Infrared Absorption Spectra of Hydrazides. II. Sodium Hydrazides

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In a previous paper[1] amide frequencies of aromatic hydrazides have been studied. In the present study, the influence on the amide frequencies of the ionized group of $CONHNCO^-$ of the substitution for a hydrogen atom of a sodium ion will be discussed.

Experimental

Diformylhydrazine was synthesized with sodium formate and hydrazine sulfate[2] and purified by recrystallization from ethanol, m. p. 155°C. Diacetylhydrazine was prepared with acetic anhydride and hydrazine hydrate[3] and purified by recrystallization from ethanol, m. p. 137°C. The syntheses of acetylbenzoylhydrazine and dibenzoylhydrazine have been described previously[1]. Sodium salts of these hydrazides were obtained by heating their ethanol solutions with sodium ethoxide and repeatedly washing them with a large quantity of ethanol. The salts obtained were examined analytically*1. Calcd. for $HCONHNCOH \cdot Na$: C, 21.8; H, 2.75; N, 25.5; Na, 20.9%. Found: C, 22.4; H, 3.16; N, 22.6; Na, 22.0%. Calcd. for $CH_3 \cdot CONHNCOCH_3 \cdot Na$: C, 34.8; H, 5.1; N, 20.3; Na, 16.7%. Found: C, 34.6; H, 5.4; N, 20.0; Na, 17.3%. Calcd. for $CH_3CONHNCOC_6H_5 \cdot Na$: C, 54.0; H, 4.53; N, 14.0; Na, 11.5%. Found: C, 54.0; H, 4.68; N, 13.8; Na, 12.1%. Calcd. for $C_6H_5CONHNCOC_6H_5 \cdot Na$: C, 64.1; H, 4.23; N, 10.7; Na, 8.77%. Found: C, 61.8; H, 4.23; N, 10.3; Na, 8.44%. Deuterium-containing salts were prepared in sealed tubes in the presence of heavy water (99.8%), of which the excess was evaporated in vacuo after the exchange reaction. A Hitachi infrared spectrophotometer type EPI-2 with a rock salt prism was used throughout the work.

Results and Discussion

Sodium Diformylhydrazine (SDFH).—The infrared absorption spectrum of diformylhydrazine[4] was reasonably explaned with a model of a transplanar configuration. It may be assumed that an ion $(HCONHNCOH)^-$ also has a planar configuration. It has only one plane of symmetry of point group C_s, and all twenty-one ($3N-6$) fundamental modes will be active in the infrared. Of these, fifteen modes are of species A′ and six of species A″. