Infrared Absorption Spectra of Hydrazides. VI. Benzoylhydrazine

By Mitsuo MASHIMA

(Received October 18, 1962)

The infrared absorption spectra of benzoylhydrazine in the solid state and in an acetonitrile solution have previously been observed by the present author¹⁾. However, the absorption bands observed could not be interpreted with certainty. In the present study, the infrared spectrum of *N*-deuterated benzoylhydrazine is examined in the rock salt region. For the sake of comparison, the infrared spectra of *N*-deuterated benzamide, cyanoacetic acid amide and its *N*-deuterated derivative are also observed. A tentative assignment of the bands of these compounds is described in the present paper. On the basis of results of the assignment, the frequencies characteristic of the $-CONHNH_2$ group are compared with those characteristic of the $-CONH_2$ group.

Experimental

The preparation and purification of benzoylhydrazine and benzamide have been described in a previous paper¹⁾. Cyanoacetic acid amide was synthesized with cyanoacetic acid ethylester and ammonia and was purified by recrystallization from ethanol, m. p., 119°C. The *N*-deuterated derivatives examined were prepared in sealed tubes in the presence of heavy water (99.8%). The excess heavy water was evaporated in vacuo. The solid spectra of all compounds were studied with potassium bromide disks. The solution spectrum of cyanoacetic acid amide was obtained with acetonitrile as a solvent and with 0.1 mm. cells in the optical path. A double-beam Hitachi infrared spectrophotometer type EPI-2 was used in the rock salt region.

Results and Discussion

Benzoylhydrazine (BH).—The infrared absorption spectra of BH and *N*-deuterated BH ($BH-d_3$) are illustrated in Fig. 1. The present author has previously investigated the frequencies characteristic of the $-CONHNH_2$ group²,³⁾. Cyanoacetylhydrazine²⁾, for example, has the following bands due to the $-CONHNH_2$ group: NH_2 or NH stretching, 3320, 3180 cm^{-1}; amide I, 1698 cm^{-1}; NH_2 bending, 1625 cm^{-1}; amide II, 1534 cm^{-1}; NH_2 twisting, 1313 cm^{-1}; amide III, 1258 cm^{-1}; NH_2 wagging, 1105 cm^{-1}; NH_2 rocking 1009 cm^{-1}.

The 1664 cm^{-1} band of BH was taken as the amide I band in a previous paper¹⁾. This assignment is supported by the fact that $BH-d_3$ has the corresponding band at 1627 cm^{-1}, the ν_H/ν_D ratio being 1.023. BH has an intense band at 1618 cm^{-1}, and this band is displaced by a band at 1209 cm^{-1} on *N*-deuteration, the ν_H/ν_D ratio being 1.338. Therefore, the 1618 cm^{-1} band may surely be assigned to the NH_2 bending vibration, $\beta(NH_2)$. For BH a shoulder band at 1527 cm^{-1}, which is accompanied by the band at 1582 cm^{-1}, vanishes on *N*-deuteration. $BH-d_3$ has a new band at 1416 cm^{-1}. In cyanoacetylhydrazine the amide II band at 1534 cm^{-1} is displaced by a band at 1451 cm^{-1} on *N*-deuteration. Therefore, the 1527 cm^{-1} band of BH is very probably to be assigned to the amide II band, and the 1416 cm^{-1} band of $BH-d_3$ may probably be taken as the amide II′ band. The 1349 cm^{-1} band of BH has not yet been assigned with certainty. This band vanishes on *N*-deuteration and $BH-d_3$ has a new band at 1098 cm^{-1}, the ν_H/ν_D ratio being 1.229. Therefore, it seems that the 1349 cm^{-1} band may best be assigned to the NH_2 twisting vibration ($\tau(NH_2)$) because it is close in frequency to the corresponding band at 1313 cm^{-1} of cyanoacetylhydrazine. BH has two additional moderately strong bands, which disappear on *N*-deutration, at 1118 and 987*¹ cm^{-1}. These two bands are considered to correspond to the bands at 936 and 897 cm^{-1} for $BH-d_3$ and are close in frequency to the bands at 1105 and 1009 cm^{-1} of cyanoacetylhydrazine. Therefore, they are considered to be assigned to the NH_2 wagging and rocking vibrations, ($\omega(NH_2)$ and $\gamma(NH_2)$) respectively. BH has a very weak band at 1250 cm^{-1}, which disappears on *N*-deuteration, and $BH-d_3$ has a new band at 1058 cm^{-1}, the ν_H/ν_D ratio being 1250/1058 (1.182). In consequence, the 1250 cm^{-1} band is can probably best be assigned to an amide III band.

