Infrared Absorption Spectra of Hydrazides. IV Some Monoacid Hydrazides

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Although Jensen[1] studied the infrared absorption spectra of some monoacid hydrazides, he examined the bands in the 6 and 3 μ regions only. The infrared spectrum of benzoylhydrazine was previously observed by the present author[2], but the absorption bands obtained could not be interpreted with confidence.

In the present study the spectra of some monoacid hydrazides in the solid state and in acetonitrile solutions are examined in the rock salt region and the frequencies characteristic of the $-CONHNH_2$ group are considered.

Experimental

Formyl-[3], acetyl-[4], cyanoacetyl-[5], propionyl-[6], butyryl-[7] and isovaleryl-hydrazine[8] were synthesized with ethyl esters of corresponding acids and hydrazinehydrate and were purified by recrystallization from ethanol or ether; m. p., 54, 67, 110, 40, 45, 68°C, respectively. *N*-Deuterated cyanoacetylhydrazine was prepared in sealed tubes in the presence of heavy water (99.8%), the excess of which was evaporated in vacuum.

The spectra were taken with a double-beam Hitachi infrared spectrophotometer, type EPI-2, with rock salt prisms. Potassium bromide disks were employed for taking the spectra of solids, and the solution spectra were examined in acetonitrile.

Results and Discussion

Cyanoacetylhydrazine (CAH). — The solid spectra of CAH and *N*-deuterated CAH (CAH-d_3) and the solution spectrum of CAH are illustrated in Fig. 1. The absorption bands of CAH are interpreted without much difficulty by comparing the spectrum with those of cyanoacetyl-acetylhydrazine (CAAH)[9], hydrazine[10] and its derivatives[11,12].

The 3000 cm^{-1} Region. — The most intense band among the bands in this region is found at 3180 cm^{-1} for solid CAH, while a corresponding band is observed at 2380 cm^{-1} for solid CAH-d_3, the value of ν_H/ν_D being 1.336. This is probably due to the N–H stretching vibration of the –CONH– group, because CAAH[9] has also a NH band at 3190 cm^{-1} which is displaced by a band at 2370 cm^{-1} on *N*-deuteration, the ν_H/ν_D ratio being 1.346. The NH_2 stretching vibrations ($\nu(NH_2)$) of the hydrazine residue will also give rise to bands in this region. Hydrazine[10] in the solid state has two bands, ascribed to $\nu_a(NH_2)$ at 3315 cm^{-1} and to $\nu_s(NH_2)$ at 3204 cm^{-1}. Monomethylhydrazine[11] in the liquid state shows three Raman lines, 3317, 3245 and 3177 cm^{-1}, which have been ascribed to NH or NH_2 stretching

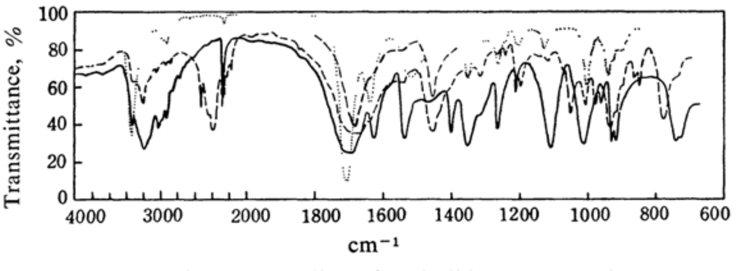

Fig. 1. Infrared spectra of cyanoacetylhyrazine (solid curve) and its *N*-deuterated derivative (dashed curve) in KBr disks and cyanoacetylhydrazine in the CH_3CN solution (dotted curve).

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1) J. B. Jensen, *Acta Chem. Scand.*, **10**, 667 (1956).

2) M. Mashima, This Bulletin, **35**, 332 (1962).

3) G. Pellizzari, *Gazz. chim. ital.*, **24**, II, 225 (1894).

4) T. Curtius and T. S. Hofmann, *J. prakt. Chem.*, [2] **53**, 524 (1897).

5) V. Rothenburg, *Ber.*, **27**, 687 (1894).

6) T. Curtius and H. Hille, *J. prakt. Chem.*, [2] **64**, 404 (1901).

7) R. Stolle and G. Zinsser, ibid., [2] **69**, 489 (1904).

8) T. Curtius and H. Hille, ibid., [2] **64**, 411 (1901).

9) M. Mashima, This Bulletin, **35**, 423 (1962).

10) D. A. Giguere and I. D. Liu, *J. Chem. Phys.*, **20**, 136 (1952).

11) D. W. E. Axford, G. J. Janz and K. E. Russell, ibid., **19**, 704 (1951).

