Chem. Pharm. Bull. 12(10)1207~1217(1964)

UDC 615.778.47-011 : 547-386

168. Kozo Nagano, Hisashi Kinoshita, and Akiko Hirakawa : Metal Complexes of Isonicotinoylhydrazine and Related Compounds. V.*1 Infrared Absorption Spectra of Isonicotinoylhydrazine and Related Compounds.

(*Faculty of Pharmaceutical Sciences, University of Tokyo**2)

In the course of elucidating the structures of metal complexes of isonicotinoylhydrazine (INH) and related compounds, the infrared absorption spectra of the complex crystals were investigated.*1 For that purpose, the authors intended to examine in detail the bands of ligands themselves, the N-deuterated derivatives, the hydrochlorides and the N-deuterated hydrochlorides.

A molecule of INH and related compounds, with several exceptions, is composed of an N-substituted amide group, a terminal amino group of hydrazide and an aromatic ring. The characteristic bands of *trans*-planar N-monosubstituted amides have been reported by many investigators, and the amide I band at 1650 cm^{-1} has been assigned to the C=O stretching frequeny. Fraser, *et al.*[1] first pointed out that the C-N stretching, and N-H in-plane bending vibrations have considerable interaction in the amide II and III bands which appear at 1550 and 1270 cm^{-1} respectively. Miyazawa, *et al.*[2] further confirmed the assignment by the normal vibration calculation, and found that the amide IV band at ca. 630 cm^{-1} is assigned to the O=C-N deformation vibration, and that the amide V and VI which appear at ca. 730 and 600 cm^{-1} respectively are to the interaction of the N-H out-of-plane bending, and C=O out-of-plane bending vibrations. For N-deuterated *trans*-planar N-substituted amides, the amide I, II′, III′, IV, V′, and VI′ occur at ca. 1645, 1450, 970, 630, 510, and 620 cm^{-1} respectively. Some investigators have treated the amide I, II, and III bands of several INH derivatives,[3,4] and other hydrazides[5] according to the assignment. The bands of the antisymmetric and symmetric $-NH_2$ stretching, and >NH stretching vibrations appear in the 3400~3000 cm^{-1} region, and those of the $-ND_2$ and >ND stretching vibrations in the 2400~2200 cm^{-1} region. Though these bands are useful in estimating the degree of N-deuteration, little information is available about the structures of metal complex crystals. For this reason assignments of the spectra are restricted in the 1700~690 cm^{-1} region.

Hirakawa (née Yamaguchi)[6] has shown that the deformation vibrations of the non-planar $-NH_2$ group are composed of bending, twisting (inactive or weak) and wagging vibrations and that their frequencies are in the region of 1600, 1300, and 800 cm^{-1} respectively. On the other hand, Hirakawa[7] and Suzuki[8] have shown that the deformation vibrations of the planar $-NH_2$ group are composed of bending, rocking, wagging (out-of-plane bending) and twisting (inactive) vibrations and that the bands arising from them appear at ca. 1600, 1150, 720, and 500 cm^{-1} respectively. The corresponding bands of N-deuterated derivatives occur in the lower frequencies, and their wave number ratios come to ca. 1.3.

---

*1 Part IV : This Bulletin, **12**, 1192 (1964).

*2 Motofuji-cho, Bunkyo-ku, Tokyo (長野晃三, 木下 恒, 平川暁子).

1) R. D. B. Fraser, W. C. Price : Nature, **170**, 490 (1952).
2) T. Miyazawa, T. Shimanouchi, S. Mizushima : J. Chem. Phys., **24**, 408 (1956); T. Miyazawa : Nippon Kagaku Zasshi, **76**, 341, 1018 (1955); *Ibid.*, **77**, 171, 321, 526, 619 (1956).
3) H. Fujiwara : Yakugaku Zasshi, **78**, 823 (1958).
4) S. Imado : *Ibid.*, **81**, 342 (1961).
5) M. Mashima : Bull. Chem. Soc. Japan, **35**, 332, 338, 423, 1882 (1962).
6) A. Yamaguchi : Nippon Kagaku Zasshi, **80**, 1105, 1109 (1959).
7) *Idem* : *Ibid.*, **78**, 1467 (1957).
8) I. Suzuki : Bull. Chem. Soc. Japan, **33**, 1359 (1960).

The spectra of aromatic rings, benzene,[9,10] benzene-d,[10] benzene-1,4-d_2,[10] toluene,[11] pyridine,[12,13,15] pyridine-2-d,[14] pyridine-3-d,[14] pyridine-4-d,[14] and γ-picoline,[16] have been assigned by many investigators. Following their results, the bands of the ring double-bonds stretching vibrations occur in the region of 1600~1350 cm^{-1}, those of the C-H in-plane bending vibrations in the region of 1350~1000 cm^{-1}, those of the ring vibrations at ca. 1000 cm^{-1} and those of the C-H out-of-plane bending vibrations in the region of 1000~650 cm^{-1}.

