Infrared Absorption Spectra of Hydrazides.
III. Hydrazides of Aliphatic Acids

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In a previous paper[1] the amide frequencies characteristic of the hydrazides of aromatic acids were discussed, and for the ion (RCONHNCOR')$^-$ [2] amide I, II and III bands were observed within the normal frequency ranges for secondary amides. The present investigation was undertaken to determine the characteristic frequencies of the hydrazides of aliphatic acids. Solid spectra of diformylhydrazine and its *N*-deuterated derivative[3] of diacetylhydrazine, its mono-hydrate, and of their deuterated derivatives[4] have already been published. For the present study, the spectra of dipropionylhydrazine, dibutyrylhydrazine, diisovalerylhydrazine, formyl-acetylhydrazine, and cyanoacetyl-acetylhydrazine were examined in the solid state and in solution. The solution spectrum of diacetylhydrazine was also observed, diformylhydrazine in solution could not, however, be examined because of its sparing solubilities in solvents suitable to observation in infrared spectra.

Experimental

Dipropionylhydrazine was prepared with propionic anhydride and hydrazine hydrate[5] and was purified by recrystallization from benzene, m. p. 136°C. Dibutyrylhydrazine was synthesized by the reaction of butyrylhydrazine with iodine in ethanol[6] and was purified by recrystallization from benzene, m. p. 163°C. Diisovalerylhydrazine was synthesized with isovalerylhydrazine and iodine in ethanol[7] and was purified by recrystallization from benzene, m. p. 180°C. Formyl-acetylhydrazine was synthesized with formylhydrazine and acetic anhydride[8]

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[1] M. Mashima, This Bulletin, **35**, 338 (1962).

[2] M. Mashima, ibid., **35**, 332 (1962).

[3] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956); also see T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 341 (1955).

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

[5] T. Curtius and H. Hille, *J. prakt. Chem.*, [2] **64**, 406 (1901).

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

[7] T. Curtius and H. Hille, ibid., [2] **64**, 414 (1901).

[8] G. Heller, ibid., [2] **120**, 60 (1929).

and was purified by recrystallization from ethanol, m. p. 96°C. Cyanoacetyl-acetylhydrazine was synthesized with cyanoacetylhydrazine and acetic anhydride⁹⁾ and was purified by recrystallization from ethanol, m. p. 171°C. The synthesis of diacetylhydrazine has been described previously²⁾. The method of preparation of compounds containing deuterium was similar to that described previously¹⁾. Solution spectra were obtained in acetonitrile with cells of 0.1 mm. in optical path, and solid spectra were studied in potassium bromide disk with a Hitachi infrared spectrophotometer EPI-2 in the rock salt region.

Results and Discussion

Solid Spectra.—*Symmetric Hydrazides.*—The solid spectra of dipropionylhydrazine (DPH), dibutyrylhydrazine (DBuH), and diisovalerylhydrazine (DIVH) are shown in Fig. 1, in which the solid spectrum of diacetylhydrazine (DAH) is also represented for purposes of comparison. Let us consider mainly the N–H stretching band and the amide I, amide II and amide III bands because they may be characteristic of the hydrazides.

By comparison of the spectra with those of diformylhydrazine (DFH)³⁾ and DAH⁴⁾, the following assignments are possible:

All of these hydrazides have a very intense band near 3200 cm^{-1} which is easily assigned to the N–H stretching vibration ν(N–H) and a rather weak band near 3030 cm^{-1} which is also attributed to ν(N–H). The assignment of the former was confirmed by *N*-deuteration; e. g., *N*-deuterated DPH has a band at 2380 cm^{-1} which corresponds to the 3200 cm^{-1} band of DPH, the ratio ν_H/ν_D being 1.34. The latter disappears from the solution spectra, as is indicated in a following section. Therefore, it is probably also associated with ν(N–H).

