Infrared Absorption Spectra of Hydrazides. I. Hydrazides of Aromatic Acids

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The infrared absorption spectra of a number of mono-substituted amides and their related compounds have been studied[1], and the characteristic bands of mono-substituted amides have been reported on in detail[2]. Bands amide I, amide II and amide III in the rock salt region have been associated with CONH group of non-cyclic secondary amides. Amide frequencies of difomylhydrozine[2,3] and diacetylhydrazine[2,4] have recently been studied, and amide I and amide II bands have been observed to shift abnormally to the lower frequencies in the spectra of these hydrazides. However, the number of the hydrazides examined has been rather limited. The aim of the present study is to examine in detail the amide bands of various aromatic hydrazides containing a CONHNHCO group.

Experimental

Acetylbenzoylhydrazine was synthesized with acetic anhydride and benzoylhydrazine[5] and purified by recrystallization from ethanol, m. p. 171°C. Benzoylhydrazine was prepared with ethylbenzoate and hydrazine hydrate[6] and purified by recrystallization from benzene, m. p. 111°C. Trichloroacetylbenzoylhydrazine was synthesized with trichloroacetylchloride and benzoylhydrazine[7] and purified by recrystallization from benzene, m. p. 164°C. Dibenzoylhydrazine was synthesized with benzoylchloride and hydrazine hydrate[8] and purified by recrystallization from ethanol, m. p. 238°C. Benzamide was prepared by recrystallization of the material of G. R. grade from ethanol, m. p. 130°C. *N*-Deuterated derivatives examined were prepared in sealed tubes in the presence of heavy water (99.8%). The excess of heavy water was evaporated in vacuo.

The spectra of hydrazides which were insoluble in non-polar solvents, such as carbon disulfide and carbon tetrachloride, were obtained with acetonitrile as a solvent and cells of 0.1 mm. in the optical path. The solid spectra of all compounds were studied with potassium bromide disk. A double-beam Hitachi infrared spectrophotometer Type EPI-2 was used in the rock salt region.

Results and Discussion

Acetylbenzoylhydrazine (ABH).—The infrared absorption spectra of ABH are given in Fig. 1, in which a solid curve shows the solid spectrum, a dotted curve, the solution spectrum and a dashed curve, the spectrum of *N*-deuterated ABH (ABH-d_2) in the solid state. The solution spectrum of ABH was obtained with a saturated solution (ca. 0.1 mol./l.) in acetonitrile.

The 3000 cm^{-1} Region. — Two strong bands were found at 3180 and 3000 cm^{-1} in the spectrum of solid ABH. Probably an ABH molecule is planar in the solid state, and the two

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1) See, for instance, L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Company, Ltd., London (1954).

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

3) 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, *J. prakt. Chem.*, [2] **50**, 280 (1894).

6) T. Curtius, ibid., [2] **50**, 278 (1894).

7) L. Spiegel and P. Spiegel, *Ber.*, **40**, 1739 (1907).

8) R. Stolle and A. Benrath, *J. prakt. Chem.*, [2] **70**, 268 (1904).

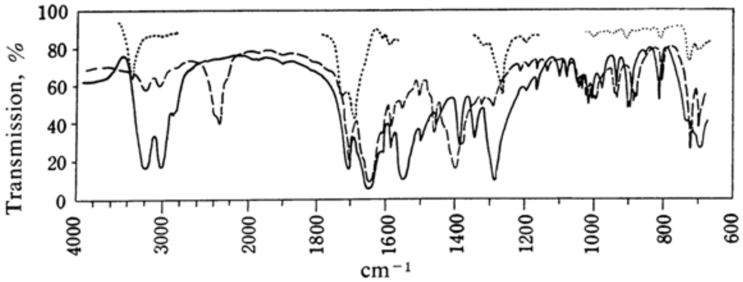

Fig. 1. Infrared absorption spectra of ABH in the rock salt region. The solid curve indicates the solid spectrum, the dotted curve partly represented is the solution spectrum of ABH (0.1 mol./l., 0.1 mm. cell), and the dashed curve shows the spectrum of ABH-d$_2$ in the solid state.