12) E. R. Shull, J. L. Wood, J. G. Aston and D. H. Rank, ibid., **22**, 1191 (1954).

vibrations, while 1,1-dimethylhydrazine[12] shows two Raman lines, 3330 and 3141 cm^{-1}, assigned to $\nu(NH_2)$. In this region, CAH has a band at 3320 cm^{-1} and CAH-d_3 has an isolated band at 2510 cm^{-1} and a shoulder band at 2430 cm^{-1}. The 3320 cm^{-1} band is very close in frequency to the 3315 cm^{-1} band ($\nu_a(NH_2)$) of solid hydrazine; its counterpart is found at 2510 cm^{-1} in the CAH-d_3 spectrum, the ν_H/ν_D ratio being 1.323. Therefore, the 3320 cm^{-1} band may be ascribed to $\nu_a(NH_2)$. On the other hand, the $\nu_s(NH_2)$ absorption is expected to appear near 3200 cm^{-1} because solid hydrazine has a corresponding band at 3204 cm^{-1}. However, we can not observe the corresponding band because of the overlap of the intense band at 3180 cm^{-1}, which was already ascribed to $\nu(NH)$. CAH-d_3 has, however, a band at 2430 cm^{-1} which is probably to be ascribed to $\nu_s(ND_2)$. For phenylacetic acid hydrazide, Jensen[1] obtained three bands, at 3300, 3175 and 3000 cm^{-1}, in the solid state, but he did not make detailed assignments of them. The former two bands are very close in frequency to the 3320 and 3180 cm^{-1} bands of CAH respectively. In the present study the assignment of the 3180 cm^{-1} band to the NH stretching vibration of the –CONH– group depends also on the fact that CAH in acetonitrile has a band at 3320 cm^{-1} which is very close in frequency to the $\nu(NH)$ band at 3310 cm^{-1} of CAAH[9] in the same solvent

In this region, CAH has several more weak bands. Of these, three bands are shifted to lower frequencies on *N*-deuteration, but a reasonable interpretation of them is not easy on the basis of the present observations only. On the other hand, a sharp band at 2925 cm^{-1} and a shoulder band at 2860 cm^{-1} are probably to be ascribed to the CH_2 stretching vibrations, because the corresponding bands are found at 2930 and 2870 cm^{-1} for CAH-d_3.

A band at 2265 cm^{-1} of CAH is easily assigned to $\nu(C\equiv N)$, because CAH-d_3 has a corresponding band at 2270 cm^{-1} and CAAH[9] absorbs at 2270 cm^{-1}.

The 1700～700 cm^{-1} Region. — The amide group, –CONH–, is contained in a CAH molecule, so CAH will show amide I, II, III and IV absorptions in this region[13]. CAH has a very strong and broad band with a center at 1698 cm^{-1} and CAH-d_3 has a corresponding band at 1680 cm^{-1}, the ν_H/ν_D ratio being 1.010. Therefore, the 1698 cm^{-1} band of solid CAH may surely be assigned to the amide I band. In the acetonitrile solution, CAH has the corresponding band at 1704 cm^{-1}.

CAH has a band at 1534 cm^{-1} which corresponds in intensity to the band of CAH-d_3 at 1451 cm^{-1}, the ν_H/ν_D ratio being 1.057. A corresponding band is also found at 1513 cm^{-1} for CAH in acetonitrile. CAAH[9] has an amide II band at 1497 cm^{-1}, and CAAH-d_2 has an amide II′ band at 1413 cm^{-1}, the ν_H/ν_D ratio being 1.059. Thus, the 1534 cm^{-1} band of CAH is undoubtedly to be ascribed to the amide II band.

Although the amide III band is expected to appear in the 1300～1250 cm^{-1} range, its identification will be considered with the assignments of the NH_2 deformation vibrations.

Let us now consider the location of the NH_2 deformation vibrations. Yamaguchi[14] has shown that the deformation vibrational modes of the non-planar $-NH_2$ group (e. g., of methylamine and hydrazine) are composed of bending, twisting and wagging vibrations and that the absorption bands due to them occur near 1600, 1300 and 800 cm^{-1} respectively. On the other hand, the deformation vibrations of the planar $-NH_2$ group are composed of bending, rocking, wagging and twisting vibrations. Urea[15] in the solid state has the bands at 1629 and 1603 cm^{-1} (bending), 1150 cm^{-1} (rocking), 719 cm^{-1} (wagging) and 500 cm^{-1} (twisting). Oxamide[16] in the solid state has these four bands at 1608, 1103, 792 and 678 cm^{-1} respectively. Therefore, the presence of the non-planar $-NH_2$ group may probably be detected by the presence of the NH_2 deformation band near 1300 cm^{-1}. Yamaguchi[14] has assigned the 1275 cm^{-1} band of hydrazine vapor to the NH_2 twisting vibration. For solid hydrazine Giguere and Liu[10] have obtained the 1320 cm^{-1} band, which corresponds to the 1275 cm^{-1} band of hydrazine vapor. Axford and others[11] obtained an absorption band at 1308 cm^{-1} for methylamine in the liquid state, but they could not reasonably assign the band. For liquid 1, 1-dimethylhydrazine, Shull and others[12] have observed a strong band at 1321 cm^{-1} which they ascribed to a CH_3 bending vibration. However, this assignment is doubtful because liquid trimethylhydrazine[12] has no band corresponding to it. The band of these hydrazine derivatives near 1300 cm^{-1} is probably due to the non-planar NH_2 deformation vibration.