A hydrochloride molecule of INH and related compounds, with several exceptions, is composed of a N-substituted amide group, a monosubstituted ammonium group and a pyridinium group. The amide I, II, III, II′, and III′ bands are similarly observed but shift slightly according to the change of the electronic state due to the ammonium and pyridinium groups. Tsuboi, *et al.*[17] have reported the bands of the $-NH_3^+$ degenerate deformation, $-NH_3^+$ symmetric deformation, $-NH_3^+$ rocking, $-ND_3^+$ degenerate and symmetric deformation and $-ND_3^+$ rocking vibrations for many α-amino acids in the regions of 1660~1567, 1544~1445, 1293~1064, 1206~1056, and 1015~710 cm^{-1} respectively. It has been reported[18,19] that the band at ca. 1600 cm^{-1} of pyridine shifts towards higher frequency by ca. 40 cm^{-1} and becomes stronger in intensity when it changes to the hydrochloride and to the deuterochloride. As to the C-H in-plane and out-of-plane bending vibrations, it is inferred that the bands of pyridine hydrochloride and its deuterochloride resemble to those of benzene and benzene-d respectively. From such an analogy, tentative assignments of vibrational spectra of pyridine (Py), Py·HCl[20] and Py·DCl[20] can be made as shown in Table I.

On the basis of those spectral data described above, tentative assignments of vibrational spectra of INH, nicotinoylhydrazine (NH), picolinoylhydrazine (PH), benzoylhydrazine (BH), *p*-nitrobenzoylhydrazine (PNBH), isonicotinamide (INA), 1-isonicotinoyl-1-methylhydrazine (N-Me-INH), nicotinamide (NA), picolinamide (PA), their N-deuterated derivatives, their hydrochlorides and their N-deuterated hydrochlorides were carried out as shown in Tables II~X. 1-Isonicotioyl-2-methylhydrazine (N′-Me-INH) was omitted owing to instability of the compound and insufficiency of reference data about the methylated terminal amino group of hydrazide.

Experimental

Materials——INH, NH, PH, BH, PNBH, INA, N-Me-INH, NA and PA were the same as those used in Part IV.*1 INH-d_3, NH-d_3, PH-d_3, BH-d_3, PNBH-d_3, INA-d_2, N-Me-INH-d_2, NA-d_2 and PA-d_2 were prepared by drying solutions of the corresponding compounds in D_2O from the frozen state. Hydrochlorides of INH, NH, PH, BH, PNBH, INA, NA and PA were prepared by passing dry HCl through solutions of the corresponding compounds in EtOH. N-Me-INH·2HCl was the same as that described in Part II.[21] The results of elemental analyses of C, H and N coincided with the following formulae and the melting points were measured: INH·2HCl, m.p. 280~283°;[3,22] NH·2HCl, m.p. 225~227°;[23]

9) C. R. Bailey, C. K. Ingold, H. G. Poole, C. L. Wilson: J. Chem. Soc., **1946**, 222.
10) F. A. Miller, B. L. Crawford, Jr.: J. Chem. Phys., **14**, 282, 292 (1946).
11) N. Fuson, C. Garrigou-Lagrange, M. L. Josien: Spectrochim. Acta, **16**, 106 (1960).
12) C. H. Kline, Jr., J. Turkevich: J. Chem. Phys., **12**, 300 (1944).
13) L. Corrsin, B. J. Fax, R. C. Lord: *Ibid.*, **21**, 1170 (1953).
14) F. A. Andersen, B. Bak, S. Brodersen, J. Rastrup-Andersen: *Ibid.*, **23**, 1047 (1955).
15) G. Zerbi, B. Crawford, Jr., J. Overend: *Ibid.*, **38**, 127 (1963).
16) D. A. Long, W. O. George: Spectrochim. Acta, **19**, 1777 (1963).
17) M. Tsuboi, T. Takenishi, A. Nakamura: *Ibid.*, **19**, 271 (1963).
18) B. Witkop: Experientia, **10**, 420 (1954); J. Am. Chem. Soc., **76**, 5597 (1954).
19) H. Shindo: Kagaku-no Ryoiki, Zokan No. 28, p. 186 (1958), Nankodo Co., Tokyo.
20) K. Matsuo, M. Tsuboi: Unpublished data.
21) Part II: This Bulletin, **11**, 797 (1963).
22) H. Mayer, J. Mally: Monatsch., 33, 401 (1912).
23) T. Curtius, E. Mohr: Ber., **31**, 2493 (1898).