The symmetric hydrazides have the most intense band among their absorption bands near 1600 cm^{-1}. The amide I band was found at 1610 cm^{-1} for DFH³⁾ and at 1598 cm^{-1} for

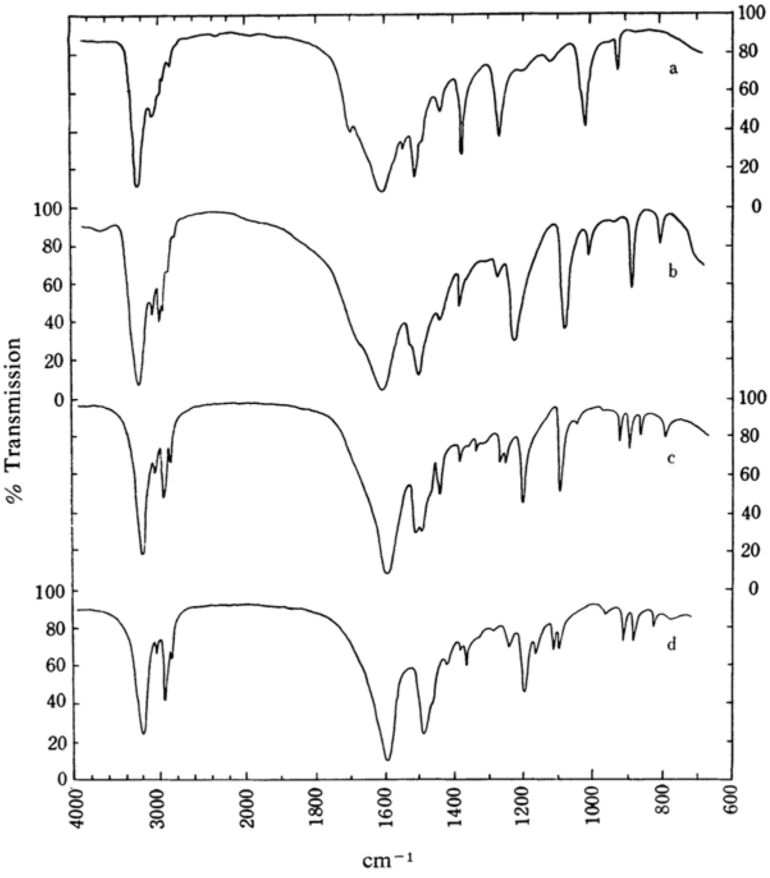

Fig. 1. Infrared spectra of the symmetric hydrazides in KBr disk.
a; DAH, b; DPH, c; DBuH, d; DIVH

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9) V. Rothenburg, *Ber.*, **27**, 688 (1894).

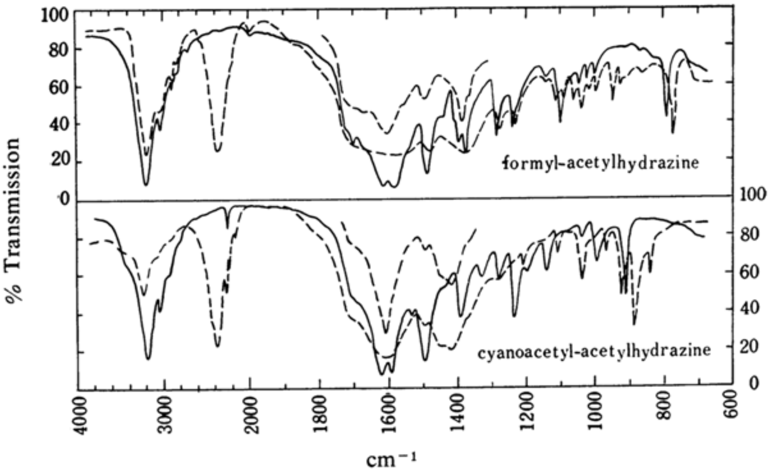

Fig. 2. Infrared spectra of asymmetric hydrazides in KBr disk. Solid curves show the spectra of hydrazides and dashed curves indicate the spectra of *N*-deuterated derivatives.

