rials are present (cf. Table II) but the method is applicable by slight correction.

The present method utilizes colorimetric determination of the insecticide DDVP but the color developed by Dibrom is more labile than that of DDVP. While the determination value of DDVP is hardly affected in the presence of other insecticides, the value of Dibrom is greatly affected by other insecticides, as shown in Table II, but no examination has yet been made on a method for separatory determination. Periodical change of the concentrate, and relationship between the kind of emulsifier and rate of decomposition of Dibrom are still in the stage of preliminary investigation. Further examinations are being continued.

The authors wish to express their thanks to Goro Tatsui, Director of Research Laboratory of Chugai Pharmaceutical Co., Ltd., for permission to publish this work. They are indebted to many coworkers in the Laboratory for their earnest assistances.

Summary

A colorimetric method for the determination of DDVP is modified to adapt for the determination of Dibrom, which based on the color complex formed between Dibrom and acetone in the presence of alkali. The values obtained from this method showed good agreement with the values from the infrared absorption spectral method. Periodical change of 5% Dibrom emulsifiable concentrate was studied at 100, 70, 60, and 50° by this colorimetric method, and statistical treatment was made to presume the days required until 10% reduction at 30, 25, and 20°. Experiments were further made to see whether these values would agree when the concentrates were maintained at room temperature. From this result, the days required until 10% reduction at room temperature were 1.5, and 3~4 months in the emulsifiable concentrate containing 5% of *epi*-chlorohydrin and the one not containing it, respectively. These values showed good agreement with the values obtained from the statistical treatment. *epi*-Chlorohydrin has no stabilizing effect on Dibrom or rather promotes decomposition. Dibrom in the emulsifiable concentrate is fairly stable when nonionic emulsifier alone is present, but undergoes fairly rapid decomposition in the presence of anionic emulsifier alone.

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UDC 547.582.4 : 543.422.4

110. **Shigeru Yoshida**: Infrared Spectra of Benzamide, its *p*-Substituted Derivatives, Pyridinecarboxylic Acid Amides and Pyrazinamide.*1

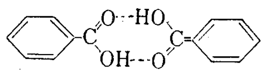
(*Takamine Research Laboratory, Sankyo Co., Ltd.**2)

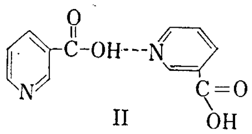
Infrared absorption spectra of benzamide, *p*-substituted benzamides, picolinamide, nicotinamide, isonicotinamide and pyrazinamide will be dealt with in this paper. The infrared spectra of benzoic acid, its *p*-substituted benzoic acids, pyridinecarboxylic acids and pyrazinecarboxylic acid has been previously reported,1) indicating that benzoic acids form dimeric structure (I), which was observed usually in aliphatic carboxylic acids; and that pyridinecarboxylic acids and pyrazinecarboxylic acids with nitrogen atoms in their nuclei form an intramolecular hydrogen bond structure (II) between carboxylic acid and nitrogen atom in the nucleus, without forming dimeri c structure. Especially, a carboxylic acid which possesses a nitrogen atom at *ortho*-position such as picolincarboxylic acid and pyrazinecarboxylic acid, forms intermolecular hydrogen bond structure (III).

The structural difference between benzoic acid, its *p*-substituted derivatives, and pyridinecarboxylic acids, pyrazinecarboxylic acids, was indicated by their characteristic absorption spectra. A similar difference of crystal structure may be considered to exist among benzamide, pyridinecarboxylic acid amides and pyrazinamide, therefore an investigation has been undertaken in order to find out whether any difference could be observed in this work.

Among the amides employed in this work, X-ray diffraction of benzamide,[2)] nicotinamide[3)] and pyrazinamide (α-type)[4)] had been already studied. The result proved that benzamide formed quite a similar dimeric structure (IV) to benzoic acid and combined in numerous hydrogen bonding.

Nicotinamide forms hydrogen bonding between the nitrogen atom in the nucleus and the amino group, and to this amino group combined the carbonyl group of another molecule in hydrogen bonding as it is observed in the case of nicotinic acid. That is to say, one molecule of nicotinamide combined with the other four molecules in hydrogen bond of the following structure (V).


I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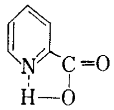
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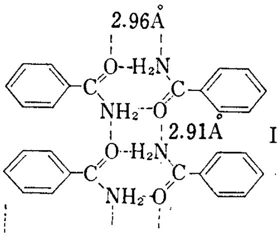

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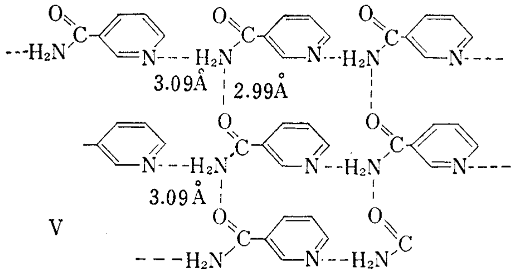
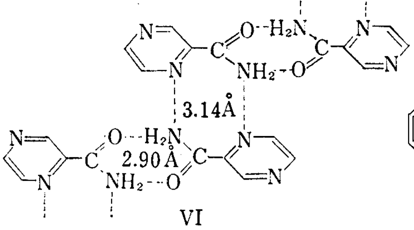
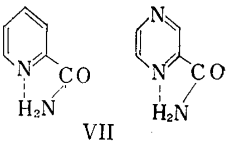


V



VI


VII

α-Type of pyrazinamide possesses a dimeric structure similar to benzamide, however, the type of hydrogen bond between dimers is different.