PH·2HCl, m.p. 218~220°; BH·HCl, m.p. 185~187°;[24] PNBH·HCl, m.p. 265~268°; INA·HCl, 260~262°;[25] N-Me-INH·2HCl, m.p. 238~240°;[26] NA·HCl, m.p. 240~242°; PA·HCl, m.p. 216~218° (All melting points are decomp.). N-Deuterated hydrochlorides were prepared by drying solutions of the corresponding hydrochlorides in D_2O from the frozen state.

Infrared Absorption Spectra——The IR absorption spectra were obtained using a Koken Model DS-301 spectrophotometer with a NaCl prism in the Nujol mulls, hexachlorobutadiene (HCB) mulls and/or KBr disks. The adopted methods are described in the bottom lines of Tables.

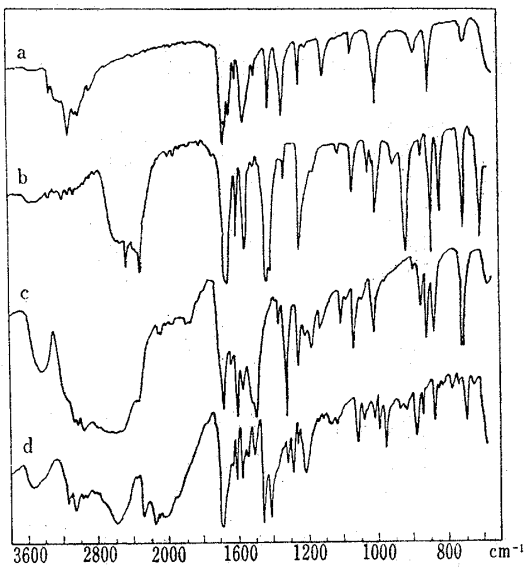

Fig. 1a. Isonicotinoylhydrazine (INH) (KBr disk)
b. INH-d_3 (KBr disk)
c. INH·2HCl (KBr disk)
d. INH-d_3·2DCl (KBr disk)

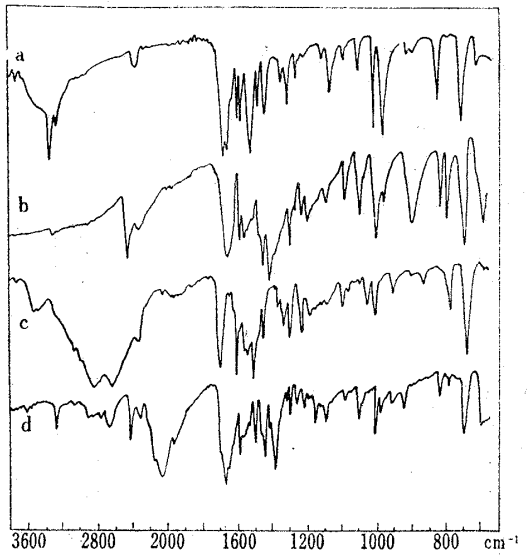

Fig. 2a. Picolinoylhydrazine (PH) (KBr disk)
b. PH-d_3 (Nujol mull, HCB mull)
c. PH·2HCl (KBr disk)
d. PH-d_3·2DCl (Nujol mull, HCB mull)

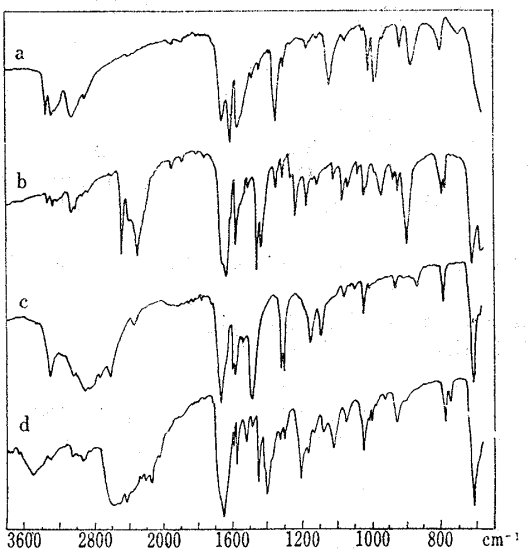

Fig. 3a. Benzoylhydrazine (BH) (KBr disk)
b. BH-d_3 (Nujol mull, HCB mull)
c. BH·HCl (KBr disk)
d. BH-d_3·DCl (KBr disk)

