH)
1065(W)	1055	
1037(W)	1045	β(CH)

Table VIII (continued)

Frequency		Interpretation
IR (cm^{-1}) in KBr	Raman (cm^{-1})	
986(M)	991	Ring, b_2 γ(CH)
958(W)	--	γ(CH)
854(W)	855	γ(CH)
845(W)		
772(S)	777	X-sens.
765(S)		γ(CH)
737(M)	740	
665(W)	665	γ(NH) of NH_2 group, φ(CC)
628(W)	632	α(CCC)
565(VW)	563	
530(M)	533	X-sens.
520(sh)	--	φ(CC)
435(M)		
408(M)	415	φ(CC)
360(M)	--	X-sens.
300(W)	--	
--	217	X-sens.

Table IX Vibrational Frequencies and Assignment For 2-Picoline

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3085(M)		$a_1\nu(CH)$, $b_1\nu(CH)$
3070(M)		
3046(M)	3047(P)	$a_1\nu(CH)$, $b_1\nu(CH)$
3025(M)		
3015(M)	3015(dp)	
2982(M)		$\nu(CH)$ assym. CH_3
2958(M)	2960(P)	$\nu(CH)$ sym. CH_3
2922(M)	2918(P)	
2860(W)	2860	
1592(S)	1595(dp)	$\nu(CC)$
1570(M)	1573(dp)	
1560(W)		$\nu(CC)$
1540(W)		
1480(VS)	1475	$\nu(CC,CN)$
1475(sh)	1475	
1465(M)		
1460(M)		
1450(M)		
1440(M)		$\nu(CC,CN)$
1435(W)		$\gamma(CH)$ sym. CH_3

Table IX (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1375(W)	1376(wp)	ν(CC, CN), γ(CH) sym. (CH_3)
1295(M)	1295(dp)	β(CH)
1284(W)		
1235(W)	1235(P)	x-sens.
1150(M)	1150(dp)	
1142(W)		β(CH)
1099(W)	1100(dp)	β(CH)
1050(M)	1050(sp)	β (CH), CH_3 rock
1045(W)		
995(W)	995(sp)	Ring
987(W)		
972(W)		γ(CH)
940(VW)		γ(CH)
883(VW)		γ(CH)
800(VW)	800(P)	X-sens.
753(VS)		γ(CH) umbrella
730(M)		
729(W)		ϕ(CC) trigonal
718(VW)		
629(W)	630(dp)	α(CCC)

Table IX (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
548(VW)	548(P)	X-sens.
470(W)		φ(CC)
403(W)		φ(CC)
359(W)		X-sens.
--	209	X-sens.

Table X Vibrational Frequencies and Assignment For 3-Picoline

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3670(W)		
3420(M)		
3087(M)		ν(CH)
3056(S)	3054(P)	$a_1 \nu$(CH), $b_1 \nu$(CH)
3030(VS)		ν(CH)
3000(S)		
2980(S)	2995(dp)	ν(CH) assym. (CH_3)
2925(S)	2925(P)	ν(CH) sym. (CH_3)
2885(M)		
2835(M)		
2742(W)	2747(P)	
2610(W)		
2570(VW)		
2460(VW)		
2380(VW)		
2350(VW)		
2260(VW)		
2230(VW)		
1965(W)		
1910(W)		

Table X (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1860(W)		
1840(VW)		
1765(W)		
1720(W)		
1660(W)		
1605(M)		
1595(M)	1592(dp)	ν(CC)
1575(VS)		ν(CC)
1477(VS)	1477(dp)	ν(CC,CN)
1468(S)		
1452(S)		δ(CH) assym. (CH_3)
1415(VS)		ν(CC,CN)
1385(M)	1385(P)	δ(CH) sym. (CH_3)
1340(W)		ν(CC,CN)
1332(W)		
1285(M)	1286	β(CH)
--	1262	
1245(W)		
1227(M)	1232(P)	X-sens.
1190(VS)	1195(P)	β(CH)
1165(W)	1153(dp)	

Table X (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1128(M)		
1106(M)	1107(P)	β(CH)
1041(M)	1046(P)	β(CH),γ(CH) CH_3 rock
1028(VS)		Ring
995(W)		
987(W)		γ(CH)
941(VW)		γ(CH)
923(VW)		γ(CH)
800(W)	805(P)	X-sens.
788(VS)		γ(CH)
708(VS)		φ (CC)
628(VS)	632(dp)	α(CCC)
575(W)		
538(W)	540(P)	X-sens.
515(VW)		
488(W)		
457(M)	460(dp)	φ (CC)
400(M)	402(dp)	φ (CC)
338(W)	340(dp)	X-sens.
--	222(dp)	X-sens.

Table XI Vibrational Frequencies and Assignment For 4-Picoline

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3670(M)		
3420(S)		
3070(S)		
3050(sh)	3048(P)	ν(CH)
3040(S)	3029	$a_1\nu$(CH), $b_1\nu$(CH)
3010(S)	2982	ν(CH)
2990(S)		
2967(M)	2959(dp)	ν(CH) assym. CH_3 group
2923(M)	2921(P)	ν(CH) sym. CH_3 group
2895(M)		
2860(M)		
2735(W)		
2460(W)		
1935(W)		
1855(W)		
1794(W)		
1755(VW)		
1665(M)		
1604(VS)	1603	ν(CC)
1566(S)	1566	ν(CC)

Table XI (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1510(M)		
1495(S)	1495(P)	ν(CC,CN)
1490(M)		
1445(S)	1449(dp)	γ(CH) assym. CH$_3$ group.
1415(M)		ν(CC,CN)
1380(S)	1378(P)	γ(CH) sym. CH$_3$ group.
1365(M)		ν(CC,CN)
1340(W)		
1289(W)	1282	β(CH)
1225(M)		
1220(S)	1223(P)	β(CH)
1212(M)	1212	X-sens.
1113(VW)		
1090(VW)		β(CH)
1070(M)	1068	β(CH)
1042(W)		γ(CH) CH$_3$ rock
1000(M)	1000(P)	
994(S)	994	Ring
990(W)		
985(W)		
972(M)	969	γ(CH)

Table XI (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
940(W)	937	
872(W)	866	$b_2\gamma(CH)$, $a_2\gamma(CH)$
800(VS)	806(P)	$b_2\gamma(CH)$, X-sens.
727(M)		$\varphi(CC)$
710(W)		
670(W)	669	$\alpha(CCC)$
525(M)		
518(M)	519(P)	
511(M)	514	X-sens.
488(VS)		$\varphi(CC)$
--	384	$\varphi(CC)$
--	341	X-sens.
--	211	X-sens.

