Infrared Absorption Spectra of Hydrazides. V. Oxal-, Malon- and Succin-Hydrazides

By Mitsuo MASHIMA

(Received August 11, 1962)

In a previous paper[1] the infrared frequencies characteristic of the $-CONHNH_2$ group have been reported on. The present investigation has aimed at obtaining further evidence about the characteristic frequencies of the $-CONHNH_2$ group. The infrared absorption spectra of oxal-, malon- and succin-hydrazides and their *N*-deuterated species in the solid state were examined in the rock salt region. For the sake of comparison, the infrared absorption spectra of hydrazioxlyl, hydrazimalonyl, hydrazisuccinyl and oxamide acide hydrazide were also examined. The results of these measurements are reported in this paper, and the frequencies characteristic of the $-CONHNH_2$ group are considered on the basis of these experimental results.

Experimental

Oxal-, malon- and succin-hydrazides were synthesized with ethyl esters of corresponding acids and hydrazine hydrate and were purified by recrystallization from ethanol (m. p., 236, 150, 167°C respectively). Oxamide acid hydrazide was synthesized by the reaction of oxalic acid ethylester amide and hydrazine hydrate and was purified by recrystallization from water (m. p., 220°C). Hydrazioxalyl and hydrazisuccinyl were synthesized by the reactions of oxal- and succin-hydrazides respectively, with sodium nitrite in the acetic acid solution. Hydrazimalonyl was prepared by heating malon-hydrazide with acetic acid. These compounds were purified by repeatedly washing the precipitates obtained with a quantity of ethanol; they were neither melted nor decomposed up to 280°C. The *N*-deuterated derivatives examined were prepared in sealed tubes in the presence of heavy water (99.8%), the excess of which was evaporated in a vacuum.

The infrared spectrophotometer used to obtaining the absorption spectra is an Hitachi infrared spectrophotometer Type EPI-2 with rock salt prisms. Potassium bromide disks were used to obtain the solid spectra.

Results and Discussion

Oxalhydrazide (OxH) and Oxamide Acid Hydrazide (OAH).—The infrared spectra of OxH, its *N*-deuterated species (OxH-d_6), and OAH are illustrated in Fig. 1. The absorption bands of these compounds were interpreted by comparison of the spectra with those of oxamide[2] and *NN'*-dimethyloxamide[3].

In the 3000 cm^{-1} region, oxamide* has two very strong bands, at 3363 and 3185 cm^{-1}, which have been ascribed to the asymmetric and symmetric NH_2 stretching vibrations. *NN'*-Dimethyloxamide[3] has a band at 3290 cm^{-1} which has been ascribed to the NH stretching vibration. OAH has three bands at 3340, 3250, and 3190 cm^{-1}. Of these three, the first and the third bands are very close in frequency to the two bands due to the NH_2 stretching vibrations for oxamide, while the second one is close in frequency to the $\nu(NH)$ band of *NN'*-dimethyloxamide. Therefore, the 3340 and 3190 cm^{-1} bands are probably to be ascribed to $\nu(NH_2)$, and the 3250 cm^{-1} band, to $\nu(NH)$.

OxH has a relatively sharp band at 3260 cm^{-1}, two broad bands at 3160 and 3000 cm^{-1}, and a shoulder band at 2780 cm^{-1}. These bands are probably due to $\nu(NH_2)$ and $\nu(NH)$, but further, detailed assignments of them are not easy. OxH-d_6 has two bands, at 2640 and 2300 cm^{-1}, which are due to $\nu(ND_2)$ or $\nu(ND)$.

The 1662 and 1606 cm^{-1} bands of OxH correspond in frequency, respectively, to the 1656 cm^{-1} band ascribed to the C=O stretching vibration and the 1608 cm^{-1} band ascribed to the NH_2 bending vibration for oxamide[2]. OxH-d_6 has a broad and intense absorption band with a centre near 1650 cm^{-1}; this band corresponds to the 1662 cm^{-1} band of OxH, the ratio of ν_H/ν_D being 1.01. The 1606 cm^{-1} band of OxH corresponds to the band at 1202 cm^{-1} for OxH-d_6, $\nu_H/\nu_D=1.336$. From these facts, the 1662 and 1606 cm^{-1} bands can surely be ascribed to the C=O stretching and the NH_2 bending vibrations respectively. These assignments are also supported by the fact that *NN'*-dimethyloxamide[3] has an amide I band at 1658 cm^{-1}, while the compound has

---

[1] M. Mashima, This Bulletin, 35, 1882 (1962).