frequencies can be ascribed to the N–H stretching vibration. The abnormally low frequencies for the N–H vibration may be attributed to the coupling between two N–H vibrations in the CONHNHCO group of point group C_{2h}. On the other hand, only one band at 3320 cm^{-1} was found in this region for the solution spectrum. Probably the molecule is nonplanar in the solution, and the increase in frequency in the solution spectrum may be due to a decrease in the interaction between the two N–H vibrations. A band corresponding to them in the spectrum of *N*-deuterated ABH was found at 2310 cm^{-1}, which band was accompanied by two shoulder bands near 2340 and 2380 cm^{-1}. They are assigned to ν(N–D). ABH also has two weak bands at 2860 and 2830 cm^{-1} which are assigned to ν(C–H). Bands corresponding to them are found at 2830 and 2800 cm^{-1} for ABH-d$_2$.

The 1700～1450 cm^{-1} Region.—ABH has two bands which must be ascribed to the C=O stretching vibration. They are 1707 and 1644 cm^{-1} in the solid spectrum and 1720 and 1683 cm^{-1} in the solution spectrum. ABH-d$_2$ has bands at 1697 and 1645 cm^{-1} corresponding to them. The splitting of ν(C=O) may be due to the interaction of two vibrations which are two related C=O groups. However, the frequencies are rather higher than those of the hydrazides studied already, i. e., at 1610 cm^{-1} for diformylhydrazine3) and 1597 cm^{-1} for diacetylhydrazine4) in the solid state. The bands of those frequencies are called amide I.

There was also a strong band at 1527 cm^{-1} in the solid spectrum of ABH ascribed to the amide II band. A band corresponding to it is found at 1393 cm^{-1} in the spectrum of ABH-d$_2$ and called amide II$'$ according to Miyazawa et al.2), the ratio ν_H/ν_D being 1.096. It was impossible to check this band in the solution spectrum because of interference by solvent absorption.

In this region two comparatively strong bands are also found at 1607 and 1582 cm^{-1} in the solid spectrum and at 1603 and 1583 cm^{-1} in the solution spectrum. Bands corresponding to them are found at 1607 and 1581 cm^{-1} in the solid ABH-d$_2$ spectrum. These bands can be assigned to aromatic ring vibrations. Two other bands are found at 1493 and 1450 cm^{-1} in the spectrum of ABH and are also ascribed to aromatic ring vibrations. In the spectrum of ABH-d$_2$ bands corresponding to them are found at 1497 and 1453 cm^{-1} respectively.

The 1450～1200 cm^{-1} Region. — Deformation frequencies of a CH$_3$ group are expected to concern two bands in this region. In the spectrum of ABH a band at 1381 cm^{-1} may be taken as the symmetric vibration $\delta_s(CH_3)$ and a shoulder at 1442 cm^{-1} of the band at 1450 cm^{-1}, ν(aromatic C–C), is probably due to the asymmetric $\delta_{as}(CH_3)$. In the spectrum of ABH-d$_2$ the corresponding bands are found at 1372 and near 1430 cm^{-1}, which are both observed as shoulders on the low- and high-frequency sides of the 1393 cm^{-1} band, amide II$'$.

The most intense band at 1281 cm^{-1} in this region of the solid spectrum is assigned to the amide III band. A relatively weak band at 1337 cm^{-1} is also probably an amide III. Two bands corresponding to them are found at 1256 and 1313 cm^{-1} in the solution spectrum. The splitting of amide III may be due to coupling between two N–H vibrations; this finding is in accordance with that discussed already in connection with the N–H stretching frequencies.