A hydrogen bond is formed between the amino group and the carbonyl group of benzamide. However, pyrazinamide formed the following structure (VI) of hydrogen bond between the amino group and the carbonyl group in dimer form and farther between the nitrogen atom of the nucleus and the amino group.

A specially noticeable fact in the crystal structure of benzamide, nicotinamide and pyrazinamide (α-type) was that the ring plane and the amino group plane of benzamide and nicotinamide intersected at 25° angle, but that of pyrazinamide at 5° angle. Based upon these crystal structure known by X-ray diffraction studies the interpretations of the infrared absorption spectra of these crystals were made.

[*1] The paper was presented at the 7th Symposium on Infrared and Raman Spectra at Tokyo, October 13, 1960.

[*2] 1-888 Nishi-shinagawa, Shinagawa-ku, Tokyo (吉田 茂).

1) S. Yoshida, M. Asai : This Bulletin, **7**, 162 (1959).

2) B.R. Penfold, J.C.B. White : Acta Cryst., **12**, 130 (1959).

3) B.W. Wright, G.S.D. King : *Ibid.*, **7**, 283 (1954).

4) Y. Takaki, Y. Sasada, T. Watanabe : Bull. Chem. Soc. Japan, **32**, 202 (1959); Acta Cryst., **13**, 639 (1960).

Experimental

Method——Each sample of the marketed and the synthesized in this laboratory was purified by recrystallization from water for the measurement. The purity were confirmed by the measurements of their m.p.

Among the various kinds of isomers which have been known to exist in pyrazinamide, the usual isomer recrystallized from water was defined to be the α-type, and the other, sublimed under reduced pressure, was the β-type.

Picolinamide was similarly defined to be the α-type, which was recrystallized from water and the β-type, sublimed under reduced pressure.