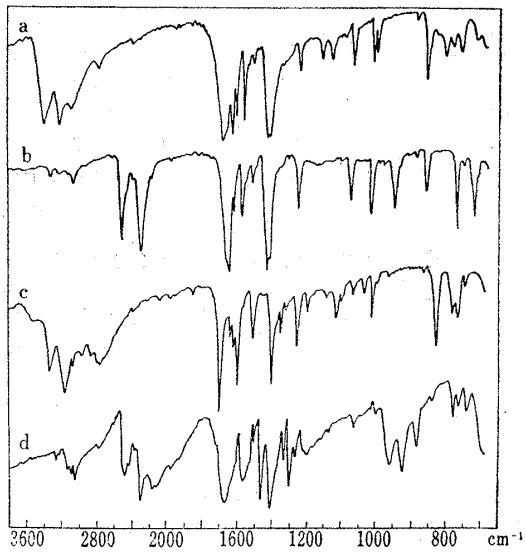

Fig. 4a. Isonicotinamide (INA) (KBr disk)
b. INA-d_2 (Nujol mull, HCB mull)
c. INA·HCl (KBr disk)
d. INA-d_2·DCl (Nujol mull, HCB mull)

24) G. Struve; J. prak. Chem., (2) **50**, 297 (1894).
25) K. W. Merz, H. Stolte: Arch. Pharm., **293**, 102 (1960).
26) J. Cymerman-Craig, D. Willis: J. Chem. Soc., **1955**, 4318.

Results and Discussion

The infrared absorption spectra of INH, INH-d_3, INH·2HCl, and INH-d_3·2DCl; PH, PH-d_3, PH·2HCl, and PH-d_3·2DCl; BH, BH-d_3, BH·HCl, and BH-d_3·DCl; and INA, INA-d_2, INA·HCl, and INA-d_2·DCl are shown in Figs. 1～4. Assignments of vibrational spectra of ligands, their N-deuterated derivatives, their hydrochlorides and their N-deuterated hydrochlorides are listed in Tables I～X.

Table I. Assignments of Vibrational Spectra of Py, Py·HCl and Py·DCl

Assignment	Py (cm^{-1})	Py·HCl (cm^{-1})	Py·DCl (cm^{-1})
Ring str.		1639	1649
〃	1580	1605	1605
〃	1572	1530	1550
〃	1482	1483	1494
〃	1439		
		1382	
〃	1375		
CH bend., in-.		1331	1305
〃	1218	1244	1272
〃	1217	1190	1210
〃	1148	1165	1161
			1122(w)[a]
〃	1068	1055	1054
Ring vib.	1029	1030(w)	1022(w)
〃	992	1000(s)	990(mb)
CH bend., out-.	981(w)		
〃	942(〃)	920(w)	928
〃	886(〃)		
			803
〃	749(s)	762	755
〃	703(〃)	687	673
Ring def.	675(w)		
〃	652(〃)		
		640(w)	
〃	605(m)	610	605
	capillary	Nujol mull	Nujol mull
		HCB mull	HCB mull

a) (vs) very strong; (s) strong; (m) medium; (w) weak; (vw) very weak; (b) broad; (sh) shoulder

Table II. Assignments of Vibrational Spectra of INH, INH-d_3, INH·2HCl and INH-d_3·2DCl

Assignment	INH (cm^{-1})	INH-d_3 (cm^{-1})	INH·2HCl (cm^{-1})	INH-d_3·2DCl (cm^{-1})
Amide I	1668	1662	1680	1693
NH_2 bend	1630			
Ring str.			1630	1633
〃	1603	1602		1610
NH_3^+ deg. def.			1604(s)	
Ring str.	1565(sh)	1557	1568	1578
〃			1543(w)	1548(w)
Amide II	1550(sb)		1510	
NH_3^+ sym. def.			1492(s)	
Ring str.	1495	1500		1498
Amide II′		1422		1455, 1416

Ring str.	1416	1407		
			1358	
Amide Ⅲ	1338		1315 (s)	
CH bend., in-.	1325 (sh)	1330		1290
〃	1236	1235, 1225	1247	1257
ND_3^+ deg. def.				1208 (s)
ND_2 bend.		1183		
NH_3^+ rock.			1183, 1157	
NH_2 rock.	1141			
ND_3^+ sym. def.				1130, 1115
		1106 (w)	1102 (m)	1105 (w)
CH bend., in-.	1062	1065	1060	1060
		1024 (m)	1038 (w)	1038 (〃)
Ring vib.	1003 (sh)	1010 (w)	1012 (m)	1012 (〃)
〃	996 (s)	1000 (s)	996 (w)	995 (m)
Amide Ⅲ′		948, 916		977
ND_3^+ rock.				934, 916
				886
NH_2 wag.	886			
CH bend., out-.	873 (w)	874 (w)	870 (m)	869
			856	
〃	845	843	837	835
ND_2 rock.		816		
CH bend., out-.		757, 752	757, 751	748
Amide Ⅴ	744 (mb)			
ND_2 wag.		706		
			683	
	KBr disk	KBr disk	KBr disk	KBr disk