In the region below 1650 cm^{-1}, CAH has five band which disappear on *N*-deuteration; they are the bands at 1625 (s), 1347 (s), 1258 (m), 1105 (s) and 1009 (s) cm^{-1}. On the other hand, CAH-d_3 has five new bands at 1192 (m), 1044 (m), 973 (m), 928 (s) and 842

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[13] See, for example, T. Miyazawa, T. Shimanouchi and S. Mizushima, ibid., **24**, 408 (1956).

[14] A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1105, 1109 (1959).

[15] A. Yamaguchi, ibid., **78**, 1467 (1957).

[16] T. A. Scott, Jr. and E. L. Wagner, *J. Chem. Phys.*, **30**, 465 (1959); see also T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 86 (1954).

(w) cm^{-1}. Of these, the 1625 cm^{-1} band of CAH will correspond to the 1192 cm^{-1} band of CAH-d_3, the ν_H/ν_D ratio being 1.363. This band is close in frequency to the band due to the NH_2 (planar or non-planar) bending vibration and, acoordingly, it is surely to be ascribed to the NH_2 bending vibration of the $-CONHNH_2$ group. The corresponding band is observed at 1636 cm^{-1} for CAH in acetonitrile.

The 1313 cm^{-1} band of CAH probably corresponds to the 1044 cm^{-1} band of CAH-d_3 ($\nu_H/\nu_D=1.257$). This is close in frequency to the 1320 cm^{-1} band of solid hydrazine[10]. As was mentioned above, the 1320 cm^{-1} band of solid hydrazine corresponds to the 1275 cm^{-1} band of hydrazine vapor[10], and the latter has been assigned to the NH_2 (non-planar) twisting vibration[14]. Therefore, the 1313 cm^{-1} band of CAH may probably be ascribed to the NH_2 twisting vibration of the $-CONHNH_2$ group. It is further concluded that the NH_2 group of CAH has the non-planar structure, because only such a group has the band near 1 300 cm^{-1} indicated above.

Next, the 1258 cm^{-1} band of CAH is considered to correspond to the 973 cm^{-1} of CAH-d_3 ($\nu_H/\nu_D=1.293$). Its value of frequency lies in the normal 1250∼1300 cm^{-1} range in which the amide III band is usually found for the secondary amides. CAAH[9] has also amide III bands at 1281 and 1235 cm^{-1}. Therefore, the 1258 cm^{-1} band of CAH is undoubtedly to be ascribed to the amide III band. CAH in acetonitrile has also a corresponding band at 1258 cm^{-1}.

The 1105 cm^{-1} band of CAH probably corresponds to the 928 cm^{-1} band of CAH-d_3, the ν_H/ν_D ratio being 1.190. CAH in acetonitrile has a corresponding band at 1122 cm^{-1}. Such a strong band as the 1105 cm^{-1} one may not be observed near 1100 cm^{-1} for CAAH[9] and cyanoacetate acid amide[*1]. It is, therefore, concluded that the 1105 cm^{-1} band is not due to a vibration of the $N{\equiv}C{-}CH_2{-}CO{-}$ group, which is the group contained in CAH, CAAH and cyanoacetic acid amide. In consequence, the 1105 cm^{-1} band has to be due to a vibration of the hydrazine residue. Hydrazine in the vapor state has the bands at 966, 933 cm^{-1} (doublet) and 780 cm^{-1} which have been ascribed[14] to the NH_2 wagging vibrations of different species (B and A) respectively. The bands corresponding to the former have been observed at 1078, 1072 cm^{-1} for solid hydrazine by Giguere and Liu[10]. The 1105 cm^{-1} band of CAH is close in frequency to the 1078, 1072 cm^{-1} bands of solid hydrazine. Therefore, it is probably to be ascribed to the NH_2 wagging vibration of the hydrazine residue.

The band at 1009 cm^{-1} of CAH probably corresponds to the 842 cm^{-1} band of CAH-d_3 ($\nu_H/\nu_D=1.198$) ; it is probably due to an NH_2 deformation vibration (perhaps rocking).

As was mentioned above, it is seen that CAH has four bands ascribed to the NH_2 deformation vibrations. This is not consistent with Yamaguchi's conclusion[14], that the deformation modes of the non-planar NH_2 group are composed of three fundamental vibrations. However, it is of interest to note that four NH_2 deformation frequencies are obtained for other monoacid hydrazides the absorption bands of which will be considered later. In spite of some doubtfulness in the assignments, we can regard these frequencies as characteristic of the $-CONHNH_2$ group.