In order to ascertain the assignments above described, the vibrations of a monosubstituted aromatic ring will be considered. Schmid,

---

1) M. Mashima, This Bulletin, 35, 332 (1962).
2) M. Mashima, ibid., 35, 1882 (1962).
3) M. Mashima, ibid., 35, 2020 (1962).

*¹ This is a mean value of the frequencies of the two peaks at 990 and 984 cm^{-1}.

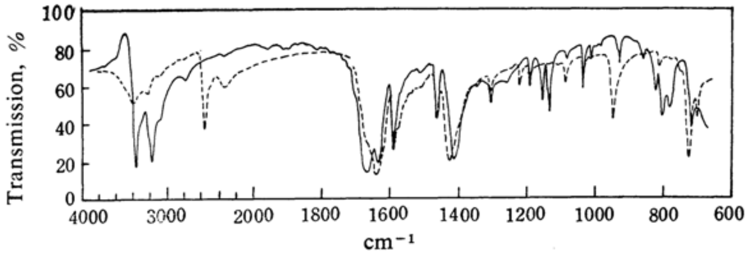

Fig. 1. Infrared spectra of $C_6H_5CONHNH_2$, ——, and $C_6H_5CONDND_2$, - - - -, in KBr disks.

Brandmeuller and Nonnenmacher[4] have made a calculation of the normal vibrations of the monosubstituted aromatic compounds. On the basis of calculations, they have proposed detailed assignments of the infrared absorption bands and Raman lines for several monosubstituted benzenes. These assignments may be referred to for an interpretation of the bands observed for BH (and also benzamide (BA), infrared spectrum of which is shown in Fig. 3) in the 1600~650 cm^{-1} region. The frequencies of this region due to an aromatic ring are summarized in Table I, in which the corresponding frequencies and their detailed assignments for toluene and chlorobenzene[4] are also represented for the sake of comparison. Four bands (near 1600, 1580, 1500 and 1450 cm^{-1}) of the monosubstituted aromatic compounds are usually used in correlation work[5], and the bands corresponding to them are easily found for BH, BA and their *N*-deuterated derivatives, as is shown in Table I. Four further bands, near 1300, 1180, 1070 and 1020 cm^{-1}, are observed for both BH and BA, and for their *N*-deuterated derivatives also. Those bands can, therefore, very probably be assigned to the in-plane C–H deformation vibrations, δ(C–H). Five of the δ(C–H) vibrations can be reasonably expected to occur, so the 1154 cm^{-1} band of BH (and the 1142 cm^{-1} band BA) is to be taken as another δ(C–H) band. However, this assignment is not certain because no band corresponding to it is found for BH-d$_3$ (nor for BA-d$_2$).

TABLE I. INFRARED FREQUENCIES OF AN AROMATIC RING (in the 1600~650 cm^{-1})

Assignment[a]	$C_6H_5CH_3$[a] liq.	C_6H_5Cl[a] liq.	BH solid	BH-d$_3$ solid	BA solid	BA-d$_2$ solid
ωB_1	1608	1570	1608	1603	1578	1574
ωA_1	1575	1585	1582	1573		
ωA_1	1497	1477	1492	1490	1497	1497
ωB_1	1452	1455	1450	1450	1451	1452
$\delta_{CH} B_1$	1250	1270	1298	1293	1296	1296
$\delta_{CH} A_1$	1179	1123	1183	1182	1180	1178
$\delta_{CH} B_1$	1157	1156	1154	—	1142	—
$\delta_{CH} B_1$	1082	1068	1070	1070	1073	1074
$\delta_{CH} A_1$	1032	1022	1024	1023	1024	1024
ωB_1	1314	1324	1320	1332	1334	1342
ωA_1	1002	1002	1002	1010	999	1000
$\omega_X A_1$	1211	1086				
$\pi_{CH} B_2$	974	982	966	967	987	987
$\pi_{CH} A_2$	966	963	917	921	917	924
$\pi_{CH} B_2$	895	903	863	—[b]	848	847
$\pi_{CH} B_2$	842	831				
$\pi_{CH} B_2$	729	740	801	797	811	801
$\omega_X A_1$	786	702	747	705	770	713
ΓB_2	694	684	690	674	705	691

a) See Ref. 4.

b) This band could not observe because it is overlapped by a more intense band at 897 cm^{-1}.

Two bands near 1330 and 1000 cm^{-1} are observed for all compounds of BH, BA and their *N*-deuterated derivatives. Therefore, these two bands also are surely assigned to the vibrations of an aromatic ring.