Table Ⅲ. Assignments of Vibrational Spectra of NH, NH-d_3, NH·2HCl and NH-d_3·2DCl

Assignment	NH (cm^{-1})	NH-d_3 (cm^{-1})	NH·2HCl (cm^{-1})	NH-d_3·2DCl (cm^{-1})
Amide Ⅰ	1677	1671	1682	1669
NH_2 bend.	1645			
NH_3^+ deg. def.			1625	
Ring str.	1598	1598	1611	1614
〃	1576	1577	1582	1589
			1535	1502
Amide Ⅱ	1548		1504 (sb)	
NH_3^+ sym. def.				
Ring str.	1478	1480	1470	1450
〃	1424			
Amide Ⅱ′		1448, 1412		1393
			1363	
CH bend., in-.		1340	1345	1348
Amide Ⅲ	1348 (vs)		1317	
				1300 (m)
ND_2 bend.		1236		
ND_3^+ deg. def.				1230
NH_3^+ rock.			1195 (mb)	
CH bend., in-.	1197	1198		1173
ND_3^+ sym. def.				1146, 1122
NH_2 rock.	1129, 1116			
			1110 (w)	
Ring vib.	1042 (w)	1051 (w)	1048	1050
〃	1033	1033	1018	1023 (w)
				992
Amide Ⅲ′		1023		973
NH_2 wag.	964, 953			

ND_3^+ rock.				931, 922
ND_2 rock.		895		
CH bend., out-.	885		863	855
			852	
〃	834	832	841	839(w)
				814(〃)
				785(〃)
Amide Ⅴ	776(wb)			
		777(w)		755(〃)
ND_2 wag.		742		
CH bend., out-.	708	705	738	725
	KBr disk	Nujol mull HCB mull	Nujol mull HCB mull	Nujol mull HCB mull

Table Ⅳ. Assignments of Vibrational Spectra of PH, PH-d_3, PH·2HCl and PH-d_3·2DCl

Assignment	PH (cm^{-1})	PH-d_3 (cm^{-1})	PH·2HCl (cm^{-1})	PH-d_3·2DCl (cm^{-1})
Amide Ⅰ	1679	1669	1710	1668
NH_2 bend.	1651			
NH_3^+ deg. def.			1610	
Ring str.	1598	1593	1592	1588
〃	1575	1565	1556	1566
Amide Ⅱ	1523		1514	
NH_3^+ sym. def.			1495(sh)	
Ring str.	1472	1479		1495
〃	1433	1454	1451	1449
Amide Ⅱ′		1416		1390
			1368	
Amide Ⅲ	1343		1336	
CH bend., in-.	1311	1311	1301	1298
ND_3^+ deg. def.				1258
CH bend., in-.	1259	1229	1235	1225
ND_2 bend.		1190		
NH_3^+ rock.			1190	
ND_3^+ sym. def.				
CH bend., in-.	1151	1148	1145(w)	1146(w)
NH_2 rock.	1128			
			1102(m)	
CH bend., in-.	1090(w)	1087(m)	1089(w)	1089(w)
Ring vib.	1050	1049	1034	1049
〃	1003	1000	1008	1000
				989
NH_2 wag.	979			
			957	955
Amide Ⅲ′		980		921
ND_2 rock.				
CH bend., out-.	905, 892(w)	902(s)		
			870	
ND_3^+ rock.				818
CH bend., out-.	822	818	794	793(w)
ND_2 wag.		798		
CH bend., out-.	752	748	749	747
〃	707	696	695(w)	701
	KBr disk	Nujol mull HCB mull	KBr disk	Nujol mull HCB mull

Table V. Assignments of Vibrational Spectra of BH, BH-d_3, BH·HCl and BH-d_3·DCl

Assignment	BH (cm^{-1})	BH-d_3 (cm^{-1})	BH·HCl (cm^{-1})	BH-d_3·DCl (cm^{-1})
Amide I	1662	1655, 1635	1679	1668
NH_2 bend.	1613			
NH_3^+ deg. def.			1604	
Ring str.	1578	1581	1587	1586
〃	1547 (sh)	1547	1536	1534
Amide II	1566		1490 (s)	
NH_3^+ sym. def.			1480	
Ring str.	1487	1495		1503
〃	1446	1454		1455
Amide II′		1435		1410
				1370 (sh)
Amide III	1352		1318	
	1338	1338		1335
CH bend., in-.	1307	1306	1306	1312
ND_2 bend.		1230		
ND_3^+ deg. def.				1220
CH bend., in-.	1185	1188	1185 (sh)	1185
NH_3^+ rock.			1175, 1148	
CH bend., in-.	1156 (w)	1156 (w)		1166 (w)
NH_2 rock.	1120			
ND_3^+ sym. def.				1138, 1114
		1105		
CH bend., in-.	1073 (w)	1078 (m)	1077 (w)	1078 (w)
		1062		
Ring vib.	1027 (w)	1033 (w)	1022 (m)	1026 (m)
〃	1006 (m)	1015, 1008 (m)	1003 (w)	1012, 1001 (w)
NH_2 wag.	995, 988			
Amide III′		973		933
ND_2 rock.		933		
CH bend., out-.	921	922	932 (w)	
	884 (s)	899 (s)	870 (〃)	
〃	801	796	794	792
ND_2 wag.		788		
ND_3^+ rock.				775
Amide V	750			
CH bend., out-.		707	708	706
	KBr disk	Nujol mull HCB mull	KBr disk	KBr disk

