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I.R. STUDIES OF PYRIDYL-SUBSTITUTED PYRAZINE COMPOUNDS

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Infra-red spectra of 22 pyridyl-substituted pyrazine and dihydropyrazine compounds are studied using their solution in carbon tetrachloride, nujol mull and potassium bromide disc techniques. Different region of strong absorptions are recognised and the characteristic abosrption are assigned.

INTRODUCTION

A number of infrared spectra of 2,2-bipyridine, 1,10-phenanthroline and their derivatives have been studied for the confirmation of identity and purity of the solid samples. The spectra of twenty two different phenanthroline complexes in 2000-600 cm^{-1} region proved to be remarkably similar, but differed appreciably from those phenanthroline[1,2]. Similar results were observed for bipyridine and some of its metal chelates.

Pyridyl-substituted pyrazine compounds related to 1,10-phenanthroline and 2,2-bipyridine have been recognised as complexing agents quite earlier[3,4], but their IR spectra have not yet been correlated. Thus the IR spectra of 22 compounds are drawn to attempt to identify the solids on the basis of their IR spectra.

EXPERIMENTAL

The preparation of the compounds I to XXII is reported else where[3,4,5]. The infrared spectra of the compounds in region 3800-625 cm^{-1} were recorded using their saturated solution in spectroscopic carbon tetrachlride, nujol mull and potassium bromide disc techniques with Unicam SP 1025 infrared spectrophoto meter.

RESULTS AND DISCUSSION

Infrared spectra of the compounds in 3800-625 cm^{-1} were obtained and results are summarized in Table 1. Four regions of strong absorption were observed which are discussed individually below:

Absorption Near 3000 cm^{-1}. The first strong absorption region above and below 3000 cm^{-1} attributed to CH streaching vibrations of pyridyl, pyrazine, dihydro-pyrazine and methyl groups is not welly resolved. The CH stretching absorption in potassium bromide disc appears as broad bands of medium or weak intensity (Fig. 1). Their solutions in carbon tetrachloride were tried without much success. With high resolution spectrophoto meter, better information on the characteristics could be obtained.

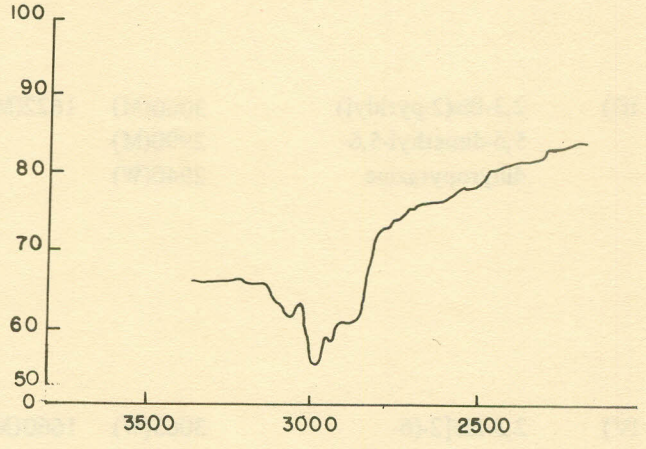

Fig. 1. Absorption Spectra of 2,3-Bis(2-pyridyl)5,6-dimethyl-5,6-dihydropyrazine in 3800-2000 cm^{-1} region.

Absorption in 1700-1300 cm^{-1} Region. First band of medium to weak intensity in dihydropyrazine compounds is assigned to C=N band of dihydropyrazine ring (Fig. 2). Similar bands have been reported earlier in dihydro and tetrahydro-pyridines[6].

All the compounds show close resemblance in absorption between 1600-1390 cm^{-1} with a number of bands due to C=C and C=N stretching vibrations in pyridyl, pyrazine and dihydropyrazine rings. The relative intensity of the bands varies from very strong to medium and the first band is the strongest. The compounds show characteristic doublet near 1600 cm^{-1} which are separated by 20 ± 5 cm^{-1}. The frequencies and the pattern of the bands do not vary appreciably when recorded in KBr disc or nujol mull. However there is a slight shift in the peaks towards lower frequencies when nujol mull techniques is used. The fre-

Table 1. Correlations in the region 3800-625 cm^{-1} of pyridyl-substituted pyrazine in KBr disc.