The 1200～690 cm^{-1} Region. — Owing to the complexity of the spectral pattern in this region, the observed bands will be assigned through a comparison of the spectrum with those of related compounds. Strong and relatively weak bands have been found in this region in the spectra of aromatic compounds; the strong bands may generally be ascribed to the out-of-plane C–H deformation vibrations. In the solid ABH spectrum the most intense

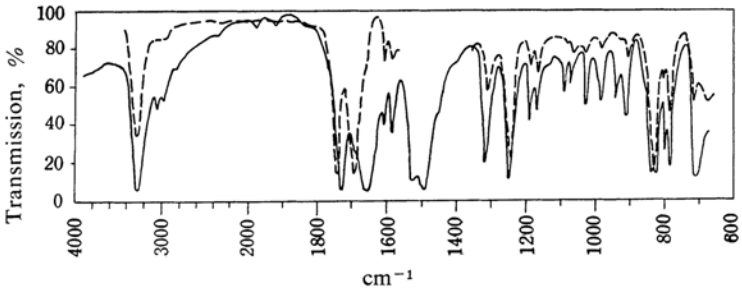

Fig. 2. Infrared absorption spectra of TCABH in the solid state (solid curve) and in a 0.2 mol./l. solution (dashed curve).

band in this region is found at 687 cm^{-1}, which band is accompanied by two well-defined shoulders at 702 and 724 cm^{-1}. ABH in solution has two bands at 691 and 717 cm^{-1}, while ABH-d$_2$ has them at 691 and 715 cm^{-1}. Since these frequencies are, in general, within or near the range of 700 ± 10 cm^{-1}[1], the two bands can be attributed to the out-of-plane C–H deformation vibrations.

The out-of-plane C–H deformation vibrations of the mono-substituted benzene ring give rise to another band generally within the range $770\sim730$ cm^{-1}[1]. Kross et al.[9] studied the influence of substituents of mono-substituted benzene on the positions of the C–H deformation bands and pointed out that the introduction of electrophilic substituents tends to increase the C–H band in frequency. A band at 803 cm^{-1} of the ABH spectrum can, therefore, be attributed to the C–H out-of-plane vibration. A band corresponding to it is found at 794 cm^{-1} in the ABH-d$_2$ spectrum.

Other relatively weak bands in this region can not be interpreted with confidence because of the complexity of the spectrum.

Trichloroacetylbenzoylhydrazine (TCABH).—The infrared absorption spectrum of TCABH was studied in the rock salt region in the solid state and in a solution in acetonitrile (0.2 mol./l.). The spectra obtained are illustrated in Fig. 2.

In the solid spectrum TCABH has a band 3280 cm^{-1} which lies in the range $3320\sim3270$ cm^{-1} characteristic to ν(N–H) of many secondary amides[1], and the band can surely be ascribed to ν(N–H). Its appearence as a single band might depend on a decrease in the interaction between two N–H stretching vibrations. However, it must be pointed out that the ν(N–H) frequency does not change in value in the solution spectrum. That is one of the characteristics of the TCABH spectrum different from the ABH spectrum shown in Fig. 1.

TCABH has its amide I bands at 1731 and 1658 cm^{-1} in the solid spectrum and at 1742 and 1694 cm^{-1} in the solution spectrum. This suggests that there is a coupling between two C=O stretching vibrations. It is very interesting to compare the amide I frequencies with those of ABH. The amide I frequencies are collected in Table II. An increase of ν(C=O) due to α-halogen substitution of organic acids has been found to be of the order of 20 cm^{-1}[1]. Such an increase in ν(C=O) is also observed here, e. g., for the higher frequency band of amide I an increase by 24 cm^{-1} is seen between the solid spectra of TCABH and ABH and an increase by 22 cm^{-1} between their solution spectra.

Let us consider next the effect of solvent on the splitting of the amide I band. In the case of ABH the spacing of the splitting is 63 cm^{-1} in the solid and 37 cm^{-1} in solution, and that for TCABH is found to be 73 cm^{-1} in the solid and 48 cm^{-1} in solution. The differences between the values of the splitting in the solid state and solution are, accordingly, relatively very close, i. e., about 25 cm^{-1}. Although obtaining nearly the same values in the splitting of the amide I bands of ABH and TCABH may be accidental because of the different environments of the molecules in the crystalline state and in solution, the phenomenon seems to be worth describing here.

Two bands corresponding to the amide II bands are observed at 1524 and 1492 cm^{-1} in the solid spectrum, and, accordingly, the coupling between two C–N stretching frequencies must be taken into account, although the doublet splitting of amide II was not seen in the ABH spectrum. In solution no amide II band was observed because of interference by the absorption of solvent.