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

[3] T. Miyazawa, ibid., **76**, 1018 (1955).

* The infrared frequencies of this compound are taken from the data published by J. A. Scott, Jr. and E. L. Wagner (Ref. 2a).

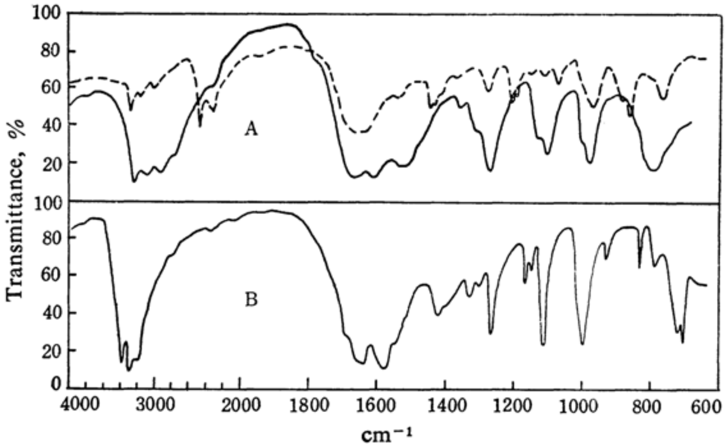

Fig. 1. Infrared absorption spectra of oxalhydrazide (curves A's) and oxamide acid hydrazides (curve B). Of the curves A's the dashed curve indicates the spectrum of *N*-deuterated specy of oxalhydrazide.

no band corresponding to the 1606 cm^{-1} band of OxH. On the other hand, OAH shows rather different absorptions in this region; i. e., it has two intense bands, at 1637 and 1583 cm^{-1}, both of which are associated with a shoulder band, at 1684 and 1532 cm^{-1} respectively. These bands are probably due to the C=O stretching and NH_2 bending vibrations, but detailed interpretations of them are not easy.

The 1522 cm^{-1} band of OxH has its counterpart at 1440 cm^{-1} in the OxH-d spectrum, the value of ν_H/ν_D being 1.057. These two bands are, respectively, very close in frequency to the amide II band at 1532 cm^{-1} for *NN'*-dimethyloxamide$^{3)}$ and the amide II' band at 1445 cm^{-1} for its *N*-deuterated specy$^{3)}$. In consequence, the 1522 cm^{-1} and 1440 cm^{-1} bands can surely be taken as the amide II and amide II' bands respectively. In this region, oxamide$^{2)}$ has no band corresponding to the amide II band, while the compound has a 1348 cm^{-1} band which has been ascribed to the C–N stretching vibration. For OAH, the 1417 and 1326 cm^{-1} bands can also be ascribed to the C–N stretching vibrations, but the assignments are not certain.

In the 1300~900 cm^{-1} range, OxH has three bands, at 1267, 1097 and 973 cm^{-1}, which correspond in frequency to the bands at 1261, 1107 and 991 cm^{-1} respectively for OAH. The three bands of OxH are apparently weakened on *N*-deuteration; they correspond, respectively, to the bands at 1067, 966 and 858 cm^{-1} for OxH-d_6. They are, therefore, due to the NH_2 or NH deformation vibrations. For OxH, the band at 1307 cm^{-1} corresponds to the band at 1108 cm^{-1} for OxH-d_6. OAH also has a band at 1296 cm^{-1}. For monoacid hydrazides, the present author has obtained three frequencies due to the NH_2 deformation vibrations, e. g., 1347, 1105 and 1009 cm^{-1} for cyanoacetylhydrazine$^{1)}$. Consequently, the bands at 1307, 1097 and 973 cm^{-1} for OxH and 1296, 1107 and 991 cm^{-1} for OAH are taken as characteristic of the –$CONHNH_2$ group. The 1267 cm^{-1} (for OxH) and 1261 cm^{-1} (for OAH) bands are close in frequency to the amide III band at 1239 cm^{-1} for *NN'*-dimethyloxamide$^{3)}$. They will, therefore, be taken as the amide III band.