	Name of compound	CH	C=N	C=C C=N	$-CH_3$	CH and ring breath	CH
I)	2,3-Bis(2-pyridyl)-5,6-diydropyrazine	3060(W) 2985(W)	1630(M)	1588(US) 1568(S) 1480(VS) 1465(W) 1448(S) 1435(S) 1335(S)	–	1290(S) 1280(W) 1240(W) 1100(VS) 1055(W) 1040(W) 998(VS)	900(M) 860(M) 820(S) 800(S) 770(M) 750(S) 705(M)
II)	2,3-Bis[2-(6-methyl pyridyl)]-5,6-dihydropyrazine	3080(M) 2930(W)	1680(M)	1590(VS) 1575(VS) 1460(VS) 1400(VS)	1375(M)	1250(M) 1200(W) 1160(S) 1120(S) 1100(M) 1060(S) 1000(M)	875(M) 810(S) 755(S)
III)	2,3-Bis(2-pyridyl) 5,6-dimethyl-5,6-dihyropyrazine	3060(M) 2990(M) 2940(W)	1622(M)	1585(VS) 1565(S) 1470(VS) 1435(S)	1380(M)	1290 (VS) 1245(M) 1150(W) 1110(S) 1095(VS) 1050(W) 1025(W) 1000(VS) 980(VS)	915(W) 820(M) 800(VS) 755(VS) 735(W) 715(M)
IV)	2,3-Bis[2-(6-methyl pyridyl)]-5,6-dimethyl-5.6-dihydropyrazine	3065(W) 2995(M) 2940(W) 2860(W)	1660(M)	1590(VS) 1575(VS) 1460(VS) 1410(S)	1378(M)	1295(S) 1260(W) 1235(W) 1180(S) 1160(M) 1105(S) 1095(M) 1035(M) 1000(S)	930(M) 890(W) 810(VS) 770(W) 755(M) 685(W)
V)	2,3-Bis(2-pyridyl)-5-methyl-5,6-dihydrc pyrazine.	3060(W) 2980(W) 2940(W)	1665 (M)	1585(VS) 1562(S) 1470(S) 1435(S) 1418(M)	1375(M)	1305(M) 1285(M) 1270(M) 1247(M) 1170(M) 1155(W) 1105(M) 1090(S) 1030(M) 1000(VS)	910(W) 860(W) 815(M) 800(VS) 778(W) 750(S) 718(W) 705(W)

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VI)	2,3-Bis[2-(6-methyl pyridyl)] -5-methyl-5,6-dihydropyrazine	3060(W) 2915(W)	1680(M)	1588(VS) 1574(VS) 1555(S) 1460(S) 1405(S)	1378(S)	1280(M) 1252(M) 1160(S) 1120(S) 1090(M) 1040(S) 1000(S)	900(M) 875(W) 832(W) 815(W) 810(VS) 792(M) 770(W) 745(S) 700(M)
VII)	2-(2-Pyridyl)-3-[2-(6-methyl pyridyl)] -5,6-dihydropyrazine	3070(M) 2965(S) 2905(W) 2850(W)	1635(M)	1585(VS) 1565 1475(S) 1460(VS) 1440(S) 1338(S)	1375(W)	1300(M) 1245(S) 1155(VS) 1110(S) 1100(VS) 1090(S) 1040(M) 995(VS)	915(M) 885(W) 820(S) 805(S) 770(S) 755(S) 710(W) 680(W)
VIII)	2,3-Bis(2-pyridyl)-5,5-dimethyl-5,6-dihydropyrazine	3060(W) 2980(W) 2940(W)	1665(M)	1590(VS) 1566(S) 1472(VS) 1435(S)	1385(M)	1300(S) 1290(M) 1260(M) 1195(M) 1155(W) 1092(VS) 1000(VS)	920(W) 905(W) 818(W) 806(S) 788(S) 765(M) 752(S) 720(W) 700(W)
IX)	2,3-Bis[2-(6-methyl pyridyl)] -5,5-dimethyl-5, 6-dihydropyrazine	2070(W) 2990(W) 2940(W)	1670(M)	1590(VS) 1562(S) 1464(S)	1380(S)	1260(M) 1200(M) 1160(M) 1115(M) 1090(M) 1000(S)	812(S) 770(S) 750(W)
X)	2,3-Bis(2-pyridyl) -pyrazine	3070(W)	–	1585(VS) 1570(S) 1555(M) 1480(S) 1445(S) 1398(VS)	–	1240(W) 1185(W) 1150(S) 1110(S) 1092(S) 1040(VS) 1000(M)	905(W) 860(S) 835(W) 800(VS) 755(S) 730(W)
XI)	2,3-Bis[2-6(-methylpyridyl)] pyrazine.	3080(W) 2930(W)	–	1590(VS) 1575(S) 1550(S) 1470(S) 1455(S) 1400(VS)	1375(M)	1290(M) 1250(S) 1200(M) 1160(S) 1120(S) 1100(S) 1065(S) 1005(S)	920(W) 900(W) 875(S) 810(VS) 755(S) 690(W)