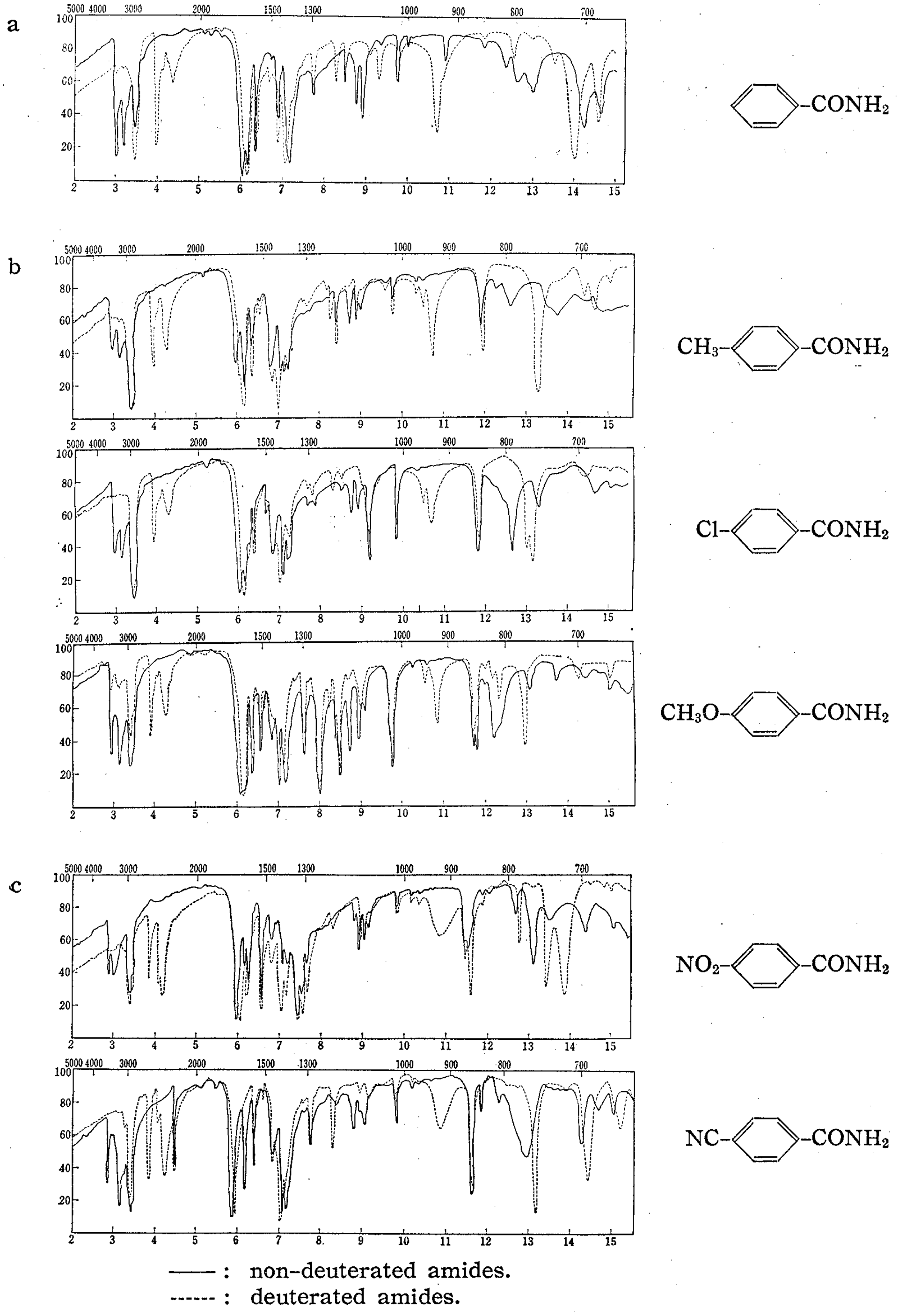


Fig. 1.

Deuteration of each amide was carried out by the method of recrystallization from deuterated water. Deuterated β-type of pyrazinamide and picolinamide was prepared by sublimation under reduced pressure. The IR measurements were made with a Perkin-Elmer Spectrophotometer, Model-21, and the width of the cell was 0.2 mm. in $CHBr_3$, 0.1 mm. in 1.5~2.5% dioxane solution and 1 mm. in 0.2~0.4% $CHCl_3$. In the latter two cases of the solution, the chart scale was employed by 20 cm./μ.

Discussion

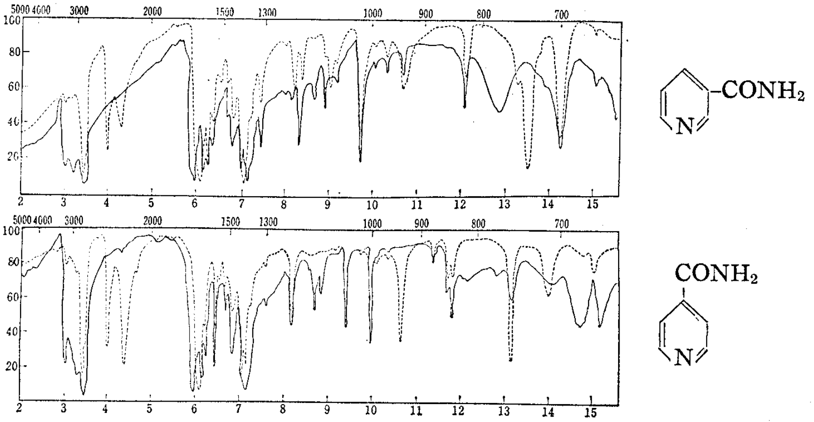
The absorption spectra of each amide and its deuterated amide in Nujol mull are shown in Figs. 1, 2, 3, and 4.

Over 3000 cm^{-1} Region——Asymmetric and symmetric stretching vibration (abbreviated to $\nu_{as\,\mathrm{NH_2}}$, $\nu_{as\,\mathrm{ND_2}}$, $\nu_{s\,\mathrm{NH_2}}$ and $\nu_{s\,\mathrm{ND_2}}$) and the values of the ratio, $\nu_{as\,\mathrm{NH_2}}/\nu_{as\,\mathrm{ND_2}}$ and $\nu_{s\,\mathrm{NH_2}}/\nu_{s\,\mathrm{ND_2}}$ are tabulated in Table 1. The value of the ratio, $\nu_{as\,\mathrm{NH_2}}/\nu_{as\,\mathrm{ND_2}}$ and $\nu_{s\,\mathrm{NH_2}}/\nu_{s\,\mathrm{ND_2}}$ in benzamide and its *p*-substituted benzamide was indicated to be 1.33~1.34 and 1.35~1.38. The values obtained were completely identical with that of aromatic amine compounds reported by S. Califano.[5] On the other hand, the values of the ratio $\nu_{as\,\mathrm{NH_2}}/\nu_{as\,\mathrm{ND_2}}$ and $\nu_{s\,\mathrm{NH_2}}/\nu_{s\,\mathrm{ND_2}}$ of isonicotinamide, nicotinamide, picolinamide (α-type) and pyrazinamide (α-type) were 1.32~1.33 and 1.33~1.35 respectively, being different from that of benzamide derivatives. However, β-type of picolinamide and pyrazinamide gave different values of 1.34 and 1.35~1.37 from the α-type compound, being equal to that of benzamide derivatives. These facts indicate that the crystal structure of benzamide derivatives and α-type of picolinamide and pyrazinamide are different, and it was considered to form a similar structure when β-type was formed.

The values of ν_{as} and ν_s of picolinamide and pyrazinamide in chloroform solution appeared to shift about 20~10 cm^{-1} to the lower frequency than the other compound. In these compounds, a presence of intermolecular hydrogen bond (VII) might be suggested, but this consideration was disproved by the following absorption spectra of the carbonyl group.