DAH*. Thus, the band near 1600 cm^{-1} is assigned to the amide I band.

The amide II band is observed near 1500 cm^{-1} for these hydrazides. A corresponding band was found at 1414 cm^{-1} for *N*-deuterated DPH, the ratio ν_H/ν_D being 1492/1414 (1.055). The value is close to 1.106 for DFH[3] and to 1.065 for DAH[4].

For hydrazides of aromatic acids[1] the amide III band was found in the normal range of secondary amides, and it split into two bands. However, no such splitting can be observed for the symmetric hydrazides of aliphatic acids; only a single amide III band is found near 1200 cm^{-1}. For *N*-deuterated DPH a corresponding band is found at 928 cm^{-1}, the ratio ν_H/ν_D being 1217/928 (1.311). The value of ν_H/ν_D is close to 1.248 for DFH[3] and to 1.333 for DAH[4].

Formyl-acetylhydrazine (FAH) and Cyanoacetyl-acetylhydrazine (CAH).—The solid spectra of FAH, CAH, and their *N*-deuterated derivatives are illustrated in Fig. 2. In the 3000 cm^{-1} region a strong band is found at 3200 cm^{-1} for FAH and at 3190 cm^{-1} for CAH. A corresponding band is found at 2380 cm^{-1} for *N*-deuterated FAH and at 2370 cm^{-1} for *N*-deuterated CAH, the values of ν_H/ν_D being 1.344 and 1.346 respectively. These bands are easily assigned to ν(N–H) by comparison of the values of frepuency and ν_H/ν_D with those of the symmetric hydrazides indicated in the foregoing section. The main band near 3200 cm^{-1} is accompanied by several shoulder bands in the spectra of FAH and CAH indicated in Fig. 2 and of DAH indicated in Fig. 1. A well-defined shoulder is found at 3020 cm^{-1} for FAH, at 3050 cm^{-1} for CAH, and at 3060 cm^{-1} for DAH. No corresponding band is found in the solution spectra, as is indicated in a following section. In consequence, the shoulder band near 3050 cm^{-1} is probably due to ν(N–H). Other shoulder bands can probably be ascribed to the C–H stretching vibrations, but we can not assign the individual shoulder band with confidence because of the complexity and the rather weak intensity of the absorption bands.

We will next consider the amide bands. DAH has a very strong band at 1598 cm^{-1} which has been ascribed to the amide I band by Yamaguchi[4], while two corresponding bands are found at 1613 and 1580 cm^{-1} for FAH and at 1623 and 1593 cm^{-1} for CAH. Both bands can undoubtedly be assigned to the amide I because they are in good agreement with the band of DAH in frequency. Yamaguchi[4] observed the solid spectra of diacetylhydrazine monohydrate and ascribed a single band at 1661 cm^{-1} to an amide I band. On the other hand, similar doublets have been observed for hydrazides of aromatic acids[1], and a further consideration will be represented later on. *N*-Deuterated FAH and *N*-deuterated CAH have only a single band at 1604 cm^{-1} and 1607 cm^{-1} respectively, both of which bands correspond to the amide I band.

FAH and CAH have amide II bands at 1483 cm^{-1} and at 1497 cm^{-1} respectively. The values of these frequencies are very close to the 1506 cm^{-1} of DAH and the 1480 cm^{-1} of DFH[3]. The assignments of these bands were confirmed by *N*-deuteration; i. e., *N*-deuterated FAH has a corresponding band at 1383 cm^{-1},

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* Yamaguchi (Ref. 4) obtained the band at 1597 cm^{-1} for DAH in Nujol.

the ratio of ν_H/ν_D being 1.072, and *N*-deuterated CAH has a band at 1413 cm^{-1}, the ratio being 1.059. These values of ν_H/ν_D are very close to those of the symmetric hydrazides indicated in the previous section, i. e., 1.106 for DFH, 1.065 for DAH, and 1.055 for DPH.