(continued. . . .)

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XII)	2,3-Bis(2-pyridyl)-5,6-dimethylpyrazine	3070 2940	–	1590(VS) 1575(S) 1485(S) 1455(S) 1410(S)	1380(S)	1290(S) 1270(M) 1250(M) 1180(S) 1120(S) 1090(S) 1060(S) 1020(S) 1000(S)	900(M) 930(M) 830(M) 750(S) 715(S)
XIII)	2,3-Bis[2-(6-methylpyridyl)]-5,6-dimethyl-pyrazine.	3090(W) 2930(W)	–	1590(VS) 1575(VS) 1455(S) 1410(VS)	1378(M)	1262(M) 1180(S) 1160(S) 1135(W) 1095(M) 1040(W) 1000(S)	890(S) 840(M) 830(M) 810(VS) 790(W) 765(W) 750(S) 690(M)
XIV)	2,3-Bis(2-pyridyl)-5-methylpyrazine	3060(W) 3020(W) 2960(W)	–	1585(VS) 1578(W) 1562(S) 1480(S) 1448(S) 1435(S) 1417(VS)	1372(S)	1275(S) 1252(M) 1170(S) 1110(VS) 1090(S) 1035(VS) 1000(S)	910(M) 830(S) 800(VS) 780(S) 752(VS) 740(W) 720(M)
XV)	2,3-Bis[2-(6-methylpyridyl)]-5-methylpyrazine.	3070(W) 2940(W)	–	1590(VS) 1575(S) 1560(S) 1455(S) 1410(S)	1375(S)	1282(S) 1245(M) 1220(W) 1162(VS) 1120(S) 1090(M) 1065(VS) 1000(S)	910(S) 875(W) 835(W) 825(W) 810(VS) 790(W) 755(S) 745(S) 705(W) 690(W)
XVI)	2-(2-Pyridyl)-3-[2-(6-methyl pyridyl)] pyrazine.	3070(M) 3000(W) 2960(W)	–	1590(VS) 1572 1550(S) 1480(S) 1445(S) 1400(VS)	1375(M)	1250(M) 1190(M) 1155(S) 1115(VS) 1100(S) 1090(S) 1065(S) 1050(M) 1035(M) 1000(S)	890(W) 870(S) 835(S) 800(S) 785(W) 750(S) 710(M) 660(M)