The $CH_2\langle$ deformation vibrations are probably to be found in this region. For the $CH_2\langle$ deformation frequencies, Nakagawa[17] has proposed the following ranges : 1450∼1350 cm^{-1} for bending, 1350∼1100 cm^{-1} for wagging, 1250∼1000 cm^{-1} for twisting, and 1000∼700 cm^{-1} for rocking. CAH has 1396, 1347, 1205 and 1009[*2] cm^{-1} bands, which are scarcely changed in frequency on *N*-deuteration. CAH-d_3 has corresponding bands at 1397, 1347, 1206 and 1000 cm^{-1}. These four bands lie in the four ranges indicated above ; accordingly, they are ascribed to the CH_2 bending, wagging, twisting and rocking vibrations respectively. The bending and wagging frequencies are not observed for CAH in acetonitrile because of interference due to solvent absorption, but the bands due to the latter two vibrations are found at 1197 and 997 cm^{-1} respectively.

Bands ascribed to the skeletal ($CH_2{-}CO$, $NC{-}CH_2$ and $N{-}N$) stretching vibrations and the $O{=}C{-}N$ deformation vibration (amide IV) are expected to appear in this region. The N–N stretching frequency of 1143 cm^{-1} has been obtained for CAAH[9], but no band corresponding to it is observed for CAH because of its location on the sloping back ground of the much more intense band at 1105 cm^{-1}. On the other hand, CAH-d_3 has a very weak band at 1112 cm^{-1} which is probably to be ascribed to the N–N stretching vibration. Hydrazine[10] absorbs at 1098 cm^{-1} (vapor) and 1124 cm^{-1} (solid). The 1098 cm^{-1} band has been ascribed to the N–N stretching vibration[14]. The corresponding band was observed at 1110 cm^{-1} for HCONDNHCOH[18], at 1165 cm^{-1} for

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[*1] Its infrared absorption spectrum will be published elsewhere.

17) I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 76, 540 (1955).

[*2] It seems probable that this band arises from the NH_2 deformation band overlapping the CH_2 deformation band.

18) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 76, 341 (1955).

TABLE I. INFRARED FREQUENCIES OF CYANOACETYLHYDRAZINE AND ITS *N*-DEUTERATED DERIVATIVE (in cm^{-1})

Assignment	Cyanoacetylhydrazine Solid	Cyanoacetylhydrazine in CH_3CN	Its *N*-deuterated derivative Solid
$\nu_a(NH_2)$	3320 (m)		
$\nu(NH)$, $\nu_s(NH_2)$	3180 (vs)	3320	
	3020 (m)		
	2970 (sh)		
$\nu(CH_2)$	2925 (m)	2910	2930 (w)
	2860 (w)		2870 (w)
	2770 (w)		
$\nu_a(ND_2)$			2510 (m)
$\nu_s(ND_2)$			2430 (sh)
$\nu(ND)$			2380 (vs)
$\nu(C\equiv N)$	2265 (m)	2250	2270 (m)
			2240 (w)
			2200 (w)
			2150 (w)
Amide I	1698 (vs)	1704	1680 (vs)
$\beta(NH_2)$	1625 (s)	1636	
Amide II	1534 (s)	1513	
	1464 (b, w)		
Amide II′			1451 (s)
$\beta(CH_2)$	1396 (m)		1397 (sh)
$\omega(CH_2)$	1347 (s)	1347	1347 (w)
$\tau(NH_2)$	1313 (sh)		1312 (w)
Amide III	1258 (m)	1258	
$\tau(CH_2)$	1205 (w)	1197	1206 (m)
$\beta(ND_2)$			1192 (m)
$\omega(NH_2)$?	1105 (s)	1122	
$\nu(N\text{-}N)$			1112 (vw)
			1069 (sh)
$\tau(ND_2)$			1044 (m)
$\gamma(NH_2)$?, $\gamma(CH_2)$	1009 (s)	997	1000 (m)
Amide III′			973 (m)
$\omega(ND_2)$?			928 (s)
	932 (w)	935	
$\nu(C\text{-}C)$	924 (s)	920	912 (sh)
	913 (s)	892	892 (sh)
$\gamma(ND_2)$			857, 842 (w)
Amide IV	738 (s)		772 (s)
	723 (sh)		729 (sh)

ν; stretching; a, asymmetric; s, symmetric; β, bending; τ, twisting; ω, wagging; γ, rocking

$(CH_3CONH\text{–})_2\cdot H_2O$[19] and at 1133 cm^{-1} for formyl-acetylhydrazine[9].

CAH has bands at 932 (w), 924 (s), 913 (s), 738 (s) and 723 (sh) cm^{-1} not yet accounted for. CAH-d_3 also has four bands at 912 (sh), 892 (sh), 772 (s) and 729 (sh) cm^{-1}. Of these, the bands near 900 cm^{-1} are probably due to the C–C stretching vibrations and a band near 750 cm^{-1} can be assigned to amide IV, although their detailed assignments are not easy.

The infrared frequencies of CAH and their tentative assignments are summarised in Table I.