OxH has a strong band at 792 cm^{-1} which has not yet been accounted for. This band shifts to 757 cm^{-1} on *N*-deuteration. OAH has a band with two peaks (713 and 702 cm^{-1}); this band corresponds to the 792 cm^{-1} band for OxH. *NN'*-Dimethyloxamide$^{3)}$ has an amide IV band at 765 cm^{-1}, the frequency value of which is close to that of the 792 cm^{-1} band for OxH. Therefore, the 792 cm^{-1} band of OxH will be taken as an amide IV band. On the other hand, oxamide$^{2)}$ has a 629 cm^{-1} band which has been ascribed to the in-plane N–C=O deformation vibration. For OAH the appearance of two peaks, 713 and 702 cm^{-1}, will depend on the reduced symmetry of the molecule.

The 1124 cm^{-1} band of OxH has its counterpart at 1146 cm^{-1} in the OxH-d_6 spectrum. OAH also has corresponding bands at 1159 and 1144 cm^{-1}. They are probably dut to the N–N stretching vibration, but the assignments are not sure. OxH has more two weak bands, at 834 and 815 cm^{-1}, while no band corresponding to them has been found for OxH-d_6 in the region examined here. These two bands correspond in frequency to the bands at 824 and 783 cm^{-1} of OAH, but these can

TABLE I. INFRARED FREQUENCIES OF OXALHYDRAZIDE AND OXAMIDE ACID HYDRAZIDE (in cm^{-1})

Assignment[a]	Oxamide[b]	*NN'*-Dimethyloxamide[c]	Oxamide acid hydrazide	Oxalhydrazide	Its *N*-deuterated specy
$\nu_{as}(NH_2)$	3363	—	3340 (vs)		
$\nu(NH)$	—	3290	3250 (vs)	3260 (s)	
$\nu_s(NH_2)$	3185	—	3190 (vs)	3160 (s) 3000 (s) 2780 (sh)	
$\nu(ND_2)$ or $\nu(ND)$					2640 (s) 2300 (s)
Amide I	1656	1658	1684 (sh) 1637 (vs)	1662 (vs)	1650 (b vs)
$\beta(NH_2)$ or $\beta(ND_2)$	1608	—	1583 (vs)	1606 (s)	1202 (m)
Amide II (or II')	—	1532	1532 (sh)	1522 (s)	1440 (s)
$\nu(C-N)$	1348	—	1417 (m) 1326 (m)		
$NH_2(ND_2)$ def.	—	—	1296 (w)	1307 (m)	1108 (w)
Amide III, III'	—	1239	1261 (s)	1267 (s)	1067 (w)
$\nu(N-N)$	—	—	1159 (w) 1144 (w)	1124 (w)	1146 (vw)
$NH_2(ND_2)$ def.	—	—	1107 (s)	1097 (m)	966 (s)
$NH_2(ND_2)$ def.	792	—	991 (s)	973 (s)	858 (s)
$\nu(C-C)$	—	—	925 (w) 824 (w) 783 (w)	 834 (sh) 815 (sh)	
Amide IV (O=C-N def.)	629	765	713 (s) 702 (s)	792 (s)	757 (m)

a ν and β denote stretching and bending vibrations respectively
b See Ref. 2
c See Ref. 3