Carbonyl Absorptions (Amide I Bands, Fig. 2)——The frequency of benzamide and its *p*-substituted compound became higher in the chloroform solution almost proportional to the Hammett constant of $CH_3{=}CH_3O<H{=}Cl<Cl<CN<NO_2$.

The frequency of nicotinamide, whose nitrogen atom in the nucleus had little effect in pyridine carboxylic acid amides, was the lowest, and those of isonicotinamide and picolinamide, whose negativity of nitrogen atom in the nucleus at either *ortho-* or *para-*



—— : non-deuterated amides. ------ : deuterated amides.

Fig. 2.

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5) S. Califano, R. Moccia : Gaz. Chem. Ital., 87, 805 (1957).

Table I. Asymmetric and Symmetric Streching Vibrations of NH_2 and ND_2

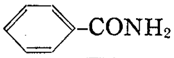
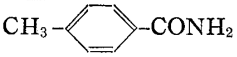
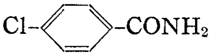
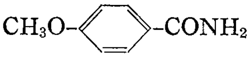
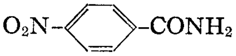
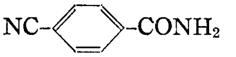
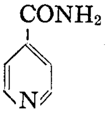
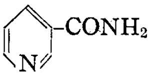
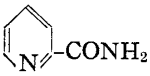
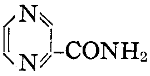
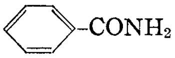
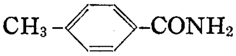
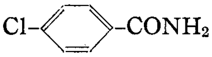
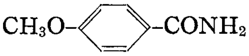
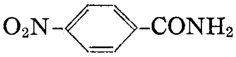
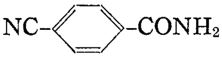
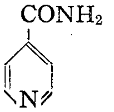
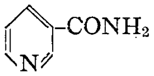
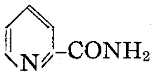
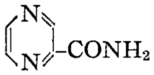
	Compounds		Nujol						CHCl$_3$ (1 mm.)	
			ν_{as} NH$_2$	ν_s NH$_2$	ν_{as} ND$_2$	ν_s ND$_2$	ν_{as} NH$_2$/ν_{as} ND$_2$	ν_s NH$_2$/ν_s ND$_2$	ν_{as} NH$_2$	ν_s NH$_2$
1			3356	3155	2525	2309	1.33	1.37	3546	3430
2			3367	3165	2525	2320	1.33	1.36	3552	3440
3			3401	3185	2538	2326	1.34	1.37	3546	3430
4			3413	3175	2558	2336	1.33	1.36	3546	3420
5			3448	3311	2577	2392	1.34	1.38	3544	3422
6			3472	3175	2591	2353	1.34	1.35	3552	3422
7			3289	3012	2488	2273	1.32	1.33	3549	3436
8			3333	3145	2525	2326	1.32	1.35	3556	3436
9		α	3436	3185	2584	2398	1.33	1.33	3534	3407
		β	3436	3185	2571	2358	1.34	1.35		
10		α	3448	3165	2565	2375	1.33	1.33	3530	3410
		β	3460	3311	2577	2411	1.34	1.37		

Table II. Carbonyl Absorptions (Amide I Bands)

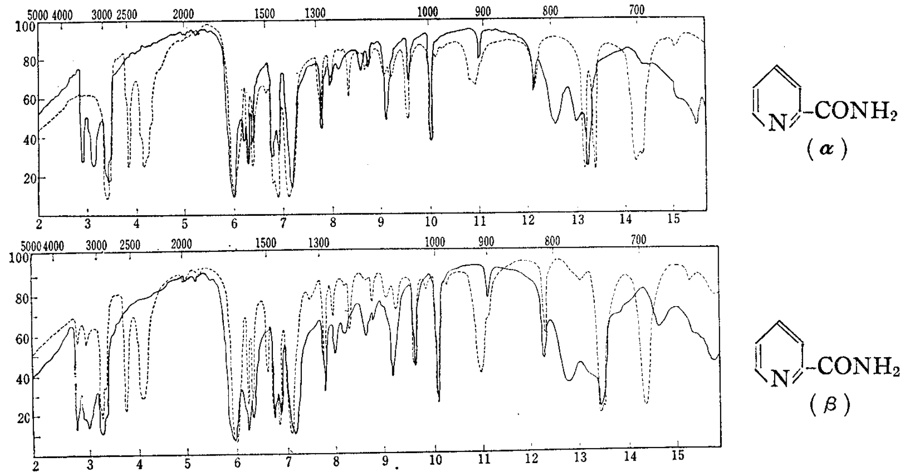
	Compounds		Nujol	Deuterated amides (Nujol)	CHCl$_3$	CHBr$_3$	Dioxan
1			1658	1634	1678	1675	1689
2			1675	1650	1675	1672	1684
3			1658	1634	1678	1675	1690
4			1645	1629	1675	1669	1678
5			1669	1648	1690	1686	
6			1703	1678	1689	1686	
7			1684	1639	1692	1689	1694
8			1695 sh, 1684	1675 sh, 1645	1686	1684	1691
9		α	1667	1667	1692	1692	1696
		β	1667	1656			
10		α	1715	1689	1698	1695	1701
		β	1684	1672			