DAH has only a single amide III band at 1260 cm^{-1}, but FAH has two corresponding bands at 1279 and 1232 cm^{-1} and CAH has two bands at 1281 and 1235 cm^{-1}. The assignment of these two bands is confirmed by the finding of corresponding bands at 946 and 924 cm^{-1} for *N*-deuterated FAH and at 962 and 918 cm^{-1} for *N*-deuterated CAH. The values of the ratio ν_H/ν_D are 1.352, 1.333 for the two bands of FAH and 1.345, 1.342 for CAH.

Vibrations relating to the CH_3, CH_2 and CH groups are also to be associated with bands in the rock salt region. The C–H stretching bands have been discussed already. Bands due to CH_3, CH_2 and CH deformation vibrations are expected to appear in the region 1450∼1350 cm^{-1}. DAH has a $\delta_a(CH_3)$ band at 1430 cm^{-1} and a $\delta_s(CH_3)$ band at 1365 cm^{-1}, and DFH[3)] has a δ(CH) band at 1368 cm^{-1}. CAH has bands at 1448, 1392, and 1331 cm^{-1}, of which the first band is assigned to $\delta_a(CH_3)$ or $\delta(CH_2)$; the second one can be ascribed to $\delta_a(CH_3)$, while the last band might possibly be due to CH_3 or CH_2 deformation vibration. In this region FAH has three bands at 1441, 1390 and 1372 cm^{-1}, of which the 1441 cm^{-1} band is easily assigned to $\delta_a(CH_3)$, while the other two bands are probably due to either $\delta_s(CH_3)$ or δ(CH). These deformation bands can not be determined in the spectra of *N*-deuterated derivatives of CAH and FAH because of the overlap of the amide II band.

Rocking vibrations of the CH_3 and CH_2 groups can also concern bands which are ordinarily shown in the range of 1200∼800 cm^{-1}. DAH has rocking CH_3 bands at 1027 and 1016 cm^{-1} **. CAH has two bands at 1041 and 996 cm^{-1} which can probably be ascribed to the rocking CH_3 or CH_2 vibrations. For *N*-deuterated CAH, corresponding bands are found at 1103 and 1030 cm^{-1}. In this region FAH has a relatively intense band at 1093 cm^{-1} and three weaker bands at 1038, 1018 and 995 cm^{-1}. *N*-Deuterated FAH has six rather weak corresponding bands. C–H out-of-plane deformation vibrations are also to be related to one of them. For sodium diformylhydrazine[2)], two bands due to the out-of-plane deformation vibrations have been obtained at 1026 and 974 cm^{-1}. In consequence, the four bands of FAH can not definitely be assigned, but it is sure that they are due to either the CH_3 rocking or the CH out-of-plane deformation vibrations.

An in-plane bending O=C–N band has been obtained at 753 cm^{-1} for DFH[3)]. The 784 cm^{-1} band of FAH is also probably due to δ(O=C–N). The corresponding band of *N*-deuterated FAH is observed at 769 cm^{-1}. Further, DFH[3)] has the out-of-plane bending N–H band at 770 cm^{-1}, while no band corresponding to it is observed for FAH. In the region examined, neither the δ(O=C–N) nor the π(N–H) is observed for CAH.