Formylhydrazine (FH).—The infrared spectra of FH in the solid state and in acetonitrile are illustrated in Fig. 2. Although the spectrum of *N*-deuterated FH could not be observed*[3], absorption bands of FH were interpreted without much difficulty by comparing the spectrum with those of diformylhydrazine (DFH)[18], formamide(FA)[20]and *N*-methylformamide (MFA)[21]. The infrared frequencies of DFH, FA and MFA have reasonably been explained with a model of a trans-planar configuration of the HCONH– group. Therefore, it will be assumed that an FH molecule also contains such a planar HCONH– group. This assumption is supported by the fact that FH has six bands very close in frequency to the bands of DFH; accordingly, these bands are immediately assigned to vibrational modes of the HCONH– group, as is indicated in Table II (upper part).

The amide I absorption will be shown near 1600 cm^{-1} because DFH has a band at 1610 cm^{-1}. FH in the solid state has a very strong band at 1674 cm^{-1} which corresponds to the band at 1689 cm^{-1} of FH in acetonitrile. The value of 1674 cm^{-1} is rather higher than that of the amide I band of DFH, but it is surely taken to be an amide I band because MFA in the solid state also has a band at 1672 cm^{-1}[21].

DFH[18] has a 3100 cm^{-1} band ascribed to the NH stretching vibration. In this region, FH in the solid state shows very intense and broad absorption with a maximum near 3210 cm^{-1}, while FH in acetonitrile has the band at 3330 cm^{-1}. FA[20] in the solide state also has a broad and strong band near 3250 cm^{-1}, which has been ascribed to the NH_2 assym. or sym. stretching vibration. The rock salt optics employed are not suitable for measurements in this region because of low resolution, but it is seen that the band near 3210 cm^{-1} of solid FH is really composed of three bands, i. e., it is accompanied by a shoulder band which could not be defined on both the high- and low-frequencies sides. Therefore, these bands are due to the NH_2 and NH stretching vibrations.

The out-of-plane CH deformation vibration may also be located in the region examined here. No band corresponding to it has been observed for DFH[18], but its sodium salt[22] has

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[19] A. Yamaguchi, ibid., 79, 880 (1958).

*[3] *N*-Deuterated FH could not be prepared by the usual exchange reaction.

[20] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **76**, 821 (1955).

[21] T. Miyazawa, ibid., **77**, 321, 619 (1956); see also I. Suzuki, This Bulletin, **35**, 540 (1962).

[22] M. Mashima, ibid., **35**, 338 (1962).

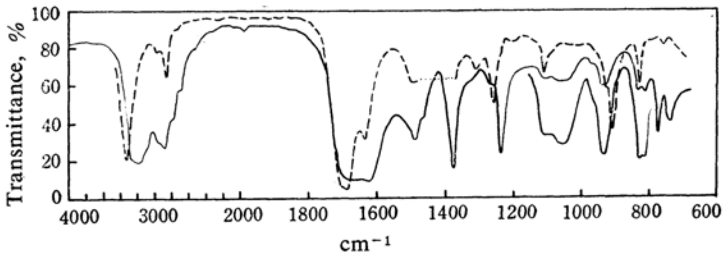

Fig. 2. Infrared spectra of formylhydrazine in the solid state (solid curve) and in the CH_3CN solution (dashed curve).

TABLE II. INFRARED FREQUENCIES OF FORMYLHYDRAZINE (in cm^{-1})

Assignment	DFH[a] Solid	DFH-d_2[a] Solid	FH Solid	FH in CH_3CN
ν(CH)	2900	2920	2880 (s)	2860 (w)
Amide II	1480	1338	1488 (m)	—[b]
δ(CH)	1368	1389	1373 (s)	—[b]
Amide III (III')	1229	985	1233 (s)	1255 (m)
π(NH)	770	—	772 (m)	
Amide IV	753	751	737 (m)	753 (vw)
ν(NH) or $\nu(NH_2)$	3100		3210 (vs)	3330 (s)
			2790 (sh)	
			2700 (sh)	
Amide I	1610	1605	1674 (vs)	1689 (vs)
$\beta(NH_2)$			1632 (vs)	1635 (m)
			1463 (sh)	
NH_2 deformation			1262 (vw)	1305 (w)
NH_2 deformation			1104 (vw)	1106 (w)
π(CH)			1050 (w)	
ν(N–N) ?			927 (w)	921 (w)
				907 (m)
NH_2 deformation			826 (w)	826 (w)
			807	

ν, stretching; δ, in-plane deformation; π, out-of-plane deformation; β, bending

a See Ref. 18

b Could not observe because of interference due to solvent absorption

a band at 1026 cm⁻¹. FA[20)] and MFA[21)] in the solid states have a CH band at 1060 cm⁻¹ and 1015 cm⁻¹ respectively. In this region FH has a weak band at 1050 cm⁻¹ which is probably to be ascribed to the out-of-plane CH deformation vibration.

Let us now consider the location of the NH_2 deformation vibrations and the N–N stretching vibration of the hydrazine residue. Solid FH has a strong band at 1632 cm⁻¹ which is very close in frequency to the 1625 cm⁻¹ band (ascribed to the NH_2 bending vibration) of CAH. FH in acetonitrile has a corresponding band at 1635 cm⁻¹. Thus, the 1632 cm⁻¹ band may be ascribed to the bending vibration.