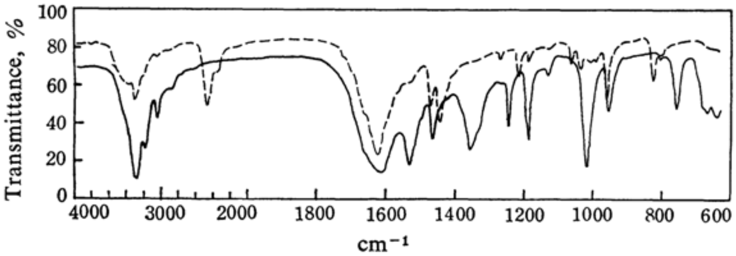

Fig. 2. Infrared absorption spectra of succinhydrazide (solid curve) and its *N*-deuterated specy (dashed curve).

not be interpreted with confidence. For OAH a weak band at 925 cm^{-1} is probably to be attributed to the C–C stretching vibration, which is infrared active because of the asymmetric character of the molecule.

The observed frequencies for OxH and OAH and their tentative assignments are summarized in Table I, in which the infrared frequencies of oxamide and *NN'*-dimethyloxamide are also represented for the sake of comparison.

Succinhydrazide (SH).—For this compound the frequencies characteristic of the $-CONHNH_2$ group were rather easily obtained. The solid spectra of SH and its *N*-deuterated specy (SH-d_6) are illustrated in Fig. 2, and the tentative assignments of the absorption bands are given in Table II.

In the 3000 cm^{-1} region, SH has three strong or moderately strong bands, at 3270, 3160 and 3030 cm^{-1}, all of which are apparently weakened on *N*-deuteration. Their counterparts are found at 2440 and 2340 cm^{-1} in the SH-d_6 spectrum. They can, therefore, be ascribed to NH_2 or NH stretching vibrations. Since an SH molecule has a hydrazine residue, it can reasonably be expected that three bands due to the N–H bond stretching vibrations appear in this region. However, detailed assignments of the observed bands are impossible on the basis of present observations only.

Next, we will concern ourselves with the location of the CH_2 deformation vibrations. For $X-XH_2-CH_2-X$ type molecules, Nakagawa[4]

---

[4] I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 602 (1956).

TABLE II. INFRARED FREQUENCIES OF SH AND SH-d_6 IN THE ROCK SALT REGION (in cm^{-1})

Assignment	SH	SH-d_6
$\nu(NH_2)$ or $\nu(NH)$	3270 (s) 3160 (m) 3030 (m)	
$\nu(ND_2)$ or $\nu(ND)$		2440 (s) 2340 (m)
Amide I or $\beta(NH_2)$	1624 (vs)	1620 (vs)
Amide II (II′)	1528 (s)	1441 (s)
$\beta(CH_2)$	1462 (m)	1466 (m)
NH_2 deformation	1353 (s) 1328 (sh)	
$\omega(CH_2)$	1258 (m)	1265 (w)
Amide III	1240 (m)	
$\beta(ND_2)$		1212 (m)
NH_2 deformation	1181 (s)	
$\tau(CH_2)$	1126 (w)	1128 (vw)
ND_2 deformation or Amide III′		1059 (w) 1032 (w)
NH_2 deformation	1012 (s)	
ν(C–C)	948 (m)	957 (m)
ND_2 deformation		820 (m)
$\gamma(CH_2)$	800 (vw)	798 (w)
Amide IV ?	751 (m) 674 (sh) 662 (m) 638 (m)	

ν; stretching, β; bending, ω; wagging, τ; twisting, γ; rocking

has obtained the following ranges for the CH_2 deformation frequencies; 1400∼1450 cm^{-1} for bending, 1200∼1350 cm^{-1} for wagging, 1050∼1250 cm^{-1} for twisting, and 700∼1000 cm^{-1} for rocking. For SH, the band at 1462 cm^{-1} is near the range for CH_2 bending vibrations, and its value of frequency is scarcely changed on *N*-deuteration. In consequence, it may be assigned to the CH_2 bending vibration. The band at 1258 cm^{-1} corresponds to the band at 1265 cm^{-1} of SH-d_6 and they both fall in the range for the CH_2 wagging vibrations; accordingly, they are assigned to the CH_2 wagging vibration. SH has a further weak band at 1126 cm^{-1} which is scarcely changed in frequency on *N*-deuteration and which falls in the range for the CH_2 twisting vibrations. Thus, the 1126 cm^{-1} band may be assigned to the CH_2 twisting vibration. The weak band at 800 cm^{-1}, which also is scarcely changed in frequency on *N*-deuteration, falls in the range for the CH_2 rocking vibration. Consequently, the 800 cm^{-1} band is assigned to the CH_2 rocking vibration. However, SH has a further band falling in the 700∼1000 cm^{-1} range. This is the band at 948 cm^{-1}, which is also scarcely changed in frequency on *N*-deuteration. Although the 948 cm^{-1} band is tentatively assigned to the C–C stretching vibration, an alternative assignment (to the CH_2 rocking vibration) is also possible.