Furthermore, the splitting of the amide III band is also observed; i. e., two bands appear at 1317 and 1248 cm^{-1} in the solid spectrum and at 1305 and 1241 cm^{-1} in the solution spectrum. Thus, it can easily be concluded

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

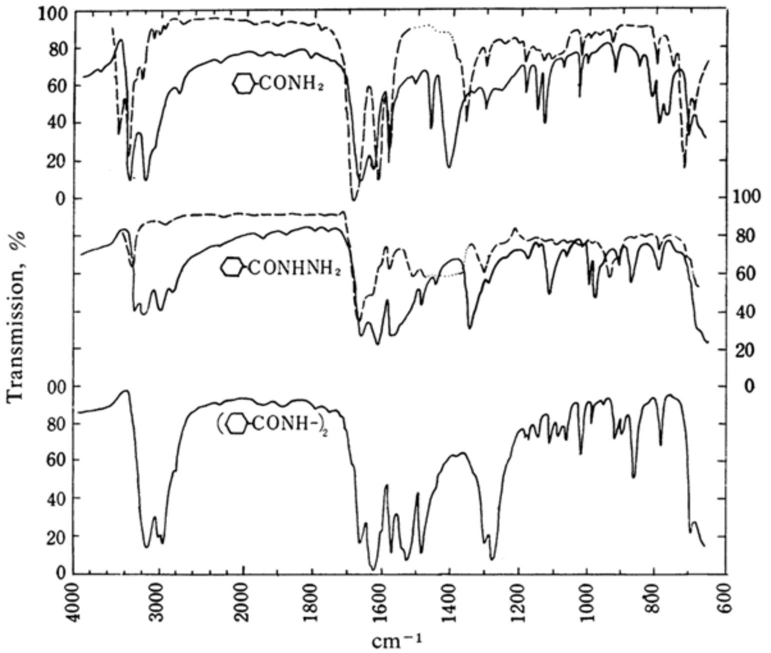


Fig. 3. Infrared absorption spectra of hydrazides and benzamide. The solid curves indicate the solid spectra in KBr disk, and the dashed curves show the solution spectra in acetonitrile.

that there is also a coupling between the two amide III frequencies of the CONHNHCO group.

In the solid spectrum TCABH has a very intense band with two peaks at 835 and 824 cm^{-1}, and a band corresponding to it is found at 827 cm^{-1} in the solution spectrum. This band may be due to the C–Cl stretching frequencies since no corresponding band is observed in the ABH spectrum, as is indicated in Fig. 1.

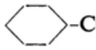
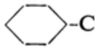
Other bands, especially due to vibrations of the aromatic ring, will be considered in the next section.

Dibenzoylhydrazine (DBH) and Relating Compounds. — The infrared absorption spectra of DBH and its related compounds are shown in Fig. 3, in which solid curves show the solid spectra and dashed curves indicate the solution spectra. The solution spectrum of DBH could not be observed because no appropriate solvent was found.

The 3000 cm^{-1} Region.—DBH has two intense bands at 3170 and 2980 cm^{-1} which may be assigned to N–H vibrations analogous to the bands at 3180 and 3000 cm^{-1} of ABH mentioned already. In the solid state benzamide also has two absorption bands of an NH_2 group at 3330 and 3140 cm^{-1}, to which correspond two bands at 3460 and 3350 cm^{-1} in the solution spectrum. These bands are naturally due to the asymmetric and symmetric N–H stretching frequencies. On the other hand, benzoylhydrazine (BH) has three bands at 3280, 3180 and 3010 cm^{-1}, of which the latter two bands have nearly the same frequencies as those of DBH and ABH. Moreover, it is interesting to see that only one band, at 3350 cm^{-1}, in the solution spectrum of BH corresponds to those three NH bands. The primary amides having an NH_2 group indicate generally two bands in the solid state and in solution1). They are also found in the benzamide absorption, while BH containing an NH_2 group adjacent to the CONH group has the three bands as mentioned above. It is impossible to give a reasonable interpretation for such a feature of ν(N–H) of BH without further observations, but the following explanation may tentatively be presented. In the solid state at least two of the three NH vibrations of BH may interact with each other, and hence bands similar to those of DBH and ABH may appear. The coupling between the two N–H vibrations decreases in solution, and hence BH has only one N–H band. The N–H stretching frequencies of the hydrazides and their related compounds are collhcted in Table I.