The infrared frequencies of FA have been reasonably explained[20)] by use of the model of the planar structure of the $-CONH_2$ group; the compound shows the NH_2 deformation frequencies as follows: 1610 cm⁻¹ (bending), 1110 cm⁻¹ (rocking), and 800 cm⁻¹ (wagging). As has been indicated already, CAH has the end group $-NH_2$, being non-planar in structure, and it has four bands, 1625, 1347, 1105 and 1009 cm⁻¹, due to the NH_2 deformation vibrations. FH has several weak or shoulder bands not yet accounted for. Of these, the very weak band at 1262 cm⁻¹ is expected to be due to a fundamental vibrational mode because the band corresponding to it is observed at 1305 cm⁻¹ for FH in acetonitrile. This band probably corresponds to the 1347 cm⁻¹ band of CAH; it will be ascribed to the NH_2 deformation vibration. Two further bands at 1104 and 927 cm⁻¹ and the doublet band (826, 807 cm⁻¹) have their respective counterparts in the solution spectrum as represented in Table II. Of these three, the 1104 cm⁻¹ band and the doublet

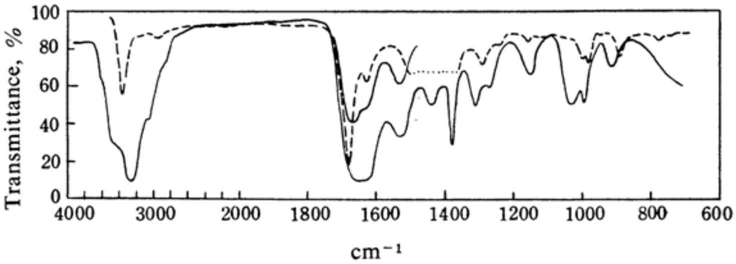

Fig. 3. Infrared spectra of acetylhydrazine in the solid state (solid curve) and in the CH_3CN solution (dashed curve).

band are very close in frequency to the 1110 cm⁻¹ (NH_2 rocking) and 800 cm⁻¹ (NH_2 wagging) bands of FH respectively. These two bands are probably to be ascribed to the NH_2 deformation vibratios and the band at 927 cm⁻¹, to the N–N stretching vibration, but these assignments, of course, are not certain.

The infrared frequencies of FH and their tentative assignments are summarized in Table II, in which the frequencies of DFH are also indicated for the sake of comparison.

Acetyl-, Propionyl-, *n*-Butyryl- and Isovalerylhydrazine. — The infrared spectra of acetylhydrazine (AH) in the solid state and in the acetonitrile solution are illustrated in Fig. 3. The spectrum of its *N*-deuterated species could not be observed*4, but the absorption bands of AH were interpreted by a comparison of the spectrum with those of diacetylhydrazine19), *N*-methylacetamide23) and cyanoacetylhydrazine. The infrared frequencies of AH and their tentative assignments are summarized in Table III.

TABLE III. INFRARED FREQUENCIES OF AH (in cm⁻¹)

Assignment	$CH_3CONHNH_2$	
	Solid	in CH_3CN
$\nu(NH_2)$ or $\nu(NH)$	3420 (sh)	
	3270 (vs)	3360 (s)
	3050 (sh)	
	2860 (w)	
Amide I	1673 (vs)	1684 (vs)
$\beta(NH_2)$	1633 (sh)	1633 (m)
Amide II	1535 (s)	
$\delta_a(CH_3)$	1443 (b, m)	
$\delta_s(CH_3)$	1382 (s)	
Amide III or	1316 (m)	1295 (m)
NH_2 deformation	1276 (sh)	
NH_2 deformation	1154 (m)	1163 (w)
NH_2 deformation	1034 (m)	998 (m)
$\gamma(CH_3)$	994 (m)	986 (m)
$\nu(C-CH_3)$	909 (m)	894 (m)
		780 (w)

ν, stretching; β, bending; δ, deformation; γ, rocking; a, asymmetric; s, symmetric

In the solid state, AH has a very strong band at 3270 cm⁻¹, which is accompanied by two shoulder bands at 3420 and 3050 cm⁻¹. These bands are probably to be ascribed to the NH_2 or NH stretching vibrations. The band corresponding to them is found at 3360 cm⁻¹ for AH in acetonitrile.

The very strong band at 1673 cm⁻¹ of solid AH corresponds to the 1684 cm⁻¹ band of AH in acetonitrile; it may surely be taken as an amide I band. The band at 1535 cm⁻¹ is easily taken as an amide II band. Further, it is expected that an amide III band will appear near 1300 cm⁻¹. Solid AH has two bands at 1316 and 1276 cm⁻¹. They will correspond to the band at 1295 cm⁻¹ of AH in acetonitrile. An amide III band has been obtained at 1261 cm⁻¹ for diacetylhydrazine19), 1258 cm⁻¹ for cyanoacetylhydrazine and 1312 cm⁻¹ for *N*-methylacetamide23). Therefore, one of the two bands, 1316 and 1276 cm⁻¹, is probably to be taken as an amide III band.