Table XII Vibrational Frequencies and Assignment For 4-Ethylpyridine

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3952(W)		
3939(W)		
3909(W)		
3859(W)		
3842(W)		
3809(W)		
3790(W)		
3777(W)		
3680(W)		
3638(W)		
3507(sh)		
3405(M)		
3290(sh)		
3200(W)		
3158(W)		
3121(W)		
3119(W)		
3100(W)		
3069(M)		$a_1\nu$(C-H), $b_1\nu$(C-H)
--	3040(P)	ν(C-H)

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
3023(S)		ν(C-H)
2989(sh)		
2979(sh)		
2971(VS)	2975(P)	ν(CH) assym. (CH_2)
2939(S)	2938(P)	ν(CH) assym. (CH_3)
2897(M)	2897(P)	ν(CH) sym. (CH_2)
2879(S)	2883(P)	ν(CH) sym. (CH_3)
2839(sh)		
2830(W)	2815(?)	
2741(W)	2740(P)	
2629(W)		
2542(VS)		
2477(W)		
2420(W)		
2300(W)		
2281(W)		
2208(W)		
2130(W)		
2100(W)		
2006(W)		
1980(VW)		

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1943(W)		
1936(W)		
1909(VW)		
1850(VW)		
1828(VW)		
1794(VW)		
1779(VW)		
1750(VW)		
1736(VW)		
1720(VW)		
1690(W)		
1666(W)		
1650(W)		
1638(W)		
1619(sh)		
1601(VS)	1604(dp)	ν(CC)
1595(sh)		
1577(sh)		
1556(M)	1562(dp)	ν(CC)
1546(sh)		
1540(sh)		

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1535(W)		
1529(W)		
1509(W)		
1498(sh)	1498(P)	
1494(M)	1498(P)	ν(CC,CN)
1474(sh)		
1467(sh)		
1459(S)	1455(dp)	δ(CH)scissering (CH_2)
1449(sh)		
1439(M)		δ(CH) assym. (CH_3)
1430(sh)		
1424(sh)		
1420(sh)		
1413(VS)		ν(CC,CN)
1400(W)		
1380(sh)		
1375(M)	1375(dp)	δ(CH) sym. (CH_3)
1370(W)	1370(dp)	ν(CC,CN)
1363(sh)		
1340(W)		
1321(W)	1320(P)	

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1313(W)	1314(P)	
1308(sh)		
1297(VW)		
1290(VW)	1292(dp)	β(CH)
1272(VW)		
1265(VW)	1262(P)	
1247(VW)		
1240(W)	1243(P)	γ(CH)wagging and twisting modes overlapped(CH_2)
1231(sh)		
1220(S)		X-sens.
1212(sh)	1210(P)	β (CH)
1208(sh)		
1200(W)		
1191(W)		
1178(VW)		
1160(VW)		
1143(W)		
1133(W)		
1124(W)		
1120(W)		

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
1113(W)		
1100(W)	1105	γ(CH) CH_3 rock
1081(W)		
1070(M)	1070(P)	β(CH)
1061(sh)	1062(P)	β(CH)
1050(sh)		
1049(W)		
	1045(P)	
1040(W)		γ(CH) CH_3 rock
995(S)	997(P)	
971(W)		γ(CH)
955(S)	---	Ring, ν(C-C) of (CH_2-CH_3)
921(VW)		γ(CH)
890(W)		
872(W)	880(P)	γ(CH)
850(sh)		
828(VS)		
820(VS)		γ(CH)
802(sh)	798(P)	
790(M)		γ(CH) rocking mode (CH_2)

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
778(S)	778(P)	X-sens.
763(M)		
750(W)		
736(W)		ϕ(CC)
715(M)	715(P)	
705(M)		
691(W)		
680(W)		
669(M)	670(P)	
662(M)		α(CCC).
616(M)		
595(W)		
573(S)		ϕ(CC)
569(S)		
556(sh)		
550(sh)		
529(M)		
520(M)	525	
509(sh)		
495(S)	495(P)	X-sens.
475(sh)		

Table XII (continued)

Frequency		Interpretation
IR (cm^{-1}) Liquid	Raman (cm^{-1})	
470(sh)		
460(W)		
454(W)		
421(M)		
400(M)	395(P)	φ(CC)
388(M)		
378(M)		
371(W)		
359(M)		α(CCC) of (pyr-CH_2-CH_3)
354(W)		
343(W)		
338(M)		
329(M)		
323(W)		
318(W)		
304(M)		
300(sh)		
291(M)		X-sens.
280(W)		
269(W)		
254(W)	260	X-sens.

Table XIII Fundamental Vibrational Frequencies of Pyridine and 2-Substituted Pyridines

symmetry species			assignments	Vibrational Frequencies (cm^{-1})				
				Pyridine	2-Me-pyr.	2-F-pyr.	2-Cl-pyr.	2-Br-pyr.
A'	(A_1)	z_1	ν(CH)	3054	3085	3097	3075	3070
		z_2	ν(CH)	3054	3046	3075	3060	3050
		k	ν(CC)	1583	1592	1598	1580	1573
		m	ν(CC,CN)	1482	1480	1510*	1452	1450
		a	β(CH)	1218	1142	1143	1150	1150
		b	β(CH)	1068	1050	1047	1045	1043
		p	Ring	992	995	995	994	989
		q	X-sens.	3036	1235	1247	1120	1105
		r	X-sens.	1030	800	828	727	702
		t	X-sens.	605	548	558	428	312
	(B_1)	z_4	ν(CH)	3080	3085	3097	3075	3070
		z_5	ν(CH)	3036	3046	3075	3060	3050
		l	ν(CC)	1572	1560	1579	1568	1563
		n	ν(CC,CN)	1439	1440	1434*	1420	1422
		o	ν(CC,CN)	1375	1375	1375*	1366	1350
		e	β(CH)	1288	1295	1302	1288	1282