Other relatively weak bands in this region probably are due to C–H stretching frequencies, but their full assignment can not yet be completely given.

TABLE I. ν(N-H) VALUES IN cm^{-1}

Molecule	Solid	In CH_3CN
 $-CONHNHCOCl_3$	3280, 3050	3280
 $-CONHNHCOCH_3$	3180, 3000	3320
 $-CONH-)_2$	3170, 2980	—
 $-CONHNH_2$	3280, 3180, 3010	3350
 $-CONH_2$	3340, 3140	3460, 3350

The Amide Frequencies. — DBH has bands at 1669 and 1636 cm^{-1}. Although DBH is examined only in the solid state, these two bands may be ascribed to C=O stretching frequencies (amide I) by comparison of the solid spectrum with those of TCABH and ABH.

Benzamide also has two bands at 1656 and 1623 cm^{-1} in the solid spectrum, while in the solution spectrum, bands corresponding to them are seen at 1682 and 1608 cm^{-1}. The 1656 cm^{-1} band is assigned to an amide I, and the 1623 cm^{-1} band to NH_2 deformation vibration.

In this region BH also has two bands at 1664 and 1618 cm^{-1} in the solid state, of which the latter is more intense, while in the solution spectrum a band at 1672 cm^{-1} is stronger than that at 1634 cm^{-1}. BH has an NH_2 group, and an NH_2 deformation vibration will give rise to a band near 1590 cm^{-1} as sustituted hydrazines[10]. In addition to it, an amide I band should also be found in this region. The 1664 cm^{-1} band of solid BH may correspond to the 1672 cm^{-1} band in solution, and, accordingly, it is probably due to the C=O vibration. On the other hand, the 1618 cm^{-1} band of solid BH probably corresponds to the 1634 cm^{-1} band in solution, but it is difficult to discuss its assignment from the present observation only. For instance, three absorption bands characteristic to mono-acid hydrazides in this region were reported by Jensen[11], and one of them was seen to appear at 1620 cm^{-1}. Moreover, a band of the same frequency was seen in solution.

DBH has a band at 1535 cm^{-1} which can undoubtedly be assigned to an amide II band since the frequency is very close to that of the corresponding band of ABH. This region of the spectrum of BH is complicated by bands due to the vibrations of the aromatic ring. Nevertheless, it is not difficult to find bands due to the ring vibrations by comparison of the spectrum with those of relating compounds. The ring absorption bands will soon be discussed. BH has an intense band at 1568 cm^{-1} which is accompanied by a band at 1527 cm^{-1}. In the solution spectrum a corresponding band may appear in the lower frequencies, but it would be impossible to observe it because of interference by solvent absorption.

DBH has bands at 1305 and 1285 cm^{-1} of which the latter is stronger, and they are both ascribed to amide III bands by comparison of frequencies and their relative intensities with those of the corresponding bands of ABH. This suggests that there also is the coupling of two identical vibrations of the CONHNHCO group. In the solid state BH has an intense band isolated at 1349 cm^{-1} which is higher than the amide III frequencies of secondary amides. The frequency value decreases to 1311 cm^{-1} in the solution spectrum. Benzamide has an intense absorption at 1403 cm^{-1}, while a band at 1356 cm^{-1} is considered to correspond to it in the solution spectrum. This frequency is within the range of 1420~1400 cm^{-1} in which many primary amides have bands of frequencies characteristic to them[1]. The amide frequencies shown by the hydrazides examined are collected in Table II. Frequencies of BH and benzamide similar in value to them are also indicated in the lower part on the table.

In order to ascertain the assignment of characteristic bands of these hydrazides, absorption bands due to the ring vibrations will be discussed. The identification of these bands was made by a comparison of the spectra of all materials examined.