The out-of-plane C–H deformation vibrations (π(C–H)) are expected to occur in the region below 1000 cm^{-1} because they have been obtained in that region for the monosubstituted aromatic compounds[4], as is shown in Table I. The 966 cm^{-1} band of BH, which is observed as a shoulder band at the foot of the more intense band at 987 cm^{-1}, corresponds in frequency to the band at 967 cm^{-1} for BH-d$_3$. BA also has a very weak band at 987 cm^{-1} which is considered to correspond to the 966 cm^{-1} band of BH. The band near 920 cm^{-1} is observed for BH, BA and all of their *N*-deuterated derivatives. The 863 cm^{-1} band of BH corresponds in frequency to the band at 848 cm^{-1} for BA and 847 cm^{-1} for BA-d$_2$, while for BH-d$_3$ the corresponding band can not be ascertained because it is overlapped by the more intense band at 897 cm^{-1} which was already assigned to the γ(ND$_2$) vibration. Thus, the 966, 917 and 863 cm^{-1} bands of BH

---

[4] E. W. Schmid, J. Brandmeuller and G. Nonnenmacher, *Z. Elektrochem.*, **64**, 726 (1960).

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Company, Ltd., London (1954).

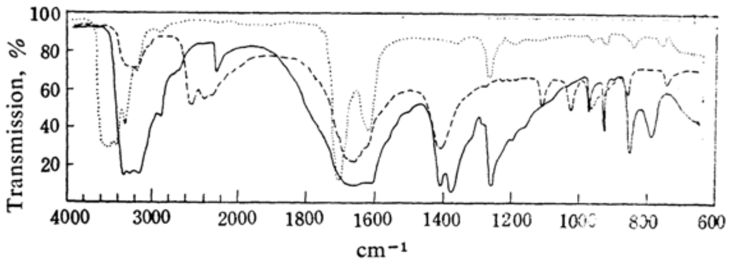

Fig. 2. Infrared spectra of $CNCH_2CONH_2$ in the solid state, ——, and in CH_3CN, ……, and $CNCH_2COND_2$ in the solid state, ----.

TABLE II. INFRARED FREQUENCIES OF BH AND THEIR ASSIGNMENTS

Assignment[a]	BH Solid	BH-d_3 Solid
$\nu(NH_2)$ or $\nu(NH)$	3280 (s)	
	3180 (s)	
	3010 (s)	
	2870 (w)	
		1652 (sh)
Amide I	1664 (vs)	1627 (vs)
$\beta(NH_2)$	1618 (vs)	
ν(C-C)	1608 (sh)	1603 (sh)
ν(C-C)	1582 (s)	1573 (s)
Amide II	1527 (sh)	
		1507 (w)
ν(C-C)	1492 (w)	1490 (w)
ν(C-C)	1450 (w)	1450 (s)
Amide II′		1416 (s)
$\tau(NH_2)$	1349 (s)	
	1320 (sh)	1332 (w)
δ(C-H)	1298 (w)	1293 (w)
Amide III	1250 (vw)	
$\beta(ND_2)$		1209 (m)
δ(C-H)	1183 (w)	1182 (w)
	1154 (vw)	
$\omega(NH_2)$	1118 (m)	
$\tau(ND_2)$		1098 (w)
δ(C-H)	1070 (w)	1072 (w)
Amide III′		1058 (vw)
δ(C-H)	1024 (vw)	1023 (vw)
$\gamma(NH_2)$	990 (m)	
	984 (m)	
π(C-H)	966 (vw)	967 (w)
$\omega(ND_2)$		936 (w)
π(C-H)	917 (w)	921 (w)
$\gamma(ND_2)$		897 (m)
π(C-H)	863 (m)	
	801 (m)	797 (w)
	747 (w)	
	690 (s)	705 (s)
		674 (s)

a) ν; stretching, β; bending, δ; in-plane deformation, π; out-of-plane deformation, τ; twisting, ω; wagging, γ; rocking

are considered to be assigned to the π(C–H) vibrations.

BH has three further bands at 801, 747 and 690 cm^{-1} not yet accounted for. In the region below 800 cm^{-1}, BH-d_3 has also three bands at 797, 705 and 674 cm^{-1}. For monosubstituted aromatic compounds, two bands in the 770～730 and 710～690 cm^{-1} ranges are usually used in correlation work[5]. Although a detailed assignment of the three bands of BH can not be made, it seems certain that they are due to the aromatic ring vibrations.

The infrared frequencies of BH and their assignments are summarized in Table II.