On the other hand, DAH has the 921 cm^{-1} band which is to be ascribed to the C–CH_3 stretching vibration[4)]. No corresponding band for FAH is observed, while CAH has the 914 cm^{-1} band which is assigned to ν(C–CH_3),

Table I. Infrared frequencies of FAH and CAH in the rock salt region (in cm^{-1})

Assignment[a]	DFH[b]	DAH[c]	FAH	CAH
ν(N–H)	3100	3210	3200	3190
		3060	3020	3050
ν(C–H)	2900	2980		2970
		2930	2910	
		2860	2860	
			2720	
ν(C≡N)				2270
		1695	1702	1710
			1669	
Amide I	1610	1598	1613	1623
			1580	1593
		1538		1538
Amide II	1480	1506	1483	1497
$\delta_a(CH_3)$		1430	1441	1448
$\delta(CH_2)$				
δ(C–H)	1368		1390	1392
$\delta_s(CH_3)$		1365	1372	1331?
Amide III	1229	1260	1279	1281
			1232	1235
		1195		1200
ν(N–N)			1133	1143
		1112		
r(CH_3)		1027	1093	
		1016	1038	1041
r(CH_2)			1018	996
π(C–H)			995	
ν(C–CH_3)		921		914
π(N–H)	770			
δ(C=O–N)	753		784	

a ν : stretching, δ : deformation, r : rocking, π : out-of-plane deformation, a : asymmetrical, s : symmetrical

b See Ref. 3

c See Footnote 10

** These two bands correspond respectively to the bands at 1029 and 1019 cm^{-1} obtained by Yamaguchi (see Ref. 4).

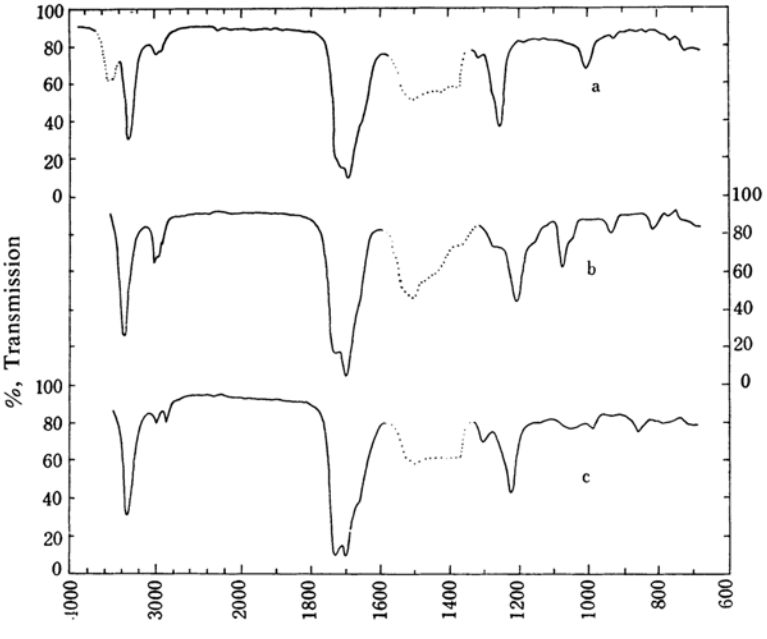

Fig. 3. Infrared spectra of the hydrazides in acetonitrile (0.1 mm. cell). a; DAH (0.1 mol./l.), b; DPH (0.2 mol./l.), c; FAH (0.2 mol./l.)

and the corresponding band of *N*-deuterated CAH is found at 881 cm^{-1}.

CAH has a further band at 2270 cm^{-1} which can possibly be assigned to the stretching C≡N vibration because the frequency hardly changes on *N*-deuteration.

DAH has four bands at 1695, 1538, 1195 and 1112 cm^{-1}, none of which was interpreted by Yamaguchi[4]. The corresponding bands of CAH are found at 1710, 1538, 1200 and 1143 cm^{-1} respectively. Of these four bands, the one near 1700 cm^{-1} is also found for FAH; it may, therefore, be a combination band involving low frequency fundamentals. The 1538, 1195 and 1112 cm^{-1} bands of DAH might also be similar combination bands. However, FAH has a weak band at 1133 cm^{-1} which corresponds to the 1143 cm^{-1} band of CAH. A band at 1100 cm^{-1} of $HCONDNHCOCH_3$[3] and the one at 1165 cm^{-1} of $(CH_3CONH-)_2\cdot H_2O$[4] were ascribed to the N–N stretching vibration. In consequence, the 1143 cm^{-1} band of CAH and the 1133 cm^{-1} band of FAH may possibly be ν(N–N). A corresponding band of *N*-deuterated CAH is not observed, while for *N*-deuterated FAH a band is found at 1143 cm^{-1}.