AH in the solid state has two bands at 1443 and 1382 cm⁻¹. They may surely be ascribed to the CH_3 asym. and sym. deformation vibrations, for the corresponding bands have been found at 1433 and 1368 cm⁻¹ for solid diacetylhydrazine19) and at 1413 and 1373 cm⁻¹ for *N*-methylacetamide23) in the carbon tetrachloride solution.

The CH_3 rocking and C–CH_3 stretching vibrations may be located without difficulty in the spectrum of AH. *N*-Methylacetamide23) in carbon tetrachloride has two bands, at 1040 and 987 cm⁻¹, which have been ascribed to the CH_3 rocking vibrations. They correspond to the bands at 1050 and 1001 cm⁻¹ for solid *N*-methylacetamide23). The compound has, further, a C–CH_3 stretching band at 881 cm⁻¹ in carbon tetrachloride solution and at 892 cm⁻¹ in the solid state23). Diacetylhydrazine19) also has

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*4 *N*-Deuterated acetylhydrazine could not be prepared by the usual exchange reaction.

23) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958); see also T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 171, 321, 619 (1956).

CH_3 rocking bands at 1029 and 1019 cm^{-1} and a C–CH_3 stretching band at 921 cm^{-1}. In the region of 1100~800 cm^{-1}, solid AH has three bands at 1034, 994 and 909 cm^{-1}; bands corresponding to them are found at 998, 986 and 894 cm^{-1} respectively for AH in acetonitrile. The value of 909 cm^{-1} is considered to be basis enough for ascribing the band to the C–CH_3 stretching vibration, because in the solid state *N*-methylacetamide and diformylhydrazine have the C–CH_3 stretching band at 892 and 921 cm^{-1} respectively, as has been mentioned above. This assignment is also supported by the fact that a similar frequency shift in the change of states is seen between the 909 cm^{-1} band of AH and the C–CH_3 stretching band at 892 cm^{-1} of solid *N*-methylacetamide. Two other bands, 1034 and 994 cm^{-1}, may be interpreted as follows: if the 1034 cm^{-1} band of solid AH corresponds to the 998 cm^{-1} band of the compound in solution, the value of the frequency shift is 36 cm^{-1}, which value is relatively larger than that of the CH_3 rocking vibration of *N*-methylacetamide. On the other hand, the 994 cm^{-1} band of solid AH is, in the value of frequency, 8 cm^{-1} larger than its 986 cm^{-1} band in solution. This value of the frequency shift is in accordance with that of the CH_3 rocking bands of *N*-methylacetamide. In consequence, the 994 cm^{-1} band of AH is ascribed to the CH_3 rocking vibration and the 1034 cm^{-1} band is due to another vibrational mode.

TABLE IV. INFRARED FREQUENCIES OF PROPIONYL-, *n*-BUTYRYL- AND ISOVALERYLHYDRAZINE (in cm^{-1})

$CH_3CH_2\cdot CONHNH_2$ Solid (KBr disk)	$CH_3CH_2CH_2\cdot CONHNH_2$ Solid (KBr disk)	$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CHCH_2\cdot CONHNH_2$ Solid (KBr disk)
3250 (vs)	3230 (vs)	3300 (vs)
	3160 (sh)	3190 (m)
3030 (m)	3000 (m)	3050 (w)
2965 (m)	2920 (s)	2950 (s)
2880 (sh)	2840 (m)	2875 (w)
1640 (b, vs)	1645 (b, vs)	1682 (sh)
		1632 (vs)
1523 (s)	1532 (s)	1542 (s)
1464 (m)	1467 (m)	1473 (m)
1436 (sh)	1439 (sh)	1441 (w)
		1392 (sh)
1374 (m)	1380 (m)	1378 (s)
		1337 (sh)
	1331 (m)	1321 (m)
1280 (m)	1288 (m)	
1242 (m)	1261 (m)	1269 (w)
	1222 (m)	1226 (m)
1150 (w)	1158 (m)	1159 (sh)
		1124 (vw)
	1085 (b, m)	1087 (m)
	1055 (w)	
1067 (m)	1044 (m)	
1027 (m)	1016 (s)	1017 (s)
		998 (sh)
954 (s)	932 (b, m)	955 (m)
		933 (m)
899 (w)	898 (w)	887 (m)
	877 (sh)	
801 (w)	806 (vw)	837 (m)
	772 (vw)	762 (w)
	748 (w)	
	696 (w)	

Solid AH has four more bands, at 1633, 1316 (or 1276), 1154 and 1034 cm^{-1}, not yet acounted for. These four bands correspond, respectively, to the bands at 1625, 1347, 1105 and 1009 cm^{-1} of cyanoacetylhydrazine. The 1633 cm^{-1} band is surely to be ascribed to the NH_2 bending vibration, while the latter three bands are due to the NH_2 deformation vibrations.