Cyanoacetic Acid Amide (CAA).—The infrared absorption spectra of CAA and CAA-d_2 in the solid state are illustrated in Fig. 2, in which the spectrum of CAA in acetonitrile is also shown. Recently Suzuki[6] studied the infrared spectra of $HCONH_2$ and its three kinds of deuterated derivatives in the 3600～300 cm^{-1} region. He also made a calculation of the normal vibrations for these four kinds of molecules. Suzuki[7] further observed the infrared spectra of CH_3CONH_2 and its three kinds of deuterated derivatives in the 1800～300 cm^{-1} region. He made a calculation of the normal vibrations for those four kinds of molecules and discussed in detail the nature of the absorption bands observed. An assignment of the absorption bands of CAA can, therefore, rather easily be made by a comparison of the spectrum with those of $HCONH_2$ and CH_3CONH_2.

The 3000 cm^{-1} Region. — CAA in the solid state has two strong bands at 3330 and 3140 cm^{-1}. Since these two bands are close in frequency to the 3330 and 3190 cm^{-1} bands of $HCONH_2$[6], they can surely be assigned to the asymmetric and symmetric NH_2 stretching vibrations, $\nu_a(NH_2)$ and $\nu_s(NH_2)$. The fact that they move to higher frequencies in an acetonitrile solution is consistent with the above assignments. CAA-d_2 has $\nu_a(ND_2)$ and $\nu_s(ND_2)$ bands at 2505 and 2350 cm^{-1} respectively. The $\nu(CH_2)$ vibrations are also considered to give rise to bands in this region.

---

[6] I. Suzuki, This Bulletin, 33, 1359 (1960).
[7] I. Suzuki, ibid. 35, 1279 (1962).

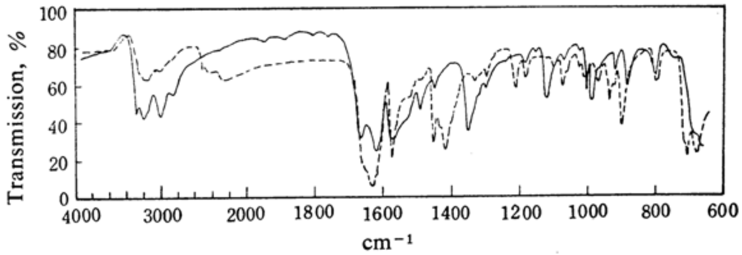

Fig. 3. Infrared spectra of $C_6H_5CONH_2$, ——, and $C_6H_5COND_2$, ----, in KBr disks.

In fact, CAA has two weak bands at 2930 and 2760 cm^{-1} which are probably to be ascribed to the $\nu(CH_2)$ vibrations.

The 2250 cm^{-1} band of CAA is surely to be assigned to the $\nu(C\equiv N)$ vibration because CAA-d_2 has a corresponding band at 2260 cm^{-1}, which is observed as a shoulder band accompanied by the band at 2350 cm^{-1}.

The 1700～700 cm^{-1} Region. — In this region the amide bands and NH_2 deformation bands are expected to appear. In primary amides the amide I band has been obtained near 1650 cm^{-1} [5]. CAA has also the amide I band at 1675 cm^{-1} (solid) and 1703 cm^{-1} (in acetonitrile). The band corresponding to it is shown at 1655 cm^{-1} in CAA-d_2. The 1615 cm^{-1} band of CAA disappears on *N*-deuteration, and CAA in acetonitrile has also a corresponding band at 1618 cm^{-1}. Suzuki[7] has shown that the 1632 cm^{-1} band of CH_3CONH_2 is mainly associated with the NH_2 bending vibration and that the 1189 cm^{-1} band of CH_3COND_2 is to be assigned to an almost pure ND_2 bending vibration. He[6] has also obtained the pure $\beta(NH_2)$ band at 1608 cm^{-1} for $HCONH_2$ and the $\beta(ND_2)$ band at 1118 cm^{-1} for $HCOND_2$. CAA-d_2 has the band at 1100 cm^{-1} instead of the 1615 cm^{-1} band of CAA. Therefore, the 1615 cm^{-1} band is undoubtedly assigned to be to the $\beta(NH_2)$ vibration and the 1100 cm^{-1} band of CAA-d_2, to the $\beta(ND_2)$.