The observed frequencies of FAH and CAH and their assignments are summarized, with those of DFH[3] and DAH[10], in Table I.

Solution Spectra.—The solution spectra of DPH, DAH and FAH are illustrated in Fig. 3 because they are typical.

All the hydrazides examined have a band near 3300 cm^{-1} which is probably due to a monomeric ν(N–H). Further, the hydrazides generally have the amide I band near 1690 cm^{-1} and a well-defined shoulder band on the high-frequency side. However, only FAH has two bands of nearly the same intensity. In spite of this, they are easily assigned to the amide I band, but further consideration will be given to the problem in a following section. The amide II band may not be observed in the solution spectra because of interference by solvent absorption. A band near 1200 cm^{-1} can be assigned to the amide III band because the frequencies are very close to the amide III band of the hydrazides in the solid state.

Characteristic Bands.—The N–H stretching and amide frequencies of the hydrazides of aliphatic acids and *N*-methyl acetamide are summarized in Table II.

In the solid state, simple *N*-mono-substituted amides show a very strong band (amide I) in the range 1680∼1630 cm^{-1}, a strong band (amide II) in the range 1570∼1515 cm^{-1} and a relatively weaker band (amide III) in the range 1305∼1200 cm^{-1} [11]. Sodium hydrazides[2] with only one CONH group showed the amide I band in the normal range of secondary amides. The decrease in the

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[10] For this compound the values of frequencies are obtained in the present study although their assignments depend on the work by Yamaguchi (see Ref. 2).

TABLE II ν(N-H) AND AMIDE FREQUENCIES IN cm^{-1}.

Molecules and State		ν(N-H)	Amide I	Amide II[a]	Amide III
$(HCONH-)_2$	Solid[b]	3100	1605	1480	1229
$(CH_3CONH-)_2$	Solid	3210, 3060	1598	1506	1260
in CH_3CN (ca. 0.1 M)		3320	1699, 1683	—	1234
$(C_2H_5CONH-)_2$	Solid	3200, 3030	1600	1492	1217
in CH_3CN (ca. 0.2 M)		3310	1718, 1690	—	1197
$(C_3H_7CONH-)_2$	Solid	3190, 3040	1593	1499[c]	1202
in CH_3CN (saturated)		3330	1723, 1693	—	—[d]
$(C_4H_9CONH-)_2$	Solid	3210, 3040	1598	1492	1204
in CH_3CN (saturated)		3330	1720, 1691	—	—[d]
$HCONHNHCOCH_3$	Solid	3200, 3020	1613, 1580	1483	1279, 1232
in CH_3CN (ca. 0.2 M)		3310	1731, 1698	—	1222
$CNCH_2CONHNHCOCH_3$	Solid	3190, 3050	1623, 1593	1497	1281, 1235
in CH_3CN (ca. 0.2 M)		3310	1737, 1707	—	—[d]
$CH_3CONHCH_3$	Solid[b]		1653	1566	1301
in CH_3CN (0.47 M)[e]		3398	1676[f]	1547	1286

a) In solutions this band could not be observed because of interference by solvent absorption.
b) See Ref. 2
c) This is a mean value of the frequencies of two peaks at 1507 and 1491 cm^{-1}.
d) These were too weak to detect.
e) See Ref. 12
f) This is the value in a solution of 0.116 mol./l.