Let us next consider the absorption spectra of propionyl-, *n*-butyryl- and isovaleryl-hydrazine. They are illustrated in Fig. 4, in which the spectra of corresponding symmetric diacid

TABLE V. INFRARED FREQUENCIES CHARACTERISTIC TO THE GROUP –$CONHNH_2$ (in cm^{-1})

Assignment	H-X[a]	CH_3-X	$CNCH_2$-X	CH_3CH_2-X	$CH_3CH_2CH_2$-X	$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CHCH_2$-X
NH_2 or NH stretching	3210	3270	3320 3180	3250	3230	3300
Amide I	1674	1673	1698			1682
				1640[b]	1645[b]	
NH_2 bending	1632	1633	1625			1632
Amide II	1488	1535	1534	1523	1532	1542
NH_2 deformation	1262	1316	1313	1280	1331	1321
Amide III	1233	1276	1258	1242	1288	1269
NH_2 deformation	1050	1154	1105	1150	1158	1159
NH_2 deformation	826 807	1034	1009	954	1006	1017

a X is the group –$CONHNH_2$

b Observed the very strong band with a center near those

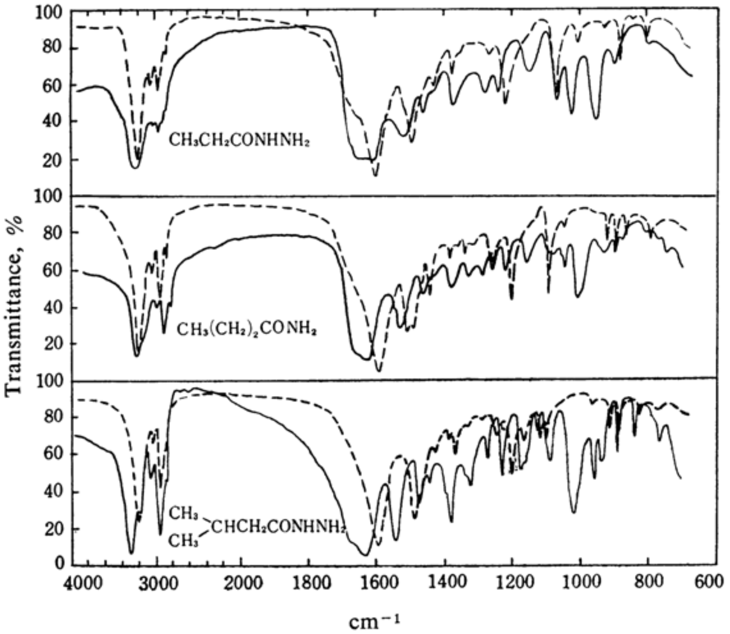

Fig. 4. Infrared spectra of the monoacid hydrazides being indicated (in KBr disks). Solid curves show the spectra of the monoacid hydrazides and dashed curves show the spectra (represented for comparison) of the corresponding diacid hydrazides.

hydrazides are represented for purposes of comparison; the infrared frequencies of these monoacid hydrazides are summarized in Table IV.

All of these hydrazides have a very strong band near 3250 cm^{-1}, which may be ascribed to the NH_2 or NH stretching vibrations. In the 1630~1680 cm^{-1} range, these hydrazides are expected to have an amide I band and a band due to the NH_2 bending vibration. These two bands are not separated from each other for propionyl- and *n*-butyrylhydrazine; i. e., they have a very broad and strong band with a center near 1640 cm^{-1}. On the other hand, isovalerylhydrazine has a very strong band at 1632 cm^{-1} which is accompanied with a shoulder band at 1682 cm^{-1}; these two bands are taken, respectively, as a band due to the NH_2 bending vibration and an amide I band. In the region below 1350 cm^{-1}, the spectral patterns of these hydrazides are rather complex, but we can find four bands corresponding to the 1316, 1276, 1154 and 1034 cm^{-1} bands of AH. They are summarized, with other frequencies characteristic of the $-CONHNH_2$ group, in Table V.

Characteristic Frequencies.—As may be seen from Table V, the frequencies characteristic of the $-CONHNH_2$ group were obtained as follows: 1) An amide I band is found near 1670 cm^{-1} for the monoacid hydrazides when examined in the solid state. 2) An amide II band is also shown near 1530 cm^{-1}. 3) All the monoacid hydrazides examined here have a band near 1630 cm^{-1} ascribed to the NH_2 bending vibration. 4) In the region below 1350 cm^{-1}, these hydrazides have four bands which may also be taken as bands characteristic of the $-CONHNH_2$ group. Of these four, one band near 1250 cm^{-1} is probably to be taken as an amide III band. However, the detailed assignment of these four bands is difficult on the basis of the present observations only. The present author plans to examine the infrared absorptions for other monoacid hydrazides and related compounds. 5) A strong band due to the NH_2 or NH stretching vibrations is found near 3250 cm^{-1}.

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