Primary amides usually have a moderately strong band in the 1420～1400 cm^{-1} range[5]. For CH_3CONH_2[7] the 1404 cm^{-1} band was ascribed to the C–N stretching vibration (ν(C–N)) interacting with other kinds of normal vibrations. In CH_3COND_2 the ν(C–N) band moves to a higher frequency and appears at 1427 cm^{-1}. The ν(C–N) band has been obtained at 1309 cm^{-1} for $HCONH_2$ and 1338 cm^{-1} for $HCOND_2$[6]. It is noticeable that a frequency shift of the ν(C–N) band of $HCONH_2$ and CH_3CONH_2 on *N*-deuteration is in the direction shown by the corresponding shift of the ν(C–N) band for urea[8] and oxamide[9], as is summarized in Table III. CAA has two strong bands at 1408 and 1378 (more intense) cm^{-1}. One of them is considered to be due to the CH_2 bending vibration, $\beta(CH_2)$. Cyanoacetylhydrazine[2] has the $\beta(CH_2)$ band at 1396 cm^{-1}, which is rather closer in frequency to the 1408 cm^{-1} band than to the 1378 cm^{-1} band of CAA. Therefore, the 1408 cm^{-1} band is considered to be assigned to the $\beta(CH_2)$ vibration, and the 1378 cm^{-1} band may be assigned to the ν(C–N) vibration. On the other hand, CAA-d_2 has a relatively broad and intense band with its absorption maximum near 1398 cm^{-1}. This band is considered as the ν(C–N) band overlapped by the $\beta(CH_2)$ band near 1400 cm^{-1}. In that case, the 1378 cm^{-1} band of CAA moves to a higher frequency on *N*-deuteration. This frequency shift is in accordance (in direction and value) with those of the ν(C–N) band of compounds containing the –$CONH_2$ group, as may be seen from Table III.

TABLE III. THE FREQUENCY SHIFT OF THE ν(C–N) BAND ON *N*-DEUTERATION

Compound	Frequency	Frequency shift
Urea[a]	1464	+26
Urea-d_4	1490	
Oxamide[b]	1348	+26
Oxamide-d_4	1374	
Formamide[c]	1309	+29
Formamide-d_2	1338	
Acetamide[d]	1404	+23
Acetamide-d_2	1427	
Cyanoacetic acid amide[e]	1378	+20
Cyanoacetic acid amide-d_2	1398	
Benzamide[e]	1408	+12
Benzamide-d_2	1415	

a) See Ref. 8
b) See Ref. 9
c) See Ref. 6
d) See Ref. 7
e) The present observations

---

8) A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, (1467 (1957).

9) 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).

CAA has a further intense band at 1259 cm^{-1} which is displaced by a band at 1016 cm^{-1} on *N*-deuteration. In an acetonitrile solution CAA has a corresponding band at 1264 cm^{-1}. For CH_3CONH_2[7] the NH_2 rocking vibration ($\gamma(NH_2)$), which interacts a little with the ν(C–N) vibration, has been found at 1152 cm^{-1}, while for CH_3COND_2 it has been shown that the $\gamma(ND_2)$ vibration takes part in both the 934 and 809 cm^{-1} bands. $HCONH_2$[6] has the $\gamma(NH_2)$ band at 1090 cm^{-1}, while $HCOND_2$ has the $\gamma(ND_2)$ band at 912 cm^{-1}. Therefore, the 1259 cm^{-1} band of CAA is considered to be assigned to the $\gamma(NH_2)$ vibration and the 1016 cm^{-1} band of CAA-d_2, to the $\gamma(ND_2)$ vibration.

Next the CH_2 deformation vibrations, except for the $\beta(CH_2)$ vibration already considered, must be assigned. For cyanoacetylhydrazine[2] the 1347, 1205 and 1009 cm^{-1} bands have been assigned, respectively, to the CH_2 wagging, twisting and rocking vibrations, $\omega(CH_2)$, $\tau(CH_2)$ and $\gamma(CH_2)$. CAA has three weak bands at 1320, 1197 and 972 cm^{-1} which are probably to be assigned, respectively, to the $\omega(CH_2)$, $\tau(CH_2)$ and $\gamma(CH_2)$ vibrations. For CAA-d_2 the $\omega(CH_2)$ and $\tau(CH_2)$ bands can not be observed. However, the $\gamma(CH_2)$ vibration of CAA-d_2 is considered to interact with the $\gamma(ND_2)$ vibration, and two bands appear at 953 and 1016 cm^{-1} assigned above to $\gamma(ND_2)$.