Table XIII (continued)

symmetry species			assignments	Vibrational Frequencies (cm^{-1})				
				Pyridine	2-Me-pyr.	2-F-pyr.	2-Cl-pyr.	2-Br-pyr.
		d	β(CH)	1085	1099	1098	1085	1079
		s	α(CCC)	652	629	620	618	615
		u	X-sens.	1148	359	388*	310	260
A"	(A_2)	h	γ(CH)	986	972	962*	960	960
		g	γ(CH)	891	883	872*	881	880
		w	φ(CC)	375	403	418*	410	405
	(B_2)	j	γ(CH)	940	940	937*	935	932
		f	γ(CH)	886	753	787*	763	760
		v	φ(CC)	744	729	732*	724	725
		y	φ(CC)	700	470	477*	480	470
		x	X-sens.	405	209	230	188	174
					(C-F)	520	(C-Cl) 410	(C-Br) 405 sym. 312 assym.
(CH_3) group			ν(CH) sym. (CH_3)		2958			
			ν(CH) assym.		2982			
			γ(CH) assym.		1435			
			γ(CH) sym.		1375			
			δ(CH) CH_3 rock		1050			

* An additional bands.

Table XIV Fundamental Vibrational Frequencies of Pyridine and 3-Substituted Pyridines

symmetry species			assignments	Vibrational Frequencies (cm^{-1})				
				Pyridine	3-Me-pyr.	3-F-pyr.*	3-Cl-pyr.	3-Br-pyr.
A'	(A_1)	z_1	ν(CH)	3054	3087	3069	3079	3075
		z_2	ν(CH)	3054	3056	3058	3050	3052
		k	ν(CC)	1583	1595	1594	1573	1574
		m	ν(CC,CN)	1482	1477	1480	1463	1463
		a	β(CH)	1218	1190	1187	1190	1190
		b	β(CH)	1068	1041	1038	1040	1025
		p	Ring	992	1028	1023	1015	1008
		q	X-sens.	3036	1227	1247	1093	1087
		r	X-sens.	1030	800	818	728	705
		t	X-sens.	605	538	535	428	319
	(B_1)	z_4	ν(CH)	3080	3056	3069	3079	3075
		z_5	ν(CH)	3036	3030	3058	3050	3052
		l	ν(CC)	1572	1575	1584	1569	1557
		n	ν(CC,CN)	1439	1415	1425	1415	1417
		o	ν(CC,CN)	1375	1340	--	1320	1320
		e	β(CH)	1288	1285	1308	1225	1220
		d	β(CH)	1085	1106	1095	1107	1095

Table XIV (continued)

symmetry species			assignments	Vibrational Frequencies (cm^{-1}) Pyridine	3-Me-pyr.	3-F-pyr.	3-Cl-pyr.	3-Br-pyr.
		s	α(CCC)	652	628	616	612	614
		u	X-sens.	1148	338	--	294	246
A"	(A_2)	h	γ(CH)	986	987	982	980	980
		g	γ(CH)	891	923	--	915	915
		w	φ(CC)	375	400	410	404	400
	(B_2)	j	γ(CH)	940	941	--	943	945
		f	γ(CH)	886	788	--	795	792
		v	φ(CC)	744	708	702	698	699
		y	φ(CC)	700	457	--	460	447
		x	X-sens.	405	222	244	199	190
	(CH_3) group		ν(CH) assym.		2980			
			ν(CH) sym.		2925			
			γ(CH) assym.		1452			
			δ(CH) sym.		1385			
			γ(CH) rock		1041			

* See reference (9).

Table XV Fundamental Vibrational Frequencies of Pyridine and 4-Substituted Pyridines

symmetry species			assignments	Vibrational Frequencies (cm^{-1})			
				Pyridine	4-Me-pyr.	4-Cl-pyr.*	4-Br-pyr.*
A'	(A_1)	z_1	ν(CH)	3054	3050	3076	3072
		z_2	ν(CH)	3054	3040	3048	3035
		k	ν(CC)	1583	1604	1575	1567
		m	ν(CC,CN)	1482	1495	1484	1482
		a	β(CH)	1218	1220	1219	1216
		b	β(CH)	1068	1070	1064	1062
		p	Ring	992	994	996	992
		q	X-sens.	3036	1212	1103	1091
		r	X-sens.	1030	800	712	680
		t	X-sens.	605	511	414	317
	(B_1)	z_4	ν(CH)	3080	3040	3076	3072
		z_5	ν(CH)	3036	3010	3048	3035
		l	ν(CC)	1572	1566	1564	1566
		o	ν(CC,CN)	1375	1365	1359	1339
		e	β(CH)	1288	1289	1316	1316
		d	β(CH)	1085	1090	1080	1076

Table XV (continued)

symmetry species			assignments	Vibrational Frequencies (cm^{-1})			
				Pyridine	4-Me-pyr.	4-Cl-pyr.*	4-Br-pyr.*
		s	α(CCC)	652	670	663	662
		u	X-sens.	1148	341	300	256
A"	(A_2)	h	γ(CH)	986	972	955	961
		g	γ(CH)	891	872	914	914
		w	φ(CC)	375	384	390	390
	(B_2)	j	γ(CH)	940	872	836	859
		f	γ(CH)	886	800	811	805
		v	φ(CC)	744	727	722	722
		y	φ(CC)	700	488	491	482
		x	X-sens.	405	211	182	182
(-CH_3) group			γ(CH) CH_3rock		1042		
			ν(CH) assym.		2967		
			ν(CH) sym.		2923		
			γ(CH) assym.		1445		
			γ(CH) sym.		1380		

* See reference (9).

agreement with those substances previously studied (9).