Table VI. Assignments of Vibrational Spectra of PNBH, PNBH-d_3, PNBH·HCl and PNBH-d_3·DCl

Assignment	PNBH (cm^{-1})	PNBH-d_3 (cm^{-1})	PNBH·HCl (cm^{-1})	PNBH-d_3·DCl (cm^{-1})
Amide I	1635	1625	1680	1669
NH_2 bend.	1611			
Ring str.	1598	1598	1605	1605
NH_3^+ deg. def.			1594	
		1560 (w)		
Ring str.	1530	1530		
NO_2 ant. str.	1513	1512	1534	1535
NH_3^+ sym. def.			1496 (sh)	
Amide II	1548 (m)		1484 (s)	
Amide II′		1433		1424
Ring str.	1388 (w)	1387 (w)	1400 (w)	1405 (w)
				1386

NO_2 sym. str.	1362	1359	1352	1354
Amide Ⅲ	1348		1298	
CH bend., in-.	1324	1330	1331	1333
〃	1311	1310		1312
ND_2 bend.		1222		
ND_3^+ deg. def.				1211
CH bend., in-.	1192(wb)	1168(m)	1190(m)	1164(w)
NH_3^+ rock.			1173, 1148	
				1138(〃)
ND_3^+ sym. def.				1118(s)
NH_2 rock.	1113			
CH bend., in-.	1106	1116, 1108	1116, 1110	1110(sh)
Ring vib.	1016(w)	1010(m)	1039(w)	1027(m)
〃			1010(m)	1013(w)
Amide Ⅲ′		975(wb)		933
NH_2 wag.	943			
CH bend., out-.	891	885	882	880
CN str. (NO_2)	864	866	875(sh)	876(sh)
CH bend., out-.	851	852	846	858
〃	782(w)	776	776(w)	775
ND_2 rock.		765		
Amide Ⅴ	730			
CH bend., out-.	717	716	721	717
ND_3^+ rock.				707(sh)
	KBr disk	KBr disk	KBr disk	KBr disk

Table Ⅶ. Assignments of Vibrational Spectra of INA, INA-d_2, INA·HCl and INA-d_2·DCl

Assignment	INA (cm^{-1})	INA-d_2 (cm^{-1})	INA·HCl (cm^{-1})	INA-d_2·DCl (cm^{-1})
C=O str.	1676	1639	1695	1674(b)
			1633	
NH_2 bend.	1622		1614	
Ring str.	1599	1604	1596	1574
〃	1558	1559		
〃	1494(w)	1503(w)	1496(m)	1453(s)
〃	1416(vs)	1417(vs)		
CN str.	1400(〃)	1405	1394	1410
			1336	
CH bend., in-.	1324(w)	1330(w)	1309(w)	1321(m)
				1295(s)
〃	1234	1237	1249	1254
ND_2 bend.				1200
			1190(w)	1190(mb)
NH_2 rock.	1150, 1123		1109, 1094	
CH bend., in-.	1065	1065	1060	1056
Ring vib.	1005(m)	1003(s)	1025(w)	1010(w)
〃	996(〃)		1006(m)	998(〃)
ND_2 rock.		938		956, 920
				885
CH bend., out-.	880(w)	876(w)	862(vw)	866(w)
〃	856(s)	850(m)		833(〃)
			830(s)	
NH_2 bend., out-.	796, 777		781	
CH bend., out-.	757	759	766, 744	775, 764
C=O bend., out-.	713	717		728
CH bend., out-.				693
	KBr disk	Nujol mull HCB mull KBr disk	KBr disk	Nujol mull HCB mull KBr disk

Table Ⅷ. Assignments of Vibrational Spectra of N-Me-INH, N-Me-INH-d_2, N-Me-INH·2HCl and N-Me-INH-d_2·2DCl