sh : shoulder

position, had a greater effect, were found to be equal. However, the frequency of picolinamide appeared to be higher than that of isonicotinamide, in bromoform and dioxane solutions. The frequency of pyrazinamide is similar to that of the sum of picolinamide and the difference between nicotinamide and isonicotinamide. This fact showed the participation of the nitrogen atom in the nucleus. The most striking fact in carbonyl absorption is that the frequency of α-type of pyrazinamide in Nujol was 1715 cm^{-1}, which was higher than that in either chloroform, bromoform or dioxane solutions. It might be impossible to get an explanation from the crystal structure (VI) of α-type of pyrazinamide mentioned above as to whether α-type of pyrazinamide would give higher frequency in Nujol than in solution.

Naturally, hydrogen bond of VI disappears in the solution because of monomeric formation, and therefore, the absorption in the solution should be seen as reaching a higher frequency than that of the solid. In the course of infrared spectral studied$^{1)}$ of pyridinecarboxylic acid derivatives, it was observed with 2,6-diphenylisonicotinic acid that the absorption of carbonyl group in the solid state reached a higher frequency than in the liquid.

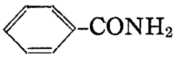
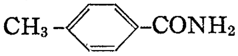
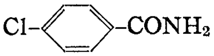
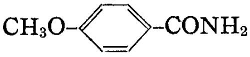
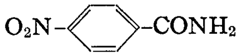
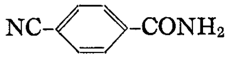
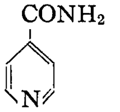
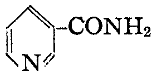
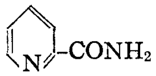
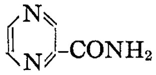
It will be interesting to know why such phenomenon may take place in these compounds.



——: non-deuterated amides. ------: deuterated amides.

Fig. 3.

Table III. Deformation Vibrations of NH_2 and ND_2 (Amide II Bands)

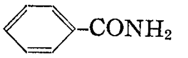
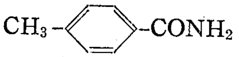
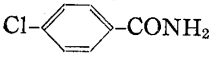
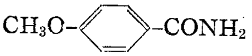
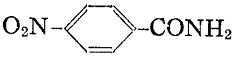
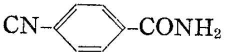
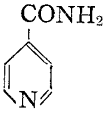
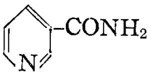
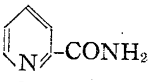
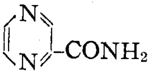
	Compounds		δ_{NH_2}	δ_{ND_2}	$\delta_{NH_2}/\delta_{ND_2}$
1			1629	1211	1.35
2			1618	1209	1.34
3			1621	1209	1.34
4			1623	1214	1.34
5			1618	1214	1.34
6			1623	1209	1.34
7			1621	1222	1.33
8			1621	1221	1.33
9		α β	1608 1603	1199 1205	1.34 1.33
10		α β	1616 1603	1224 1217	1.32 1.32

Deformation Vibration of NH_2 and ND_2 (Amide II Bands, Fig. 3)——The value of the ratio $\delta_{NH_2}/\delta_{ND_2}$ of benzamide and its *p*-substitutes was 1.35~1.34 and that of pyridinecarboxylic acid amides was 1.33, except *α*-type of picolinamide, and 1.32 for pyrazinamide. Though $\nu_{as\,NH_2}/\nu_{as\,ND_2}$ and $\nu_{s\,NH_2}/\nu_{s\,ND_2}$ of *β*-type of pyrazinamide was equal to that of benzamide, the difference of the $\delta_{NH_2}/\delta_{ND_2}$ value might be explained because the benzamide combine symmetrically with the acid amide group intramoleculary, but the *β*-type⁶⁾ of pyrazinamide, though similar to the bond type of benzamide, combine spirally but not symmetrically.

Although any analysis of *β*-type of picolinamide has not been made on crystal structure, it showed an almost similar absorption to *β*-type of pyrazinamide, therefore some similarity was supposed to exist in their crystal strucure. The appearance should be noted of one characteristic absorption band, resulting from deuteration near 1500 cm^{-1}, clearly observed for pyrazinamide and picolinamide as shown in Fig. 1. This absorption band was considered to be a deformation band⁷⁾ for ND, caused by a half-deuterated amino group. This phenomenon was also observed for benzamide and *p*-methoxybenzamide.

=C-N Stretching Vibration (Amide III Bands, Fig. 4)——Few changes were observed by the deuteration of =C-N stretching vibration and a shift to a rather lower frequency in solution was reported⁸⁾ to have been discussed and therefore the details will not be dealt with in this paper.