DISCUSSION

It would be reasonable to expect that a close analogy should exist between many of the vibrations of monosubstituted benzene derivatives and the corresponding monosubstituted pyridine derivatives. KLINE and TURKEVITCH (21) have shown that the ring vibrations of pyridine are closely parallel to those of benzene and benzene-d_6. It has further been found that the hydrogen deformation vibrations are widely different and where identifiable, they usually shift to lower frequencies going from benzene to pyridine (17, 21). The close analogy between the ring vibrations of pyridine and benzene derivatives has been discussed and is based on the spectra of mostly alkyl derivatives (22). However other work on monosubstituted benzene derivatives has indicated that some vibrations in alkyl derivatives will show extensive vibrational coupling and would not be representative for comparison purposes (6). Further, the halobenzenes would serve as a good basis for comparison studies (1, 2) with the monosubstituted pyridines. In this work investigation and comparisons are made between the vibrations of monosubstituted benzene and pyridine derivatives, as well as the different isomeric monosubstituted pyridine derivatives.

A. 4-Substituted Pyridines

Symmetry considerations suggests that the best analogies between vibrations should occur between the 4-substituted pyridines and the monosubstituted benzene derivatives. Both types of molecules belong to the C_{2v} symmetry group. Monosubstituted benzene derivatives have 30 normal modes of vibration subdivided into symmetry classes as follows.

Planar vibrations: 11 in the A_1 class and 10 in the B_1 class; nonplanar vibrations: 3 in the A_2 and 6 in the B_2 class. While all monosubstituted pyridine have 27 normal modes of vibrations, the vibrations of the 4-substituted pyridines can be subdivided into the following symmetry classes.

Planar vibrations: 10 in the A_1 class and 9 in the B_1 class; nonplanar vibrations: 3 in the A_2 class and 5 in the B_2 class. The vibrations that are "lost" in going from the benzene derivatives to the pyridine derivatives are a C-H stretching vibration (A_1), a C-H in-plane deformation (B_1) and an out-of-plane deformation (B_2).

In his classical study of monosubstituted halobenzenes (2), WHIFFEN used a code letter designation for the vibration in accordance with the approximate mode diagrams of RANDLE and WHIFFEN (1) and which has since proved very useful in comparing vibrations of monosubstituted benzene derivatives. It follows that these designations should also prove useful in comparing monosubstituted pyridines and should facilitate the comparison of vibrations of monosubstituted benzenes with the corresponding vibrations of monosubstituted pyridines. In this study, the code letter designation of WHIFFEN (2) was extended to the monosubstituted pyridines by comparing the approximate mode diagrams and approximate vibrational descriptions for the phenyl derivatives (1,2) and the pyridine derivatives (7,9). The designations of WHIFFEN, the WILSON notation (12) and the approximate descriptions of the vibrations are shown in Table XVI for the monosubstituted pyridines.

A comparison of the vibrational spectra of monosubstituted halobenzenes (2) and that of the 4-substituted halopyridines (9) in Table XV indicates that of the 30 modes of vibrations of the monosubstituted benzenes, 3 of them disappear in the corresponding pyridines (as previously discussed) and 15 vibrations are apparently analogous to the corresponding vibrations in 4-substituted pyridines; that is, the vibrations occur at nearly the same frequency. The remaining 12 vibrations of the benzene derivatives differ in frequency by 20-150 cm^{-1} from the corresponding vibrations of the 4-substituted pyridines.

Of the 10 vibrations in the A_1 symmetry class, only 3 modes are not analogous to the vibrations of monosubstituted benzenes. The two in-plane C-H bending vibrations are about 40 cm^{-1} lower in the phenyl derivatives than in the corresponding 4-substituted pyridines while the X-sensitive "q" vibration is 20 cm^{-1} lower in the phenyl derivatives.

Of the 9 vibrations in the B_1 symmetry class, there are five modes which are analogous to the corresponding vibrations of monosubstituted benzenes and four which are different. Two of them involve the (C-C, C-N) "n" and "o" stretching vibrations. The "n"

Table XVI Notation and Approximate Descriptions of Vibrations For Monosubstituted Pyridines

Symmetry group		Notation		Approximate	Symmetry Group		Notation	
4-subs.	2-subs., 3-subs.	Wilson	Whiffen	Description	4-subs.	2-subs. 3-subs.	Wilson	Whiffen
A_1	A'	2	z_1	ν(CH)	B_1	A'	20b	z_4
		20a	z_2	ν(CH)			7b	z_5
		8a	k	ν(CC)			8b	l
		19a	m	ν(CC,CN)			19b	n
				ν(CC,CN)			14	o
		9a	a	β(CH)			3	e
		18a	b	β(CH)			18b	d
		1	p	Ring				
				α(CCC)			6b	s
		13	q	X-sens.			15	u
		12	r	X-sens.				
		6a	t	X-sens.				
A_2	A"	17a	h	γ(CH)	B_2	A"	5	j
		10a	g	γ(CH)			10b	f
		16a	w	ϕ(CC)			4	v
				X-sens., ϕ(CC)			11	y
				X-sens.			16b	x

vibration is about 40 cm^{-1} lower in the 4-substituted pyridines than the corresponding monosubstituted benzene, while the "o" vibration is about 35 cm^{-1} lower in 4-chlorobenzene than 4-chloropyridine; but the 4-bromobenzene is close in frequency (i.e., about 10 cm^{-1} difference) to the 4-bromopyridine. The other 2 vibrations of the B_1 symmetry class which are not analogous are the in-plane C-H bending "e" vibration which is about 50 cm^{-1} lower in the phenyl derivatives and the in-plane (C-C-C) ring "s" deformation which is about 47 cm^{-1} lower in the phenyl derivatives.

Of the 3 vibrations of the A_2 symmetry class only one mode, the out-of-plane (C-H) deformation "g" vibration, is not analogous to the vibrations of monosubstituted benzenes. It is about 85 cm^{-1} lower in the monosubstituted benzenes than the corresponding 4-substituted pyridines.