Let us now consider the location of vibrations relating to the $-CONHNH_2$ group. This group contains the –CONH– group, so the amide I, II, III and IV bands may be expected to appear in the region examined here. In fact, very strong band at 1624 cm^{-1} is surely assigned to amide I because it corresponds in frequency and intensity to the band at 1620 cm^{-1} of SH-d_6. SH has a band at 1528 cm^{-1} which can easily be assigned to the amide II band. This assignment is supported by the observation that SH-d_6 has a corresponding band (amide II′) at 1441 cm^{-1}, the ratio of ν_H/ν_D being 1.060. The amide III band is expected to appear near 1300 cm^{-1}, but its identification will be considered with those of the bands due to the NH_2 deformation vibrations. SH apparently shows absorptions below 700 cm^{-1} and the amide IV band will apparently appear near 700 cm^{-1}, but no definite evidence can be observed in the spectra of SH-d_6 in the region examined here.

In the 700 to 1700 cm^{-1} region, five absorption bands (with the exception of the amide I and II bands) have been found for some monoacid hydrazides; these have been taken as characteristic of the $-CONHNH_2$ group[1]; e. g., for cyanoacetylhydrazine they have been observed at 1625, 1347, 1258, 1105 and 1009 cm^{-1}. Of these five the first band has been ascribed to the NH_2 bending vibration. For SH no band corresponding to it is observed because of its location near the amide I band at 1624 cm^{-1}, while SH-d_6 has a band at 1212 cm^{-1} which is probably due to the ND_2 bending vibration. SH has bands corresponding to the latter four at 1353, 1240, 1181 and 1012 cm^{-1}, all of which disappear on *N*-deuteration. The 1258 cm^{-1} band of cyanoacetylhydrazine has been taken as the amide III band; accordingly, the 1240 cm^{-1} band of SH can be assigned similarly. In the SH-d_6 spectrum, the counterpart of the 1012 cm^{-1} band is easily found at 820 cm^{-1} ($\nu_H/\nu_D=1.234$), but definite identifications of the counterparts of the other three are not easy. SH-d_6 has a further two bands at 1059 and 1032 cm^{-1} which are not present in the SH spectrum. These two bands probably correspond to two of the bands at 1353, 1240 and 1181 cm^{-1} for SH.

Malonhydrazide (MH). — The absorption spectra of MH and its *N*-deuterated specy (MH-d_6) are illustrated in Fig. 3. The obserevd frequencies of MH and MH-d_6 and their tentative assignments are summarized in Table III.

In the 3000 cm^{-1} region, a strong band at 3290 cm^{-1} and two moderately strong bands

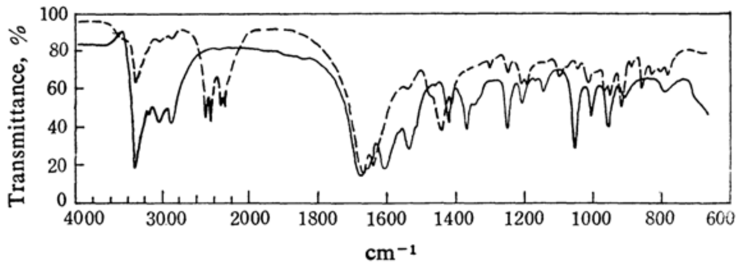

Fig. 3. Infrared absorption spectra of malonhydrazide (solid curve) and its *N*-deuterated specy (dashed curve) in the rock salt region.

at 3020 and 2870 cm^{-1} are found for MH. For MH-d$_6$ two doublet bands are found at 2480 and 2430 cm^{-1} and at 2310 and 2260 cm^{-1}. They are probably due to NH$_2$ (ND$_2$) or NH(ND) stretching vibrations; more detailed assignments are difficult on the basis of present observations only.