Table IV. =C-N Stretching Vibrations (Amide III Bands)

	Compounds		Nujol	Deuterated amide (Nujol)	$CHBr_3$
1			1401 s	1416 s	1370 s
2			1416 s	1429 s	1370 s
3			1408 s	1425 s	1366m
4			1397 s	1403 s	1370m
5			1412 s	1416 s	1374w
6			1416 s	1422 s	1370w
7			1401 s	1401 s	1372m
8			1401 s	1416 s	1374 s
9		*α* *β*	1381 s 1376 s	1408 s 1403 s	1377 s
10		*α* *β*	1381 s 1376 s	1385 s 1381 s	1361m

s: strong m: medium w: weak

It is also a remarkable fact that =C-N stretching vibration of picolinamide and pyrazinamide was present at 1380~1375 cm^{-1} and lower than that of the rest of the amides absorption at 1400~1416 cm^{-1}.

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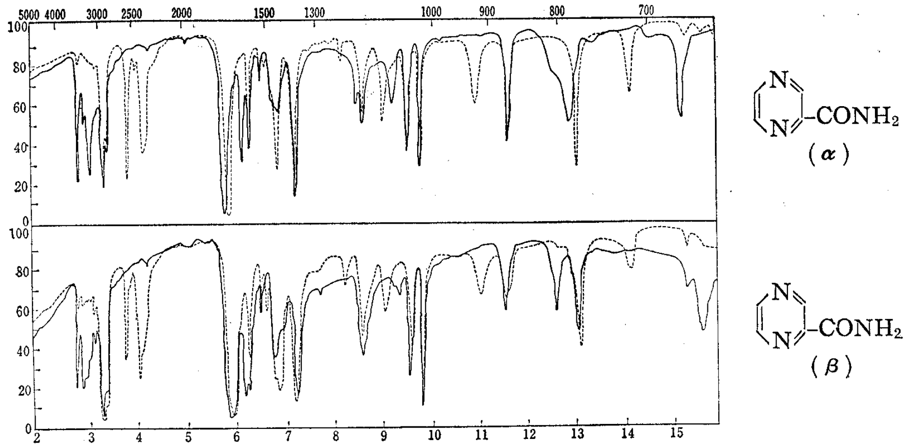
6) C. Tamura, H. Kuwano: Acta Cryst., **14**, 693 (1961).

7) T. Miyazawa: J. Chem. Soc. Japan, **76**, 821 (1955).

8) S. Pinchas, D. Samuee, *et al.*: J. Chem. Soc., **1961**, 1688 and refer to the papers cited in this reference paper.

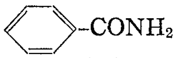
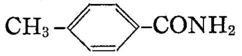
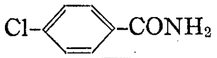
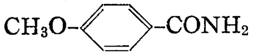
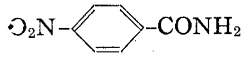
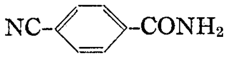
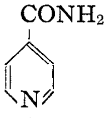
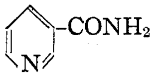
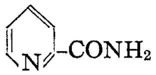
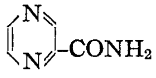


—— : non-deuterated amides. ------ : deuterated amides.

Fig. 4.

NH_2 Rocking Vibrations——The rocking vibration of NH_2 and ND_2 of each amino and the deuterated amino group is shown in Table V. It was reported by Miyazawa[8] and Evans[9] that NH_2 rocking vibration of formamide appeared around 1090 cm^{-1}, which shifted to 910 cm^{-1} on deuteration, showing 1200 of displacement ratio. In the case of formamide, only one band of NH_2 rocking vibration was reported to have been observed, but our investigation showed two separated bands clearly identified. When it was deuterated, only one band was observed, and the displacement ratio of the arithmetical mean of the two bands and the deuterated band was found to be 1.21~1.22, which corresponded almost exactly to the case of the formamide. However, the displacement ratio of such a picolinamide and pyrazinamide that possessed a nitrogen atom

Table V. NH_2 rocking Vibrations

	Compounds		Nujol	Deuterated amides (Nujol)	Displacement ratio
1			1142 s, 1122 s	938.1 s	1.22
2			1145m, 1114m	932 s	1.22
3			1145m, 1125m	936.3 s	1.21
4			1145m, 1101m	920.8 s	1.22
5			1134m, 1093m	920m, br	1.21
6			1142m, 1109m	922.5m, br	1.22
7			1149m, 1130m	939.8 s	1.21
8			1155m, (1125m)	932.8m, sh	1.22
9		α	1163w, 1143w	924.2m, br	1.25
		β	1160m, 1152m	919.1 s	1.26
10		α	1182m, (1088 s)	920.8m	1.29
		β	1091w, (1075w)	917.4m	1.27

s : strong m : medium br : broad w : weak sh : shoulder

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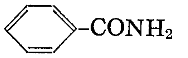
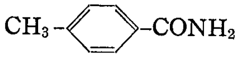
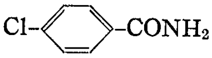
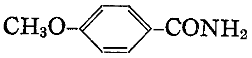
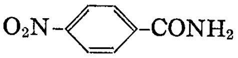
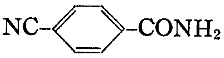
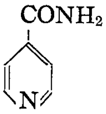
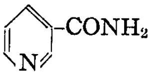
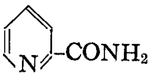
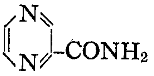
9) J.C. Evans : J. Chem. Phys., **22**, 1228 (1954).

at 2-position was 1.25~1.29, thus differing from the results obtained above. Among NH_2 rocking vibration of pyridine carboxylic acid amides and pyrazinamide, isonicotinamide was considered to possess two distinct bands, but the other compound remained still in doubt in this problem. It was uncertain as to whether α-type of picolinamide, and α- and β-type of pyrazinamide possessed two bands.