Of the 5 vibrations of the B_2 symmetry class of the 4-substituted pyridines only one mode, the X-sensitive "x" vibration, is analogous to the corresponding phenyl derivatives. Two of the remaining 4 modes are the out-of-plane bending ("j" and "f") vibrations. The "j" mode is about 140 cm^{-1} lower in the 4-substituted pyridines than the corresponding monosubstituted benzene, while the "f" mode is about 70 cm^{-1} higher in the 4-substituted pyridines than the corresponding phenyl derivatives. The other two modes are out-of-plane (C-C) ring deformations ("v" and "y" vibrations); they are lower in the phenyl derivatives than the corresponding 4-substituted pyridines (the "v" mode is about 40 cm^{-1} lower, while the "y" mode is about 25 cm^{-1} lower).

A comparison of 4-methylpyridine with the 4-halopyridines (Table XV) shows that, besides the 5 X-sensitive vibrations, there are significant frequency differences for the C-C stretching frequency in the A_1 class ("k" vibration), an in-plane C-H deformation in the B_1 class ("e" vibration) and two out-of-plane C-H deformations denoted as the "g" (A_2 class) and "j" (B_2 class) vibrations. Of these four vibrational modes, only the "k" vibration in monosubstituted benzenes shows such mass-sensitivity (2).

The correlations between the vibrations of monosubstituted benzenes and the corresponding vibrations of monosubstituted pyridines, such as the 4-substituted pyridine just discussed, can be quite useful in analyzing the vibrational spectra of other substituted pyridines. In this study, the Infrared and Raman spectra of 4-ethylpyridine has been recorded and interpreted using the correlations just discussed and spectra of related molecules.

The vibrational spectra of 4-ethylpyridine and ethylbenzene are shown in Table XVII. The correlations just discussed permit the assignment of the vibrations on the pyridine ring. Then, comparison with the spectral interpretations of ethylbenzene (23, 24, 25) should allow assignment of the vibrations arising from the ethyl moiety. It should be noted that, in the report of HARRIS and THORLEY (25), Table III incorrectly gives the range for the x-vibration as 435-460 cm^{-1} and that for the y-vibrations as 160-240 cm^{-1}. The lines in the Table for the x- and y-vibrations should actually be interchanged.

B. 3-Substituted Pyridines

The 3-substituted pyridines belong to the C_s symmetry group, and are not of the same symmetry group as the monosubstituted benzene derivatives. The C_s symmetry group contains only two symmetry species, A' containing the in-plane vibrations and A" containing the out-of-plane vibrations. However, the corresponding symmetry species for the C_{2v} symmetry group are listed (in parenthesis) in Table XV so that comparisons with the corresponding frequencies of monosubstituted phenyl derivatives and of 4-substituted pyridines are possible.

A comparison of the vibrational spectra of the 3-substituted pyridines (9) in Table XV and that of the monosubstituted halobenzenes (2) indicates that of the 30 modes of vibrations of the phenyl derivatives, 3 of them disappear (as discussed before) and 15 vibrations occur at nearly the same frequency (less than 20 cm^{-1} difference) as 3-substituted pyridines. The ramaining 12 vibrations of the phenyl derivatives are different in frequency from the corresponding 3-substituted pyridines by 20-110 cm^{-1}.

In the A' symmetry class: 3-fluoropyridine has two modes that are not analogous to the corresponding phenyl derivative, one mode is the in-plane C-H bending "a" vibration, while the other mode is the x-sensitive "q" vibration, both of them are about 30 cm^{-1} higher than that of fluorobenzene. For the 3-chloro- and 3-bromopyridines there are four modes in the A' symmetry group which are not analogous to the vibrations of the corresponding phenyl derivatives. The x-sensitive "r" vibrational mode is about 30-35 cm^{-1} higher in the pyridine derivatives

Table XVII Fundamental Vibrational Frequencies of 4-Ethylpyridine and Ethylbenzene

symmetry species			assignments	Vibrational Frequencies(cm^{-1})	
				4-ethylpyr.	ethylbenz.*
A'	(A_1)	z_1	ν(CH)	3069	3080
		z_2	ν(CH)	3040	3064
		k	ν(CC)	1601	1613
		m	ν(CC,CN)	1494	1500
		a	β (CH)	1212	1179
		b	β (CH)	1070	1031
		p	Ring	995	1003
		q	X-sens.	1220	1201
		r	X-sens.	778	772
		t	X-sens.	495	486
	(B_1)	z_4	ν(CH)	3069	3080
		z_5	ν(CH)	3023	3040
		l	ν(CC)	1556	1587
		n	ν(CC,CN)	1413	1464
		o	ν(CC,CN)	1370	1330
		e	β (CH)	1290	1245
		d	β (CH)	1061	1066
		s	α (CCC)	662	615
		u	X-sens.	291	292
A"	(A_2)	h	γ(CH)	971	964
		g	γ(CH)	921	840

Table XVII (continued)

symmetry species	assignments		vibrational frequencies(cm^{-1})	
			4-Ethylpyr.	Ethylbenz.
	w	φ(CC)	400	404
(B_2)	j	γ(CH)	872	985
	f	γ(CH)	820	747
	v	φ(CC)	736	698
	y	φ(CC)	573	556
	x	X-sens.	254	157
ν(CH) assym. (CH_3group)			2939	2950
ν(CH) sym. (CH_3 group)			2879	2890
γ(CH) assym. (CH_3 group)			1439	1456
γ(CH) sym. (CH_3 group)			1375	1377
γ(CH) CH_3 rock			1100 and 1040	1091 and 1037
ν(CH) assym. (CH_2 group)			2971	2976
ν(CH) sym. (CH_2 group)			2897	2890
γ(CH) scissoring (CH_2 grp)			1459	1456
γ(CH) wagging,twisting of $-CH_2$group			1240	1245
γ(CH) rocking (CH_2 group)			790	787
ν(CC) ($-CH_2-CH_3$ group)			955	964
α(CCC) ($-CH_2-CH_3$ group)			359	365
CH_3 torsion				216

* See reference (23, 24)

than in the corresponding monosubstituted benzene derivatives. The (C-C, C-N) stretching "n" vibration is about 30 cm^{-1} lower in the 3-substituted pyridines than the corresponding phenyl derivatives. The two in-plane C-H bending "e" and "d" vibrations of the 3-chloro- and 3-bromopyridines are not analogous to that of the corresponding monosubstituted benzenes. In the "e" vibration 3-chloro- and 3-bromopyridines are about 45 cm^{-1} lower than the corresponding phenyl derivatives, while 3-fluoropyridine is analogous to the corresponding phenyl derivative. In the "d" vibration the 3-halo-monosubstituted pyridines are about 35 cm^{-1} higher than the corresponding monosubstituted benzenes.