In the region below 930 cm^{-1} CAA has three moderately strong bands at 925, 851 and 787 cm^{-1}, and CAA-d_2 also has three bands, at 913, 848 and 731 cm^{-1}. Of these, two bands may be assigned to the C–C stretching vibrations which are expected to occur in CAA. The ν(C–C) band has been obtained at 874 cm^{-1} for CH_3CONH_2 and at 809 cm^{-1} for CH_3COND_2[7]. In cyanoacetylhydrazine[2] the 924 and 913 cm^{-1} bands were assigned to the ν(C–C) vibrations. The 925 and 851 cm^{-1} bands of CAA can, therefore, be assigned to the ν(C–C) vibrations. These assignments are supported by the fact that those band are little changed in frequency on *N*-deuteration.

The NH_2 wagging and twisting vibrations and skeletal deformation vibrations are not yet accounted for. In CH_3CONH_2[7] a broad band near 700 cm^{-1} was taken as the NH_2 wagging band overlapped with the NH_2 twisting band. $HCONH_2$[6] has the $\omega(NH_2)$ band at 750 cm^{-1}. The 787 cm^{-1} band of CAA is probably to be ascribed to the NH_2 wagging or twisting vibration because no band corresponding to it is observed for CAA-d_2. The 731 cm^{-1} band of CAA-d_2 is tentatively ascribed to the O=C–N deformation vibration, δ(O=C–N). However, this assignment is not certain because the δ(O=C–N) band has been found at 581 cm^{-1} for CH_3CONH_2[7] and 608 cm^{-1} for $HCONH_2$[6].

TABLE IV. INFRARED FREQUENCIES OF CAA AND THEIR ASSIGNMENTS

Assignment[a]	CAA Solid	CAA in CH_3CN	CAA-d_2
$\nu_a(NH_2)$	3330 (s)	3430	
	3260 (sh)	3320	
$\nu_s(NH_2)$	3140 (s)	3180	
$\nu(CH_2)$	2930 (w)	2920	
	2760 (vw)		
$\nu_a(ND_2)$			2505 (m)
$\nu_s(ND_2)$			2350 (m)
ν(C≡N)	2250 (w)		2260 (sh)
Amide I	1675 (vs)	1703	1655 (vs)
$\beta(NH_2)$	1615 (s)	1618	
$\beta(CH_2)$	1408 (s)		1398 (s)
ν(C–N)	1378 (s)		
$\omega(CH_2)$	1320 (w)		—
	1284 (vw)		
$\gamma(NH_2)$	1259 (s)	1264	
$\tau(CH_2)$	1197 (w)		—
	1165 (vw)		
	1076 (vw)		
$\beta(ND_2)$			1100 (m)
$\gamma(ND_2)$			1016 (m)
$\gamma(CH_2)$	972 (w)	964	953 (m)
ν(C–C)	925 (m)	920	913 (w)
ν(C–C)	851 (m)	842	848 (w)
$\omega(NH_2)$ or $\tau(NH_2)$	787 (m)	759	
δ(O=C–N)			731 (w)

a) ν; stretching, a; asymmetric, s; symmetric, β; bending, ω; wagging, γ; rocking, δ; in-plane deformation

The observed frequencies of CAA and their assignments are summarized in Table IV.

Benzamide (BA).—Weckherlin and Leuttke[10] observed the infrared spectrum of benzamide containing ^{15}N and aimed at defining the positions of those bands due to vibrations of the $-CONH_2$ group. In the present study the infrared spectrum of BA-d_2 was observed in the rock salt region*2. As has been mentioned already, the $-CONH_2$ vibrations may now be located rather easily.

The infrared spectrum of BA-d_2 is illustrated, along with that of BA, in Fig. 3. An assignment of the vibrations of an aromatic ring has been described already with those of BH (see Table I). In a previous paper[1] the 1656 and 1623 cm^{-1} bands of BA were taken as the amide I and the NH_2 bending bands respectively. These assignments are also supported

---

[10] S. Weckherlin and W. Leuttke, *Z. Elektrochem.*, **64**, 1228 (1960).

*2 The spectrum of BA has been published by the present author (see Ref. 1).

by the present observation for BA-d_2. BA-d_2 shows a very strong band at 1629 cm^{-1} which is surely to be ascribed to the amide I band. On the other hand, the 1623 cm^{-1} band of BH disappears on *N*-deuteration; instead of it, BA-d_2 has a new band at 1209 cm^{-1}, the ν_H/ν_D ratio being 1.342. They correspond in frequency, respectively, to the 1631 cm^{-1} band for CH_3CONH_2[7] and 1189 cm^{-1} band for CH_3COND_2[7]. The 1403 cm^{-1} band of BA shifts to 1415 cm^{-1} on *N*-deuteration. From a consideration similar to the foregoing (see Table III also), they are undoubtedly to be assigned to the ν(C–N) vibration.