Assignment	N-Me-INH (cm^{-1})	N-Me-INH-d_2 (cm^{-1})	N-Me-INH·2HCl (cm^{-1})	N-Me-INH-d_2·2DCl (cm^{-1})
NH_2 bend.	1660			
C=O str.	1625	1623	1670	1654
Ring str.			1639 (w)	1630
NH_3^+ deg. def.			1612	
Ring str.	1597	1599		
〃	1549	1548	1550	1566
NH_3^+ sym. def.			1511 (sb)	
Ring str.	1498	1501		1502
CH_3 deg. def.	1470	1470	1464	1474
Ring str.	1436	1438	1435	1456
CH_3 sym. def.	1410, 1398	1408, 1395	1382	1388
			1365 (w)	
NH_2 twist.	1344			
CH bend., in-.	1327 (w)	1326 (w)	1320 (w)	1336 (w)
CN str.	1283 (s)	1268 (s)	1292 (w)	1287 (m)
CH bend., in-.	1238	1235	1252	1262
〃	1190 (w)		1220	1216
NH_3^+ rock.			1175	
ND_2 bend.		1162		
ND_3^+ deg. def.				1159
ND_3^+ sym. def.				1131
	1111 (w)	1120 (wb)	1110 (m)	
CH_3 rock.	1088	1078	1074	1079
CH bend., in-.	1064	1062	1059	1058
			1035	
NH_2 wag.	1012			
Ring vib.	997	997	1007	998
		987 (w)		984
	965 (w)	965 (〃)	950 (wb)	952 (w)
CN str. (CH_3)	907	927		919
ND_3^+ rock.				893, 871
CH bend., out-.	879 (w)	880 (w)	879 (w)	
〃	834 (vs)	833 (s)		843 (m)
			827 (vs)	
ND_2 wag.		788		
CH bend., out-.	758	758	752	766, 752
C=O bend., out-.	746	744	736	729
CH bend., out-.	715	712		693
	KBr disk	KBr disk Nujol mull HCB mull	KBr disk	KBr disk Nujol mull HCB mull

Table Ⅸ. Assignments of Vibrational Spectra of NA, NA-d_2, NA·HCl and NA-d_2·DCl

Assignment	NA (cm^{-1})	NA-d_2 (cm^{-1})	NA·HCl (cm^{-1})	NA-d_2·DCl (cm^{-1})
C=O str.	1685	1664	1723	1699
NH_2 bend.	1617		1639	
Ring str.		1627	1625	1619
〃	1595	1597	1599	1587
〃	1575	1578	1549	
〃	1488	1492		1503
〃	1423	1425 (sh)	1465	1447

CN str.	1398	1415	1401	1419
CH bend., in-.	1342(m)	1347(m)	1346(s)	1332(m)
〃			1265	1296
ND_2 bend.		1238		1231
CH bend., in-.	1210		1184	1178
NH_2 rock.	1156, 1126		1152	
CH bend., in-.	1094(w)	1105(w)	1119, 1103	1030, 1110
Ring vib.		1042(w)	1039	1059(w)
〃	1032	1028	1016	1018
CH bend., out-.	972	972(b)	957(vw)	978
ND_2 rock.		920		957
CH bend., out-.	937		912	936
			887	
CH bend., out-.	830	839	827	841
NH_2 bend., out-.	777(mb)		790	
C=O bend., out-.		739	780	764, 742
CH bend., out-.	704	704		699
	KBr disk	Nujol mull HCB mull	KBr disk	Nujol mull HCB mull

Table X. Assignments of Vibrational Spectra of PA, PA-d_2, PA·HCl and PA-d_2·DCl

Assignment	PA (cm^{-1})	PA-d_2 (cm^{-1})	PA·HCl (cm^{-1})	PA-d_2·DCl (cm^{-1})
C=O str.	1668	1660	1710	1685
NH_2 bend.	1603		1607(vs)	
Ring str.	1590	1591		1605
〃	1570	1570	1529	1584
		1500(w)		1495(w)
Ring str.	1469	1469	1454	1448
〃	1444	1449	1435(w)	
CN str.	1392	1402	1402	1409
			1369	
CH bend., in-.	1293	1293	1316	1315
			1294(w)	1290(w)
〃	1264, 1236	1269	1241(s)	1230(b)
ND_2 bend.		1209		1138
CH bend., in-.	1146	1155	1158	1160
NH_2 rock.	1166		1127	
CH bend., in-.	1100	1106, 1090	1095(w)	
Ring vib.	1046	1047	1039, 1019	1051
〃	999	1000	1002	
			957	
ND_2 rock.		921		934
CH bend., out-.	911	915(sh)	882(w)	895(w)
〃	828	825	808	811
NH_2 bend., out-.	795		771(sh)	
				787
CH bend., out-.	769	760	758	744
ND_2 bend., out-.		706		700
	KBr disk	Nujol mull HCB mull	KBr disk	Nujol mull HCB mull