Of the 8 vibrations in the A" symmetry class, four modes are not analogous to the vibrations of the phenyl derivatives. These are the four C-H out-of-plane deformation vibrational modes. The "h" vibration for 3-bromo and 3-chloropyridines is analogous to the corresponding phenyl derivative, but in 3-fluoropyridine the frequency is about 25 cm^{-1} higher than in the corresponding monosubstituted benzene. On the other hand the "g" vibration of the 3-chloro- and 3-bromopyridines is about 85 cm^{-1} higher than the corresponding phenyl derivatives. This vibration in 3-fluoropyridine was not assigned. The out-of-plane C-H bending "j" vibration is about 42 cm^{-1} lower in the 3-substituted pyridines than the corresponding phenyl derivatives, while the "f" vibration is about 55 cm^{-1} higher in the 3-substituted pyridines than the corresponding monosubstituted benzene derivatives. The two vibrations were not assigned in 3-fluoropyridine.

A comparison of 3-methylpyridine with the 3-bromo- and 3-chloropyridines (Table XIV) shows that, besides the 5 X-sensitive vibrations, there are significant frequency differences for the C-C stretching "k" vibration, and the in-plane C-H deformation "e" vibration of the A' symmetry species. However, a comparison of the vibrations of 3-methylpyridine and 3-fluoropyridine shows that of the 5 X-sensitive vibrations and the "k" and "e" vibrations (A' type), there are frequency similarities for these two compounds in the k,q,r and t vibrations, while the 3-fluoropyridine has higher frequencies in the "e" vibration as well as the "x" vibration of the A" symmetry species. But the 3-chloro- and 3-bromopyridines have lower frequencies in the "e" and "x" vibrations than methylpyridine. In both 3-halo- and 3-methylpyridines the two out-of-plane C-H deformation denoted as "g" and "j" vibrations (A" symmetry species) have almost the same frequencies.

C. 2-Substituted Pyridines

The 2-substituted pyridines also belong to the C_s symmetry group. As in the case of the 3-substituted pyridines, the vibrations are classified into two symmetry species; i.e., A' containing the in-plane vibrations and A" containing the out-of-plane vibrations. Also, the corresponding symmetry species for the C_{2v} symmetry group are listed (in parenthesis) in Table XIII so that comparison with the corresponding frequencies of monosubstituted phenyl derivatives and of 4-substituted pyridines are possible.

A comparison of the vibrational spectra of the monosubstituted halobenzenes (2) and the 2-substituted pyridines (9) in Table XIII indicates that of the remaining 27 modes of vibrations of the phenyl derivatives, 12 vibrations occur at nearly the same frequency as the 2-substituted pyridines. The remaining 15 vibrations of the phenyl derivatives are different in frequency than the corresponding 2-substituted pyridines by 20-140 cm^{-1}.

In the A' symmetry class, for the 2-substituted halopyridine derivatives the frequencies of the two x-sensitive ("q" and "r") vibrations are about 25-35 cm^{-1} higher than in the corresponding monosubstituted benzene. In the x-sensitive "t" vibration only 2-fluoropyridine is about 40 cm^{-1} higher than fluorobenzene while 2-chloro- and 2-bromopyridines are analogous to the corresponding phenyl derivatives. The (CC,CN) stretching "m" vibration and C-H in-plane bending "a" vibration for the 2-bromo- and 2-chloropyridines vibrations are about 25 cm^{-1} lower than the corresponding phenyl derivatives, while 2-fluoropyridine vibration is analogous to the fluorobenzene. But in the C-H in-plane bending "b" vibration the 2-bromo and 2-fluoropyridines vibrations are about 25 cm^{-1} higher than the corresponding halobenzenes. While 2-chloropyridine vibration is analogous to the corresponding phenyl derivative. The other two (C-C, C-N) stretching ("n" and "o") vibrations of the 2-substituted pyridines, are not analogous to the corresponding monosubstituted benzene derivatives. In the "n" vibration the 2-substituted pyridines are about 27 cm^{-1} lower than the corresponding phenyl derivatives, while in the "o" vibration the 2-substituted pyridines are higher by 25-50 cm^{-1}. In the C-H in-plane bending "d" vibration only 2-fluoropyridine is about 30 cm^{-1} higher than fluorobenzene, but the frequencies for 2-chloro- and 2-bromopyridines are similar to those for the corresponding phenyl derivatives.

Of the 8 vibrations in the A" symmetry class for the 2-substituted pyridines, five vibrations are not analogous to the corresponding phenyl derivatives. Three of the vibrational modes are C-H out-of-plane deformations. The frequencies of the "g" vibration are about 45 cm^{-1} higher in the 2-substituted halopyridines than in the corresponding halobenzenes. The frequencies of the "j" vibration of 2-bromo, 2-chloro- and 2-fluoropyridines are about 45-55 cm^{-1} lower than the corresponding monosubstituted benzene, while in the "f" vibration the frequencies are about 25-30 cm^{-1} higher than the corresponding phenyl derivatives. The fourth mode is the out-of-plane C-C ring deformation "v" vibration which is about 40-45 cm^{-1} higher in the 2-substituted pyridines than in the monosubstituted benzenes. Finally, in the x-sensitive (out-of-plane C-C ring deformation) "y" vibration only 2-fluoropyridine is about 25 cm^{-1} lower than in the corresponding monofluorobenzene, whereas 2-chloro- and 2-bromopyridines vibrations are analogous to those of the corresponding phenyl derivatives.