MH has two very strong bands at 1669 cm^{-1} (accompanied by two ill-defined shoulder bands on the lower frequency side) and 1602 cm^{-1}. The two bands correspond to the bands at 1664 and 1636 cm^{-1} for MH-d$_6$ and are taken as amide I bands. The appearance of two bands taken as amide I bands is due to coupling two vibrations which are localized mainly on two C=O bonds. Although the NH$_2$ bending vibration is also expected to give rise to bands near 1600 cm^{-1}, definite identification is impossible because of its location near the amide I band. For MH-d$_6$, the band at 1189 cm^{-1} is probably to be ascribed to the ND$_2$ bending vibration. The 1532 cm^{-1} band of MH shifts to 1435 cm^{-1} (ν_H/ν_D = 1.068) on *N*-deuteration; it may be taken as an amide II band. For monoacid hydrazides[1], an amide III band has been observed near 1250 cm^{-1}. MH has a band at 1247 cm^{-1} which shifts to 1036 cm^{-1} on *N*-deuteration (ν_H/ν_D=1.203) and which hence may be taken as an amide III band.

Let us next consider the locations of the NH$_2$ deformation vibrations other than the bending one already accounted for. For monoacid hydrazides[1] such vibrations have been observed near 1300, 1150 and 1000 cm^{-1}. MH has three bands, at 1365 (accompanied by a shoulder band on its lower frequency side), 1139 and 1051 cm^{-1}. All these three disappear on *N*-deuteration; their counterparts are found at 1093, 962 and 918 cm^{-1} in the MH-d$_6$ spectrum, the values of ν_H/ν_D being 1.249, 1.184 and 1.145 respectively. They may, therefore, be ascribed to the NH$_2$ deformation vibrations.

TABLE III. INFRARED FREQUENCIES OF MH AND MH-d$_6$ (in cm^{-1})

Assignment	MH	MH-d$_6$
ν(NH$_2$) or ν(NH)	3290 (vs)	
	3210 (sh)	
	3020 (m)	
	2870 (m)	
ν(ND$_2$) or ν(ND)		2480 (s)
		2430 (s)
		2310 (s)
		2260 (s)
Amide I	1669 (vs)	1664 (vs)
	1602 (s)	1636 (vs)
Amide II (II′)	1532 (s)	1435 (s)
β(CH$_2$)	1418 (m)	1408 (m)
NH$_2$ deformation	1365 (m)	
	1340 (sh)	
Amide III (III′)	1247 (m)	1036 (w)
ω(CH$_2$)	1202 (w)	1203 (w)
β(ND$_2$)		1189 (m)
NH$_2$ deformation	1139 (w)	
ND$_2$ deformation		1093 (w)
		1072 (sh)
NH$_2$ deformation	1051 (s)	
τ(CH$_2$)	1002 (m)	1008 (w)
ND$_2$ deformation		962 (w)
ν(C-C)	952 (m)	948 (m)
	903 (w)	850 (m)
ND$_2$ deformation		918 (m)
γ(CH$_2$)	785 (w)	775 (w)

ν; stretching, β; bending, ω; wagging, τ; twisting, γ; rocking

In the region examined here, the CH$_2$ deformation vibrations are also expected to give rise to bands. For them Nakagawa[5] has obtained the ranges of 1350～1450 cm^{-1} (bending), 1100～1350 cm^{-1} (wagging), 1000～1250 cm^{-1} (twisting) and 700～1000 cm^{-1} (rocking) for the molecules of the CH$_2$XY type. MH has corresponding bands at 1418, 1202, 1002 and 785 cm^{-1}. None of these four is greatly changed in frequency on *N*-deuteration; i. e., MH-d$_6$ has the four bands at 1408, 1203, 1008 and 775 cm^{-1}. In consequence, they may easily be ascribed to the CH$_2$ bending, wagging, twisting and rocking vibrations respectively.