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XVII)	2-(2-pyridyl)-3-[2-(6-methyl-pyridyl)]-6-methyl pyrazine.	3070(W) 3010(W) 2950(W)	–	1590(VS) 1572(S) 1550(S) 1478(S) 1147(VS) 1425(S)	1375(S)	1280(S) 1255(M) 1168(S) 1120(S) 1100(M) 1060(VS) 1000(S)	920(M) 870(M) 830(M) 810(W) 780(M) 755(S) 720(M) 700(M)
XVIII)	2-Pyhenyl-3-(2-pyridyl) pyrazine	3060(W)	–	1585(VS) 1565(M) 1480(S) 1450(M) 1435(S) 1400(VS)	–	1290(W) 1180(W) 1157(S) 1107(VS) 1090(S) 1037(VS) 1020(S) 1000(S)	930(M) 870(S) 835(M) 795(VS) 770(VS) 710(VS)
XIX)	2,3,5,6-Tetrakis (2-pyridyl) pyrazine.	3060(W)	–	1590(VS) 1570(S) 1485(S) 1435(S) 1405(VS)	–	1290(M) 1245(M) 1155(M) 1135(S) 1100(S) 1000(M)	900(M) 815(S) 794(S) 760(S) 720(M)
XX)	2,6-Di(2-pyridyl) 3,5,di 2-(6-methyl pyridyl) pyrazine.	3060(W) 3020(W) 2970(W)	–	1590(VS) 1572(VS) 1480(S) 1442(S) 1400(VS)	1375(M)	1250(M) 1130(VS) 1095(S) 1070(S) 1042(S) 1000(S)	815(M) 800(VS) 755(S) 710(W) 690(W)
XXI)	2,3,5,6-Tetrakis 2-(6-methyl pyridyl) pyrazine	3070(W) 3000(W) 2940(W)	–	1590(VS) 1575(VS) 1475(S) 1435(S) 1405(S)	1375(W)	1275(M) 1245(M) 1165(S) 1135(S) 1078(VS) 1000(S)	905(M) 860(M) 820(VS) 805(S) 762(S) 747(M) 720(W) 682(M)
XXII)	2,3-Bis(2- pyridyl) quinoxaline.	3060(W) 3020(W)	–	1585(VS) 1565(S) 1555(S) 1480(VS) 1468(M) 1450(M) 1440(M) 1430(S) 1395(M) 1350(VS)	–	1282(VS) 1260(M) 1140(M) 1130(M) 1090(S) 1075(VS) 1000(VS) 985(S)	900(M) 925(M) 910(W) 795(VS) 765(S) 760(S) 748(S) 722(W) 710(S)

Relative intensity: VS = Very Strong; S = Strong; M = Medium; W = Weak.

Table 2. Comparison of absorption of 2,3-Bis[2-(6-methylpyridyl)] -5,6-dihydropyrazine in KBr disc and nujol mull in 1600-1350 cm^{-1}.

KBr	1590	1575	1460	1400
Nujol mull	1582	1568	1460	1392

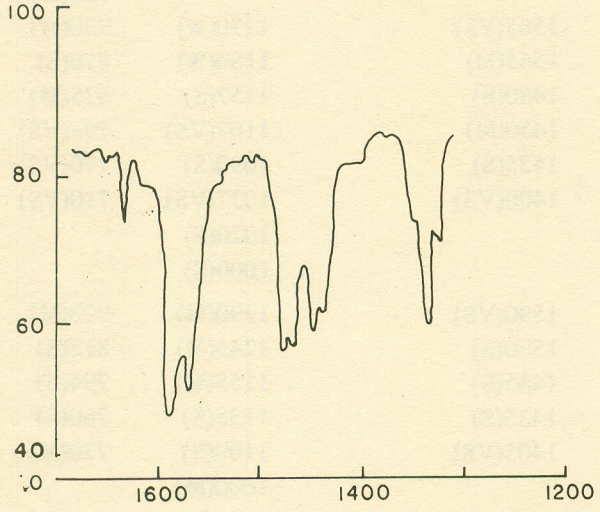


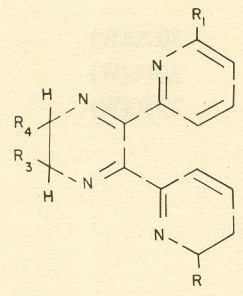
Fig. 2. Absorption Spectra of 2,3-Bis(2-pyridyl)5,6-dihydropyra-ı zine in 1700-1350 cm^{-1} KBr disc.

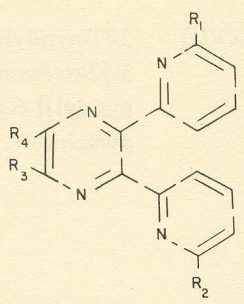
quencies for the bands in this region do not vary in a simple way with methyl substitution. However the tetra methyl substituted compounds IV and XIV indicate four bands as compared to unsubstituted basic compounds I and X which show six to seven bands in the same region. Thus it appears that the number of absorption bands in this region decreases with symmetrical multiple methyl substitution in pyridyl and pyrazine rings.