A comparison of 2-methyl pyridine with the 2-bromo- and 2-chloropyridines (Table XIII) shows that, beside the 5 x-sensitive vibrations, there are significant frequency differences for the (C-C, C-N) stretching frequency in the A' symmetry class ("m" vibration). However, only 2-bromopyridine shows a frequency difference (about 25 cm^{-1} lower than the 2-methylpyridine) for the (C-C, C-N) stretching frequency in the A' symmetry class ("o" vibration). On the other hand a comparison of the 2-methylpyridine with 2-fluoropyridine shows that out of the 5 x-sensitive vibrations there are frequency similarities for only two x-sensitive vibration in the A' symmetry class ("q" and "t" vibrations). Further, the frequencies of 2-fluoropyridine are about 25-35 cm^{-1} higher than the 2-methylpyridine in the (C-C, C-N) stretching "m" vibration (A' symmetry class), and the out-of-plane C-H deformation "f" vibration (A" symmetry class).

A comparison of 2-aminopyridine with aniline (Table XVIII) shows that, there are significant frequency differences for the X-sensitive "r" vibration in the A_1 symmetry class, and C-C stretching ("l" vibration), the (C-C, C-N) "n" stretching, the X-sensitive "u" vibration in the B_1 class, and (C-H) out-of-plane "g" deformation in the A_2 class, and (C-C) out-of-plane ring "v" deformation in the B_2 symmetry class.

Table XVIII Fundamental Vibrational Frequencies of 2-Aminopyridine and Aniline

symmetry species		assignments		Vibrational Frequencies(cm^{-1})	
				2-aminopyridine	aniline
A'	(A_1)	z_1	ν(CH)	3072	3088
		z_2	ν(CH)	3050	3050
		k	ν(CC)	1598	1600
		m	ν(CC,CN)	1488	1500
		a	β(CH)	1158	1175
		b	β(CH)	1037	1028
		p	Ring	986	996
		q	X-sens.	1278	1278
		r	X-sens.	772	810
		t	X-sens.	530	527
	(B_1)	z_4	ν(CH)	3072	3072
		z_5	ν(CH)	3020	3037
		l	ν(CC)	1560	1586
		n	ν(CC,CN)	1440	1468
		o	ν(CC,CN)	1340	1330
		e	β(CH)	1325	1312
		d	β(CH)	1120	1118
		s	α(CCC)	628	618
		u	X-sens.	360	390
A"	(A_2)	h	γ(CH)	958	959

Table XVIII (continued)

symmetry species		assignment	Vibrational Frequencies (cm^{-1})	
			2-aminopyridine	aniline
	g	γ(CH)	854	826
	w	ϕ(CC)	408	415
(B_2)	j	γ(CH)	986	970
	f	γ(CH)	765	751
	v	ϕ(CC)	665	691
	y	ϕ(CC)	520	501
	x	X-sens.	217	233
(NH_2) group		ν(NH) assym.	3445	3440
		ν(NH) sym.	3300	3360
		β(NH)	1625	1618
		ν(NH) doublet	1340and 1325	--
		ν(CN)	1278	--
		γ(NH)	665	670

* See reference (26)

D. General Comparison of Monosubstituted Pyridines and Monosubstituted Benzenes

A general comparison of 2-, 3- and 4-bromo and chloropyridines with the corresponding monosubstituted benzene derivatives (Table XIX and XX) shows that out of the 27 vibration modes of the monosubstituted pyridines there are 12 vibrational modes analogous to the corresponding phenyl derivatives. For these comparisons, symmetry species for the C_{2v} symmetry group will be used. The analogous modes include 5 vibrations in A_1 symmetry class (two C-H stretching "z_1" and "z_2" vibrations, the C-C stretching "k" vibration, the ring "p" vibration, and the x-sensitive "t" vibration), 4 vibrations in the B_1 symmetry class (two C-H stretching "z_4" vibration, and "z_5" vibrations, the C-C stretching "l" vibration, and the X-sensitive "u" vibration), 2 vibrations in the A_2 symmetry class (the out-of-plane C-H deformation "h" vibration and the out-of-plane C-C ring deformation "w" vibration), and one mode in the B_2 symmetry class (the x-sensitive "x" vibration).

A comparison of 2-, 3- and 4-chloropyridines with chlorobenzene (Table XIX) indicated that beside the previously mentioned 11 vibrational modes there is one additional vibration analogous to chlorobenzene; i.e., the in-plane C-H deformation("b" vibration) in the A_1 symmetry class.

A comparison of 2- and 3-fluoropyridines with fluorobenzene (Table XXI) indicates that of the 27 vibrational modes of the monosubstituted pyridine derivatives, 11 modes of vibration are analogous to that of monofluorobenzene. They are not the same as those previously

Table XIX COMPARISONS OF THE VIBRATIONAL SPECTRA OF THE CHLOROPYRIDINES AND CHLOROBENZENE

assignment	Vibrational Frequencies (cm^{-1})			
	2-CL-pyr	3-CL-pyr	4-CL-pyr	Cl-ph
z_1	3075	3079	3076	3071
z_2	3060	3050	3048	3050
k	1580	1573	1575	1580
m	1452	1469	1484	1477
a	1150	1190	1219	1174
b	1045	1040	1064	1026
p	994	1015	996	1003
q	1120	1093	1103	1085
r	727	730	712	701
t	428	428	414	415
z_4	3075	3079	3076	3071
z_5	3060	3050	3048	3052
l	1568	1569	1564	1580
n	1420	1415	1407	1445
o	1366	1320	1359	1326
e	1288	1225	1316	1271
d	1083	1107	1080	1068
s	618	612	663	616
u	310	294	300	297
h	960	980	955	965
g	881	915	914	830

Table XIX (continued)

Assignment	Vibrational Frequencies (cm^{-1})			
	2-CL-pyr	3-CL-pyr	4-CL-pyr	Cl-ph
w	410	404	390	400
j	935	943	836	985
f	763	795	811	740
v	724	698	722	682
y	480	460	491	467
x	188	199	182	196