---

[5] I. Nakagawa, ibid., **76**, 540 (1955).

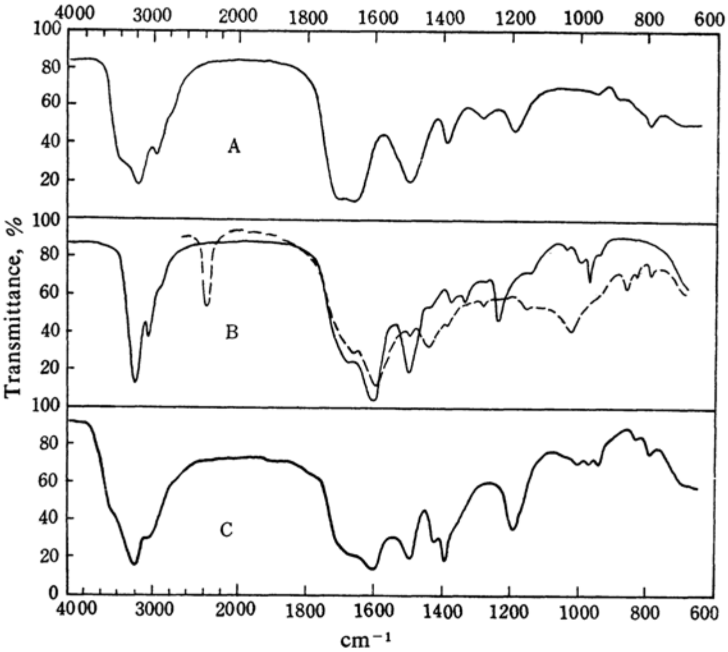

Fig. 4. Infrared absorption spectra of hydrazioxalyl (curve A), hydrazimalonyl (curves B's), and hydrazisuccinyl (curve C). Of the curves B's the dashed curve indicates the spectrum of *N*-deuterated specy of hydrazimalonyl.

For MH, two bands, at 952 and 903 cm^{-1}, are not yet accounted for. In the MH-d_6 spectrum, the former has its counterpart at 948 cm^{-1}, but the band corresponding to the latter can not be identified because of its location on the sloping background of the more intense band at 918 cm^{-1}. MH-d_6 has a rather stronger band at 850 cm^{-1}. These are probably due to the C–C stretching vibrations.

Hydrazioxalyl (HO), $(C_2H_2O_2N_2)_x$, Hydrazimalonyl (HM), $(C_3H_4O_2N_2)_x$ and Hydrazisuccinyl (HS), $(C_4H_6O_2N_2)_x$. — The solid spectra of these compounds are illustrated in Fig. 4. For HM the absorption spectrum of its *N*-deuterated specy (HM-d_2) was also examined. The so-called amide bands were identified without difficulty.

For HM, two, very strong bands are found at 1662 and 1593 cm^{-1} which correspond in intensity to the bands at 1655 and 1590 cm^{-1} for HM-d_2. The two bands, therefore, may easily be taken as amide I bands; corresponding bands are found at 1655 and 1590 cm^{-1} for HS and at 1705 and 1656 cm^{-1} for HO.

HM has a strong band at 1486 cm^{-1} which shifts to 1432 cm^{-1} on *N*-deuteration, $\nu_H/\nu_D=1.038$. The corresponding band is found at 1492 cm^{-1} for HO and 1485 cm^{-1} for HS. In consequence, they may surely be taken as amide II bands.

The amide III band is also expected to appear in the region examined here. For HM, the band at 1230 cm^{-1} shifts to 1009 cm^{-1} on *N*-deuteration, $\nu_H/\nu_D=1.219$. This band corresponds to the 1185 cm^{-1} band for HO and the 1184 cm^{-1} band for HS; these are taken as amide III bands.

For all these compounds, a strong band is found near 3160 cm^{-1}; this band is probably due to the NH stretching vibration.