BA has two moderately strong bands at 1142 and 1124 cm^{-1}, both of which vanish on *N*-deuteration. Of these, the former band has already been ascribed to the δ(C–H) vibration of an aromatic ring. The latter band may be assigned to the $\gamma(NH_2)$ vibration, because it is close in frequency to the $\gamma(NH_2)$ band at 1152 cm^{-1} for CH_3CONH_2[7]. In BA-d_2 the moderately strong band at 936 cm^{-1} is considered to correspond to the 1124 cm^{-1} band of BA, the ν_H/ν_D ratio being 1.201. The 936 cm^{-1} band of BA-d_2 is very close in frequency to the 934 cm^{-1} band of CH_3COND_2[7], which has been assigned to the $\gamma(ND_2)$ vibration interacting with the ν(C–N) vibration and others. Thus, the 936 cm^{-1} band can probably be assigned to the $\gamma(ND_2)$ vibration. The relatively strong band at 1142 cm^{-1} may be considered to arise from the δ(C–H) vibration resonating with the $\gamma(NH_2)$ vibration. Owing to the fact that the $\gamma(NH_2)$ frequency decreases in value on *N*-deuteration, the δ(C–H) band is considered to be so weakened that we can not define its position.

For BA two moderately strong bands, which vanish on *N*-deuteration, are found at 793 (more intense) and 770 cm^{-1}. One of the two bands may be assigned to the $\omega(NH_2)$ or $\tau(NH_2)$ vibration because the corresponding band has been obtained at 750 cm^{-1} for $HCONH_2$[6] and at 700 cm^{-1} for CH_3CONH_2[7]. Another band is considered to arise from one of the vibrations of an aromatic ring. In the region below 820 cm^{-1}, BA has two further bands at 811 and 705 cm^{-1}. These two bands are very close in frequency to the 801 and 690 cm^{-1} bands of BH; accordingly, they can probably be ascribed to the vibrations of an aromatic ring. In addition to these BH has a band, which is due to an aromatic ring vibration, at 747 cm^{-1}. This band is rather closer in frequency to the 770 cm^{-1} band than to the 793 cm^{-1} band of BA. Therefore, the 793 cm^{-1} band is tentatively taken as the $\omega(NH_2)$ or $\tau(NH_2)$ band. BA-d_2 has three bands, at 801, 713 and 691 cm^{-1}, and BA in an acetonitrile solution[*3] has corresponding bands at 805, 720 and 695 cm^{-1}. These three bands can probably be ascribed to the aromatic ring vibrations. BA in acetonitrile has a further band at 755 cm^{-1} which is probably to be assigned to the $\omega(NH_2)$ or $\tau(NH_2)$ vibration. The change in frequency on the change of states (793 to 755 cm^{-1}) is in the right direction for NH_2 deformation vibrations.

In the 3000 cm^{-1} region BA has two intense bands, at 3330 and 3140 cm^{-1}, which are displaced by the bands at 2525 and 2280 cm^{-1} on *N*-deuteration. Therefore, they can surely be assigned to the $\nu_a(NH_2)$ and $\nu_s(NH_2)$ vibrations respectively. A shoulder band at 3050 cm^{-1} and a weak band at 2760 cm^{-1} are scarcely changed in frequency on *N*-deuteration. These two bands are assigned to the aromatic ν(C–H)

TABLE V. INFRARED FREQUENCIES OF BA AND BA-d_2 IN THE ROCK SALT REGION

Assignment[a]	BA	BA-d_2
$\nu_a(NH_2)$	3330 (vs)	
$\nu_s(NH_2)$	3140 (vs)	
ν(CH)	3050 (sh)	3050 (w)
	2760 (sh)	2760 (vw)
$\nu_a(ND_2)$		2525 (s)
$\nu_s(ND_2)$		2280 (bw)
Amide I	1656 (vs)	1629 (vs)
$\beta(NH_2)$	1623 (s)	
ν(C–C)	1578 (s)	1574 (s)
		1563 (sh)
ν(C–C)	1497 (vw)	1497 (w)
ν(C–C)	1451 (m)	1452 (m)
	1334 (vw)	1342 (vw)
δ(C–H)	1296 (m)	1296 (w)
	1245 (w)	1237 (vw)
$\beta(ND_2)$		1209 (w)
δ(C–H)	1180 (w)	1178 (w)
δ(C–H)	1142 (m)	—
$\gamma(NH_2)$	1124 (m)	
δ(C–H)	1073 (w)	1074 (w)
δ(C–H)	1024 (m)	1024 (w)
	999 (w)	1000 (vw)
π(C–H)	987 (vw)	987 (vw)
π(C–H)	917 (vw)	924 (vw)
$\gamma(ND_2)$		936 (m)
π(C–H)	848 (w)	847 (vw)
	811 (w)	801 (w)
$\omega(NH_2)$ or $\tau(NH_2)$	793 (m)	
	770 (m)	
		738 (w)
	705 (m)	713 (s)
		691 (m)

a) ν; stretching, a; asymmetric, s; symmetric, β; bending, δ; in-plane deformation, γ; rocking, π; out-of-plane deformation, ω; wagging, τ; twisting

---

[*3] The spectrum of BA in acetonitrile has been published in a previous paper (see Ref. 1).