Ring C-H Out-of-Plane Bending Frequencies——C-H out-of-plane bending frequencies of each amide is shown in Table VI. As to the δ_{CH} of benzamide, to which Bellamy[10] and Margoshes, *et al.*[11] assigned 771 cm^{-1} and this assignment was assumed to be in adequate because of a disappearance of the band by deuteration. The absorption band at 793.7 cm^{-1}, which did not disappear even after deuteration, was supposed to be δ_{CH}. This fact was found to correspond reasonably to that of δ_{CH} of benzoic acid at 812 cm^{-1}, studied by the author.[12,14] In the *p*-substituted benzamide, it was at 840~860 cm^{-1}, which presents rather higher frequency, being highly proportional to the Hammett constant of the substitute. Although the δ_{CH} of pyridinecaboxylic acid amide and pyrazinamide was studied by Shindo,[13] it is considered to be adequate to so assign it as it was shown in the Table. The assignment of isonicotinamide was the same as that by Shindo, but the remainder are all different. Usually, δ_{CH} of carboxylic acid, ester and amide compounds appeared to have a far higher frequency[11~14] than expected, therefore it is impossible to determine the δ_{CH} in relation to the other substituted group.

TABLE VI. Ring C-H Out-of-plane Bending Frequencies

	Compounds		Nujol	Deuterated amides (Nujol)	$CHBr_3$
1			793.7m	798.1m	797.4w
2			840.3s	837.5s	840.3m, br
3			845.3s	844.6s	844.6m
4			841.0s	841.0s	843.2w
5			865.1m	862.1s	866.6w
6			859.8s	859.1s	856.2w
7			846.7m	845.3m	840.3w
8			830.6s	827.8s	826.4w
9		α	825.1m	823.0m	818.4w
		β	825.1m	822.4m	
10		α	870.3s	869.8s	860.6w
		β	877.2m	875.7m	

m : medium w : weak s : strong br : broad

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[10] L.J. Bellamy : J. Chem. Soc., **1955**, 4221.

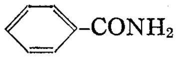
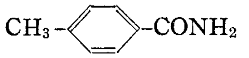
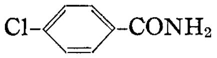
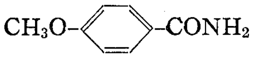
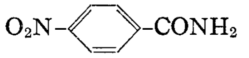
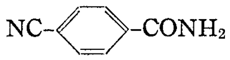
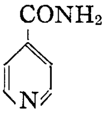
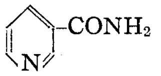
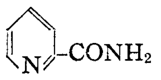
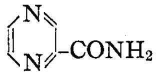
[11] R.D. Kross, V.A. Fassel, M. Margoshes : J. Am. Chem. Soc., **78**, 1332 (1956).

[12] S. Yoshida : This Bulletin, 8, 389 (1960).

[13] H. Shindo : Pharm. Bull. (Tokyo), **5**, 472 (1957).

[14] Y. Kakiuchi, *et al.* : Infrared hydrogen vibration of benzoic acid, presented at the Symposium on Infrared and Raman Spectra, October 14, 1960.

TABLE Ⅶ. Absorption Bands below 850 cm^{-1}

	Compounds		Nujol	Deuterated amides (Nujol)	$CHBr_3$
1			**810.4m**, **770.4m**, 704.2 s, 684 s	739.6m, 714.3 s, 686.8 s	709.2 s
2			**815.7w**, **793.7m, br**, 726.7m, br, 691.6m, br	751.9 s, 695.4m, 684m	830.6m, br, 749.1m
3			**789.9 s**, **751.9m**	768 s, 759.9 s	774m, 754.1m
4			**813.3 s, br**, **809.1 s, br**, 764.5w, 727.3w, 692.0w	810.4m, 772.2 s, 700.3w, 664.9w	810.4m, br, 764.5m
5			**788.6m**, **763.4 s**, 761.8m, br, 695.4m, br, 664.9m	783.7 s, 744 s, 721.5 s	757.6w, 716.3w
6			**815.7w**, **774 s, br**, 700.3m, 682.1w, 664w	760.5 s, 692.5 s, 665.8m	761w
7			**822,4w, br**, **781.3w, br**, 759.9m 709.2w, br, 680.3m, br, 659.6m	761 s, 714.3m, 664.9w	752.4w
8			**781.3 s, br**, 703.2 s	755.3m, 740.7 s, 704.2 s	771.6w, 737.5m
9		α	**794.9m, br**, **766.9m, br**, 755.3 s, 662.3m, 646.4m	795.9 s, 747.9 s, 701.8 s, 697.4 s, 665.3w	746.8 s
		β	**793.7 s, br**, **762.2 s, br**, 755.9 s, 751.9 s, sh, 692.5m, br	755.3 s, 751.9 s, 707.7 s	
10		α	**800m, br, sh**, **787.4 s**, br, 668.9 s	776.4 s, 717.4m	796.2w, 772.8m
		β	**805.2m**, 778.2 s, 666.2w, 652.7w	775.2 s, 719.4w, br, 667.7w	