Four bands produced by skeletal stretching vibrations are easily found in spite of the superposition of other strong absorption bands. They lie near 1600, 1580, 1500 and 1450 cm^{-1}, as usually found in ordinary aromatic compounds[1]. The intensity of the 1580 cm^{-1} band is seen to be enhanced in the spectra of the compounds examined. This fact is regarded as a positive indication[1] of the conjugation of the C=O bond with the aromatic ring.

Strong bands assigned to the out-of-plane C–H deformation vibrations are little difficult to detect if shifts of the bands to higher frequencies are taken into account. A band near

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[10] D. W. E. Axford, G. J. Janz and K. E. Russell, *J. Chem. Phys.*, **19**, 704 (1951); E. E. Shull, J. L. Wood, J. G. Aston and D. H. Rank, ibid., **22**, 1191 (1954).

[11] J. B. Jensen, *Acta Chem. Scand.*, **10**, 667 (1956).

TABLE II. AMIDE FREQUENCIES (in cm^{-1})

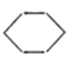
Molecule and state		Amide I	Amide II	Amide III
 -CONHNHCOCl$_3$	Solid In CH$_3$CN	1731, 1658 1742, 1694	1524, 1492 ——	1317, 1248 1305, 1241
 -CONHNHCOCH$_3$	Solid In CH$_3$CN	1707, 1644 1720, 1683	1527 ——	1337, 1281 1313, 1256
( -CONH-)$_2$	Solid	1669, 1636	1535	1305, 1285
 -CONHNH$_2$	Solid In CH$_3$CN	1664, 1618 1672, 1634	1568, 1527 ——	1349 1311
 -CONH$_2$	Solid In CH$_3$CN	1656, 1623 1682, 1608		1403 1356

TABLE III. FREQUENCIES DUE TO THE AROMATIC RING IN THE RANGE 1600~690 cm^{-1} a) (in cm^{-1})

Molecule	ν(Aromatic C-C) b)	π(C-H) b)
 -CONH$_2$	— 1578, 1497, 1451	811, 793, 770, 705
 -CONHNH$_2$	1608, 1582, 1492, 1450	801, 747, 190
( -CONH-)$_2$	1607, 1579, 1490, 1450	796, 707
 -CONHNHCOCH$_3$	1607, 1582, 1493, 1450	803, 724, 702, 687
 -CONDNDCOCH$_3$	1607, 1581, 1497, 1453	794, 715, 691
 -CONHNHCOCCl$_3$	1607, 1585, 1500, 1453	798, 783, 708

a) The values in the solid state. b) ν; stretching, π; out-of-plane deformation.

800 cm^{-1} is commonly found for all materials with a C=O group directly attached to the ring, as has been pointed out by Kross et al.[9]

The C-H in-plane deformation vibrations will concern bands in the range 1225~950 cm^{-1}, but they are not always found because of the superposion of many relatively weak bands in this region.

Characteristic Bands. — The features of the amide frequencies of the hydrazides of aromatic acids are summarized as follows: (1) The splitting of the C=O stretching vibration (amide I) is observed in both solid and solution spectra. The spacing of the splitting of these two frequencies depends on radicals attached to the CONHNHCO group. (2) The amide II absorption band is found on the lower frequency side of the normal range of the corresponding band of secondary amides. The splitting of the amide II frequency was observed for TCABH, but not for ABH and DBH. It is noteworthy that TCABH has a single N-H stretching absorption band, while ABH and DBH have two N-H bands each. (3) The splitting of the amide III absorption band is seen for all of the hydrazides examined in both solid and solution, as it is for amide I. The frequencies of these two bands are in the normal range 1305~1200 cm^{-1}, in which many secondary amides have their characteristic frequencies of vibrations[1].

Summary

The infrared absorption spectra of acetylbenzoylhydrazine, trichloroacetylbenzoylhydrazine and dibenzoylhydrazine have been studied in the rock salt region. The assignment of the amide frequencies characteristic to the hydrazides RCONHNHCOR′ and the coupling between vibrations due to two CONH groups have been discussed.

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