TABLE XX COMPARISONS OF THE VIBRATIONAL SPECTRA OF THE BROMOPYRIDINES AND BROMOBENZENE

Assignment	Vibrational Frequencies (cm^{-1})			
	2-Br-Pyr	3-Br-Pyr	4-Br-Pyr	Br-Ph
z_1	3070	3075	3072	3069
z_2	3050	3052	3035	3050
k	1573	1574	1567	1580
m	1450	1463	1482	1473
a	1150	1190	1216	1175
b	1043	1025	1062	1021
p	989	1008	992	1001
q	1105	1087	1091	1070
r	702	705	680	669
t	312	319	317	314
z_4	3070	3075	3072	3069
z_5	3050	3052	3035	3056
l	1565	1557	1556	1580
n	1422	1417	1403	1445
o	1350	1320	1339	1323
e	1282	1221	1316	1264
d	1079	1095	1076	1068
s	615	614	662	615
u	260	246	256	254
h	960	980	961	963
g	880	915	914	832

Table XX (continued)

Assignment	Vibrational Frequencies (cm^{-1})			
	2-Br-Pyr	3-Br-Pyr	4-Br-Pyr	Br-Ph
w	405	400	390	409
j	932	945	859	988
f	760	792	805	735
v	725	699	722	681
y	470	447	482	458
x	174	190	182	181

TABLE XXI COMPARISON OF THE VIBRATIONAL SPECTRA OF THE FLUOROPYRIDINES AND FLUOROBENZENE

Assignment	Vibrational Frequencies (cm^{-1})		
	2-F-Pyr	3-F-Pyr	F-Ph
z_1	3097	3069	3067
z_2	3075	3059	3053
k	1598	1594	1597
m	1510	1480	1499
a	1143	1187	1157
b	1047	1038	1020
p	995	1023	1010
q	1247	1247	1220
r	828	818	806
t	558	535	520
z_4	3094	3069	3100
z_5	3072	3058	3072
l	1579	1584	1597
n	1434	1425	1460
o	1375	--	1326
e	1302	1308	1290
d	1098	1095	1066
s	620	616	615
u	388	--	405
h	962	982	955
g	872	--	831

TABLE XXI (continued)

Assignment	Vibrational Frequencies (cm^{-1})		
	2-F-Pyr	3-F-Pyr	F-Ph
w	418	410	400
j	937	---	980
f	787	---	755
v	732	702	685
y	477	---	501
x	230	244	242

discussed for the chloro- and bromopyridines. The 11 vibrations include 4 modes in the A_1 symmetry class (the C-C stretching "k" vibration, the (C-C, C-N) stretching "m" vibration, the ring "p" vibration and the x-sensitive "r" vibration), 5 modes of vibration in the B_1 symmetry class (the C-H stretching "z_5" vibration, the C-C stretching "l" vibration, the in-plane C-H deformation "e" vibration, the in-plane (C-C-C) ring deformation "s" vibration and the x-sensitive "u" vibration), one mode of vibration in A_1 symmetry class (the out-of-plane C-C ring deformation "w" vibration), and one mode of vibration in the B_2 symmetry class (the x-sensitive "x" vibration).

On the other hand, a general comparison of 2-, 3- and 4-bromo and chloropyridines and 2-, 3-fluoropyridines with the corresponding monosubstituted benzene derivatives shows that there are 6 vibrational modes analogous to the corresponding phenyl derivatives. These include 2 vibrations in the A_1 symmetry class (the C-C stretching "k" vibration and ring "p" vibration), three vibrations in the B_1 symmetry class (the C-H stretching "z_5" vibration, the C-C stretching "l" vibration, and the x-sensitive "u" vibration), and one vibrational mode in the A_2 symmetry class (the out-of-plane ring deformation "w" vibration).

In summary, it appears that of the 27 modes of vibration for the monosubstituted pyridines, 5 vibrations are common to 2-, 3- and 4-monosubstituted halopyridines and to monosubstituted halobenzenes. Four of them are due to the ring vibrations and the other is an x-sensitive vibration. These results are in agreement with the work of KLINE and TURKEVITCH (21) who found that the ring vibrations of pyridine are closely parallel to those of benzene and monodeuterobenzene.

It has been suggested that hydrogen deformation frequencies should shift to lower frequencies going from benzene to pyridine (17, 21). the result of this study shows that in most cases, the hydrogen deformation frequencies are higher in the monosubstituted pyridine than in the corresponding monosubstituted benzene. The exceptions are of interest also. For all monosubstituted pyridine compounds, the "j" vibration is lower in the pyridine derivative than in the corresponding phenyl derivative. The frequency of the "h" vibration is essentially the same in the 2- and 4-substituted pyridine derivatives and the corresponding phenyl derivatives but is different in the 3-substituted pyridine compounds. Finally, a comparison of the hydrogen deformation frequencies between the 3-substituted pyridines and the corresponding benzenes, and between the 2-substituted pyridines and the corresponding benzenes, shows that in the former comparison, the frequencies of the "a" and "b" vibrations are the same but the frequency of the "e" vibration is lower in the pyridine molecule. But in the comparison involving the 2-substituted pyridine compounds, the frequencies of the "e" and "d" are the same for the two systems but the frequency of the "a" vibration is lower in the pyridine compounds.

CONCLUSIONS

Studies of the vibrational spectra of pyridine, 2-, 3-, and 4-substituted pyridines indicate a few similarities between these compounds and the corresponding monosubstituted phenyl derivatives which have been previously reported (8,9,11,14). Also, the location of the substituent on the ring is seen to influence the frequency of some of the vibrations, although no regular patterns could be observed. Further, other than C-H stretching vibrations, 5 vibrational modes are similar for the 1-, 2-, and 3-substituted pyridines (i.e., frequencies are independent of the location of the substituent) and analogous to the corresponding vibrations of the monosubstituted benzene compounds. The correlations between a substituted pyridine and a monosubstituted benzene are seen to be useful in making vibrational assignments on other related compounds.

SUGGESTIONS FOR FURTHER WORK

Experimental measurements of the Raman and Infrared spectra and complete vibrational assignments of 2-, 3-, and 4-iodopyridines and 3-, and 4-fluoropyridines would be very useful in further establishing the correlations suggested in the study and in establishing relations within a series of halopyridines analogous to those reported for monosubstituted halobenzenes (4, 6).

It has been suggested that the out-of-plane C-H deformation vibrations may be analogous to those of corresponding disubstituted benzene compounds (22). Vibrational spectra for these disubstituted benzene compounds should be obtained so that the comparisons could be made.

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