m : medium s : strong w : weak br : broad sh : shoulder

Below about 800 cm^{-1} Region (Table VII)——In this region, absorption of extra-band,[12] NH_2 wagging vibration, and $\delta_{O=CN}$ should exist. Miyazawa indicated that the absorption of $\delta_{O=CN}$ of formamide was found at 627 cm^{-1} for crystals and 600 cm^{-1} in liquid, being shifted to 570 cm^{-1} in liquid by deuteration, having 1.0532 of displacement ratio. $\delta_{O=CN}$ of benzamide was considered to appear at about 650 cm^{-1} and the weak absorption near 670 cm^{-1} indicated in Table Ⅶ seems to be assigned $\delta_{O=CN}$, but the assignment was impossible because the measurement in potassium bromide region was not carried out. NH_2 wagging vibration was thought to appear around at 800 cm^{-1} but any studies on displacement ratio of the band by deuteration was not reported, therefore, it might be proper to assume the absorption at 800 cm^{-1} to be the NH_2 wagging vibration, though the precise assignment was difficult. However, the absorption band which disappeared in bromoform solution was supposed to be NH_2 wagging vibration, which is indicated by Gothic in the Table. This absorption gave either one or two bands depending on the compound. NH_2 wagging vibration of formamide appeared at 800 cm^{-1} for crystal and at around 700 cm^{-1} in liquid.[8] Even though the extra-band remained unchanged or showed no absorption by deuteration, an assignment of the absorption in this region was impossible because of complexity.

The results obtained above suggested that *p*-substituted benzamide was assumed to indicate similar dimeric structure Ⅳ to benzamide, because of showing similar absorption inclination.

Isonicotinamide was considered to form a similar structure V to nicotinamide, because of having similar absorption tendency. The α-type of picolinamide was supposed to form the resembling structure Ⅵ of α-type of pyrazinamide, because of having resembling absorption inclination to α-type of pyrazinamide. β-Type of pyrazinamide was considered to benzamide structure, because of having the resembling absorption inclination, but the symmetry of structure was considered to be different.

β-type of picolinamide was supposed to have similar crystal structure to β-type of pyrazinamide.

The author's thanks are due to Prof. Miyazawa of Osaka University for helpful discussions and suggestions. The author is also indebted to Messrs. Amakasu and Higuchi for IR measurements and to Miss Sasaki for her kind assistance.

Summary

Infrared absorption spectra of benzamide, *p*-substituted benzamide, pyridinecarboxylic acid amides, pyrazinamide and their homologs were measured in Nujol mull and in solution, and the assignment of the characteristic absorption has been made. The infrared absorption spectral data suggested the crystal structure of isonicotinamide, α- and β-type of pyrazinamide and β-type of pyrazinamide.

1) Benzamide, *p*-substituted benzamides, picolinamide (β-type), and pyrazinamide (β-type) showed a similar absorption tendency and are therefore supposed to have a similar crystal structure. β-Type of picolinamide and pyrazinamide is different in symmetric center.

2) Nicotinamide and isonicotinamide showed the same absorption tendency and, therefore, the same crystal structure was formed.

3) Pyrazinamide (α-type) and picolinamide (α-type) showed the same absorption tendency and is supposed to form the same crystal structure.

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111. **Issei Iwai and Tetsuo Hiraoka**: Studies on Acetylenic Compounds. XXXI.*[1] Intramolecular Cyclization Reaction of the Acetylenic Compounds.

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There are few examples available[1)] concerning the intramolecular condensation of a triple bond to an aromatic nucleus. This time it was found that this condensation can be carried out more effectively to a variety of acetylenic derivatives by the treatment with polyphosphoric acid (PPA) under a mild condition.

Heating of 1,4-diphenyl-1-butyne (I)[2)] with PPA gave 2-phenylnaphthalene (IV), m.p. 100~101° and a liquid of b.p$_5$ 162~170° (bath temp.). The latter exhibited ultraviolet absorption bands at 220 and 285 mμ, very similar to that of 1-phenylnaphthalene (III). However, it showed an aliphatic C-H stretching absorption at 2900 cm^{-1} region in infrared spectrum. When the oily liquid, b.p$_5$ 162~170° was heated with powdered sulfur, it gave a colorless oil, b.p$_2$ 145~150° (bath temperature) in good yield, which was identified as 1-phenylnaphthalene (III) by comparing its infrared and ultraviolet spectra with

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