frequency of the amide I band may be characteristic of the hydrazides of aliphatic acids since all the hydrazides have this near 1600 cm^{-1} in the solid state. In a dilute solution the secondary amides show the amide I absorption in the range $1700\sim1670\ \text{cm}^{-1}$ 11). The hydrazides examined here have two amide I bands in acetonitrile. Thus, it may be expected that these two bands come from the coupling of two vibrations which are localized mainly on the C=O groups, as was pointed out for the hydrazides of aromatic acids in a previous paper1). Moreover, it is noteworthy that in the solution spectra the amide I band is shown at frequencies higher by ca. 100 cm^{-1} than that in the solid spectra. This fact was not seen for the secondary amides; e. g., *N*-methyl acetamide in an acetonitrile solution has an amide I band higher in frequency by ca. 20 cm^{-1} than that in the solid state.

The amide II band of the hydrazides examined here may also be characteristic. In the solid state the hydrazides have their amide II bands at ca. 1500 cm^{-1}, somewhat lower in frequency than those of secondary amides.

The amide III frequency of the hydrazides in the solid state lies near the lower limit of the normal range of $1305\sim1200\ \text{cm}^{-1}$ for bands of the secondary amides. In the solution spectra the amide III frequency decreases by ca. 20 cm^{-1}. A similar decrease is found with *N*-methyl acetamide, as is indicated in Table II.

All the hydrazides examined in the solid state have N–H stretching bands near 3200 cm^{-1} which are also lower than those of many secondary amides. Miyazawa3) postulated that the markedly decreased ν(N–H) frequency of diformylhydrazine was due to strong hydrogen bonding in the solid state. The strength of the hydrogen bond will be different from molecule to molecule. However, the hydrazides, with the exception of DFH, have a N–H band the frequency of which is very close to 3200 cm^{-1}. On the other hand, Davies et al.12) examined the infrared absorption of *N*-methyl acetamide in acetonitrile and obtained a single monomeric ν(N–H) at 3398 cm^{-1}, 80 cm^{-1} lower than that in carbon tetrachloride. Therefore, they concluded that the N–H group was markedly solvated in acetonitrile. The hydrazides in acetonitrile also have an N–H band, the frequency of which is higher by ca. 110 cm^{-1} than that of a main N–H band in the solid spectra of the hydrazides. Further, the ν(N–H) frequency of the hydrazides in acetonitrile is still lower by ca. 90 cm^{-1} than that of *N*-methyl acetamide in the same solvent. The lower value of the ν(N–H) frequency is, therefore, found in both solid spectra and solution spectra of the hydrazides examined here. Such a decrease of the ν(N–H) frequency can not reasonably be explained as the effect of strong hydrogen bonding or solvation only. Thus, the decrease of ν(N–H) in frequency can also be taken as one of the characteristics of the hydrazides examined; namely, there is a coupling between

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11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen & Co. Ltd., London (1954).

12) M. Davies, J. C. Evans and R. L. Jones, *Trans. Faraday Soc.*, **51**, 761 (1955).

two CONH groups of each hydrazide molecule in the solid state. Probably hydrazide molecules are nonplanar in solution, and the increase of the ν(N–H) frequency in the solution spectra may come from a decrease in the coupling between two CONH groups. In addition to the main 3200 cm^{-1} absorption, the hydrazides have a weak band near 3030 cm^{-1}. Its occurrence is in accordance with that of the band near 3080 cm^{-1} for the secondary amides.

Summary

The infrared absorption spectra of the hydrazides of aliphatic acids have been examined in the rock salt region. The N–H stretching frequencies are found near 3200 and 3030 cm^{-1} in the solid state and near 3320 cm^{-1} in dilute solution. The amide I band is seen near 1600 cm^{-1} in the solid state, while in solution there are two bands, near 1720 and 1690 cm^{-1}. In the solid state the amide II band appears near 1490 cm^{-1}. The amide III band is found near the lower limit of the normal range of 1305～1200 cm^{-1} for the secondary amides.

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