The present author⁶⁾ has obtained the frequencies characteristic of the –CONHNHCO– group of some diacid hydrazides; e. g., formylacetylhydrazine in the solid state absorbs at 3020 and 3200 cm^{-1} (NH stretching), 1580 and 1613 cm^{-1} (amide I), 1483 cm^{-1} (amide II), and 1232 and 1279 cm^{-1} (amide III). In the present study, bands similar to these were obtained for HO, HM and HS as is summarized in Table IV.

Characteristic Frequencies. — Oxal-, malon- and succin-hydrazide show the frequencies characteristic of the –CONHNH$_2$ group, as

TABLE IV. FREQUENCIES CHARACTERISTIC OF HO, HM AND HS (in cm^{-1})

	HO	HM	HS
ν(NH)	3160	3160	3170
Amide I	1656, 1705	1593, 1662	1590, 1655
Amide II	1492	1486	1485
Amide III	1185	1230	1184

---

6) M. Mashima, This Bulletin, 35, 423 (1962).

summarized in Table V. The characteristic frequencies of HO, HM and HS are represented in Table IV.

Amide Bands.—In the 600∼1800 cm^{-1} region mono-substituted amides[7] usually show the following bands characteristic of the trans-planar –CONH– group; the amide I band ca. 1650 cm^{-1}, the amide II band ca. 1550 cm^{-1}, the amide III band in the 1200∼1300 cm^{-1} range, and the amide IV band ca. 760 or 630 cm^{-1}. As may be seen from Table V*, the –CONH– group contained in the $-CONHNH_2$ group also exhibits the characteristic bands indicated above.

On the other hand, *NN′*-diacid hydrazides[6] show amide I, II and III bands having rather low frequency values. Further, two values of frequencies have been obtained for the amide I and III bands. In the present study also, amide bands of rather low frequencies were obtained for HO, HM and HS, while two frequency values were obtained for the amide I band, as may be seen from the Table IV. The spectroscopic evidence, therefore, suggests that the –CONHNHCO– group of HO, HM and HS has a structure similar to that of *NN′*-diacidhydrazides. The presence of two frequencies, taken as amide I bands, is probably due to the coupling of two vibrations which are localized mainly on the C=O group, as was postulated in an earlier paper[6].

TABLE V. CHARACTERISTIC FREQUENCIES OF THE $-CONHNH_2$ GROUP

	Oxal-hydrazide	Malon-hydrazide	Succin-hydrazide
Amide I	1662	1669	(1624)*
Amide II	1522	1532	1528
Amide III	1267	1247	1240
Amide IV	792	—	670
$\nu(NH_2)$ or $\nu(NH)$	3260 3160 3000	3290 3210 3020	3270 3160 3030
NH_2 deformation	1606	1602	(1624)*
NH_2 deformation	1307	1365	1353
NH_2 deformation	1097	1139	1181
NH_2 deformation	973	1051	1012

* For these see the Table II

NH_2 Deformation Absorptions. — For some aliphatic acid hydrazides[1], four frequencies characteristic of the $-CONHNH_2$ group have been obtained, in addition to the amide I, II, and III absorptions and the $\nu(HN_2)$ or $\nu(NH)$ absorptions. The highest one of the four was found ca. 1630 cm^{-1} and the second highest one in the 1260∼1350 cm^{-1} range. The other two bands were observed ca. 1150 and ca. 1000 cm^{-1}. In the present study for dicarboxylic acid hydrazides, bands corresponding to them were obtained (cf. Table V), while HO, HM and HS have no band corresponding to them. Thus, they may surely be taken as the characteristic frequencies of the $-CONHNH_2$ group. They are probably due to the NH_2 deformation vibrations, but, of course, no definite assignments can be made without a theoretical investigation of the normal vibrations.

The author is grateful to Professor Sunao Imanishi of Kyushu University for his generous permission to use the University's spectrophotometer. He is also indebted to the Ministry of Education for its financial support.

Department of Literature and Science
Saga University
Saga-city Saga

---

[7] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).

* See also Ref. 1.