Jensen[27] has reported from the X-ray analysis of INH crystal that the N-N bond length (1.41 Å) is within experimental error of the covalent radii sum (1.40 Å) and of 1.40～1.42 Å in $N_2H_6^{++}$ but significantly less than 1.45 Å in $N_2H_5^+$ or 1.46～1.47 Å in hydrazine. He has indicated, furthermore, the possibility of a pyramidal form of the

27) L. H. Jensen : J. Am. Chem. Soc., **76**, 4663 (1954).

terminal $-NH_2$ group from the difference Fourier method. It is, however, inconsistent with the infrared spectral data. The considerable double-bond character of the N-N bond and the absorption bands due to the $-NH_2$ deformation vibrations which occur at ca. 1630, 1126, and 951 cm^{-1} as shown in Tables Ⅱ, Ⅲ, Ⅳ, Ⅴ, and Ⅵ suggest that the $-NH_2$ group is almost in the same plane as the amide and the aromatic ring. On the other hand, the $-NH_2$ group of N-Me-INH appears to be non-planar.

For the reason of the less reproducibility between 950 cm^{-1} and 850 cm^{-1} in the spectra of hydrochlorides and N-deuterated hydrochlorides, further investigations are expected.

The authors express their deep gratitude to Prof. T. Kwan, Prof. M. Tsuboi and Prof. Z. Tamura for their encouragement and advice on this work. They are also indebted to Dr. Y. Kyogoku and Mrs. K. Matsuo for their pertinent advice and to Miss M. Ninomiya and Miss F. Suzuki for measurement of IR spectra.

Summary

To give reliable assignments for infrared spectra of metal complexes of isonicotinoylhydrazine and related compounds, the spectra of ligands themselves, their N-deuterated derivatives, their hydrochlorides and their N-deuterated hydrochlorides were investigated. The bands of amide, NH_2 deformation and pyridine ring vibrations were determined carefully, and some effective supports could be given to the assignments described in Part Ⅳ.

(Received May 1, 1964)

[Chem. Pharm. Bull. 12(10)1217~1224(1964)]

UDC 547.92.07

169. Kikuo Yasuda: Synthesis of 2α-Halo-4-en-3-oxo-steroids.

(*Research Laboratory, Teikoku Hormone Mfg. Co,, Ltd.*[*1])

A practical method for preparation of 2α-halo-4-en-3-oxo-steroids required for biological tests was studied.[*2]

Dehalogenation or dehydrobromination of halo-ketones (Ⅰ[1] or Ⅱ[2]) and bromine treatment of 2-ethoxalyl-4-en-3-ones (Ⅲ)[3] to the corresponding 2α-halo-4-en-3-ones (Ⅳ) are well studied. On the other hand bromination of 4-en-3-ones with N-bromosuccinimide

*1 1604, Shimosakunobe, Kawasaki (安田喜久男).

*2 Presented in part at the 18th Annual Meeting of the Pharmaceutical Society of Japan (1963).

1) B.E. Ellis, V. Petrow: J. Chem. Soc., **1956**, 1179.

2) *a*) H.H. Inhoffen, G. Zühlsdorff: Ber., **76B**, 233 (1943). *b*) C. Djerassi, C.R. Sholz: J. Am. Chem. Soc., **69**, 2404 (1947). *c*) *Idem*: J. Org. Chem., **13**, 697 (1948). *d*) C. Djerassi: J. Am. Chem. Soc., **71**, 1003 (1949). *e*) J.J. Beerboom, C. Djerassi: J. Org. Chem., **19**, 1196 (1954). *f*) R.M. Evans, J.C. Hamlet, J.S. Hunt, P.G. Jones, A.G. Long, J.F. Oughton, L. Stephenson, T. Walker, B.M. Wilson: J. Chem. Soc., **1956**, 4356.

3) *a*) J.A. Hogg, F.H. Lincoln, A.H. Nathan, A.R. Hanze, W.P. Schneider, P.F. Beal, J. Korman: J. Am. Chem. Soc., **77**, 4438 (1955). *b*) R.E. Shaub, G.R. Allen, Jr., M.J. Weiss: *Ibid.*, **81**, 4962 (1959). *c*) H.M. Kissman, A.M. Small, M.J. Weiss: *Ibid.*, **82**, 2312 (1960). *d*) G.R. Allen, Jr., M.J. Weiss: *Ibid.*, **82**, 2840 (1960). *e*) R. Joly, J. Warnant, B. Goffinet: Fr. Pat., 1,249,939, Mar. 22, 1961 (C.A., **56**, P10235d (1962)).