An absorption band observed at 1375 ± 10 cm^{-1} as expected in methyl substituted compounds is assigned to methyl bending vibrations[7,8].

Absorption in 1300-1000 cm^{-1} Region. In this region the compounds show a series of six to ten bands due to in plane hydrogen bending modes and ring vibrations near 1000 cm^{-1}[7]. A band in a narrow region of 100 ± 5 observed in all of the compounds under study is assigned to ring vibrations of pyridyl group. The bands vary in relative intensities from weak to very strong and it is difficult to correlate precisely their intensities and frequencies with substitution pattern.

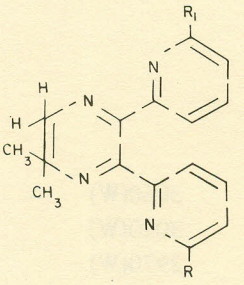
Absorption in 1000-625 cm^{-1} Region. This region covers mainly absorption due to CH out of plane deformations, ring breathing vibrations near 700 cm^{-1} and overtone of lower frequency. Therefore a number of the bands of

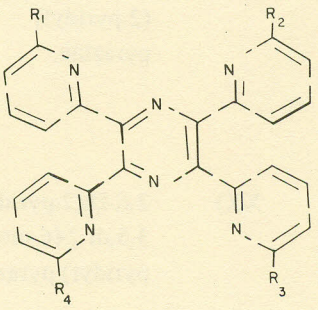




I = R_1, R_2, R_3, R_4 = H
II = $R_1, R_2 = CH_3, R_3, R_4$ = H
III = R_1, R_2 = H, $R_3, R_4 = CH_3$
IV = $R_1, R_2, R_3, R_4 = CH_3$
V = R_1, R_2, R_3, R_4 = H, $R_3 = CH_3$
VI = $R_1, R_2, R_3 = CH_3, R_4$ = H
VII = $R_1, R_3, R_4 = CH_3, R_2 = CH_3$

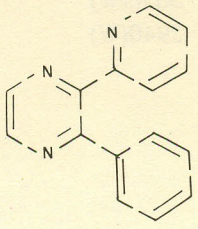
X = R_1, R_2, R_3, R_4 = H
XI = $R_1, R_2 = CH_3$; R_3, R_4 = H
XII = R_1, R_2 = H, R_3 $R_4 = CH_3$
XIII = $R_1, R_2, R_3, R_4 = CH_3$
XIV = R_1, R_2, R_4 = H, $R_3 = CH_3$
XV = $R_1, R_2, R_3 = CH_3, R_4$ = H
XVI = R_1, R_3, R_4 = H, $R_2 = CH_3$

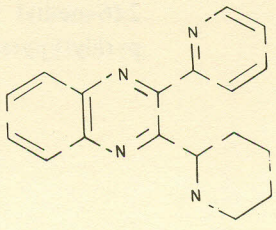




XVII = R_1, R_2 = H, $R_2, R_4 = CH_3$
VIII = R_1, R_2 = H
IX = $R_1, R_2 = CH_3$

XIX = R_1, R_2, R_3, R_4
XX = $R_1, R_2 = CH_3, R_3, R_4$ = H
XXI = $R_1, R_2, R_3, R_4 = CH_3$





varying intensities are observed and only a few strong are accounted. Katritzky[7] shows 2-alkylpyridine to absorb at 794-781 cm^{-1} and 752-746 and 2,6-dialkyl pyridine at 813-769 cm^{-1} and 752-725 cm^{-1}[8,9]. In the present investigation the compounds, I, II, V, VIII, X, XII, XIV, XIX and XXII containing 2-pyridyl groups show strong band between 806-795 cm^{-1} and 760-750 cm^{-1} and the compounds II, IV, VI, IX, XI, XIII, XV and XXI containing 6-methyl-2-pyridyl absorb within 812-805 cm^{-1} and 755-745 cm^{-1} could be assigned to the respective groups. The quinoxaline compound XXII shows the strong band

at 765 and 760 characteristic of four adjacent hydrogens in quinoxalines[10]. However a particular band for the pyrazine and dihydropyrazine rings could not be assigned with certainity, because of limited data at hand, probably there may be ascertained as additional compounds of the type becomes available.

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