TABLE VI. FREQUENCIES CHARACTERISTIC TO THE $-CONH_2$ GROUP (in the 1700～700 cm^{-1} region)

Compound	ν(C=O)	$\beta(NH_2)$	ν(C-N)	$\gamma(NH_2)$	$\omega(NH_2)$ or $\tau(NH_2)$
$HCONH_2$[a]	1690	1608	1309	1090	750
CH_3CONH_2[b]	1675	1631	1404	1152	700
$CNCH_2CONH_2$[c]	1675	1615	1378	1259	787
$C_6H_5CONH_2$[c]	1656	1623	1403	1124	793

a) See Ref. 6 b) See Ref. 7 c) Present observations

vibrations. The observed frequencies of BA and their assignments are summarized in Table V.

The present assignments for BA are in conformity with those proposed by Weckherlin and Leuttke[10] except for a few points.

Frequencies Characteristic of the $-CONHNH_2$ and $-CONH_2$ Groups. — For compounds containing the $-CONHNH_2$ group, the present author[2,3] has observed the infrared absorption spectra in the rock salt region and the frequencies characteristic of the group have been proposed. In the 1700～800 cm^{-1} region, a part of the -CONH- in the $-CONHNH_2$ group shows the amide I, II and III bands and a part of the NH_2- shows four bands due to the deformation vibrations. As has already been described in the present paper, BH also has the amide I, II and III bands at 1664, 1527 and 1250 cm^{-1} and the NH_2 deformation bands at 1618, 1349, 1118 and 987 cm^{-1}. These seven frequencies can, with confidence, be taken as characteristic of the $-CONHNH_2$ group. Of these, the amide I, II and III frequencies are within the normal ranges for the corresponding frequencies in secondary amides. On the other hand, four NH_2 deformation frequencies have been found in the 1635～1600, 1365～1260, 1180～1050 and 1050～800 cm^{-1} ranges for the ten compounds hitherto examined by the present author[*4].

Spectroscopic investigations of primary amides have been reported by many workers[5], but the vibrations of the $-CONH_2$ group have not yet been located definitely. In recent years, infrared measurements and the calculation of normal vibrations have been made for formamide and acetamide by Suzuki[6,7]. On the basis of the results of Suzuki's studies, the infrared spectra of CAA and BA were rather easily interpreted in the present paper. The frequencies characteristic of the $-CONH_2$ group may now be obtained with certainty. They are summarized in Table VI for frequencies in the 1700～700 cm^{-1} region. It may be seen from the table that the NH_2 deformation frequencies of the $-CONH_2$ group lie in the 1630～1600 (bending), 1150～1090 (rocking) and 800～700 (wagging or twisting) cm^{-1} ranges.

A comparison of the NH_2 deformation frequencies shows that the compounds containing the $-CONHNH_2$ group have a band in the 1365～1260 cm^{-1} range which is not shown by the compounds containing the planar $-CONH_2$ group. This band is close in frequency to the non-planar NH_2 twisting band which has been found at 1320 cm^{-1} for solid hydrazine[11] and at 1455 cm^{-1} for methylamine vapor[12]. Therefore, that band can very probably be ascribed to the NH_2 twisting vibration which is expected for the NH_2 group, being in a pyramidal form. A band observed in the 1635～1600 cm^{-1} range may be ascribed to the NH_2 bending vibration. It is noteworthy that the NH_2 bending band is shown in that region both by compounds containing the non-planar NH_2 group and by those containing the planar NH_2 group.

The author is grateful to Professor Sunao Imanishi of Kyushu University for his generous permission to use the spectrophotometer, and to Dr. Yoshiya Kanda of Kyushu University for his encouragement throughout the work. He is also indebted to the Ministry of Education for financial support.

Department of Literature and Science
Saga University
Saga

[*4] For spectroscopic data, see Ref. 2 and Ref. 3.

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

[12] A. P. Gray and R. C. Lord, ibid., **26**, 690 (1957); A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **80**, 1105 (1959).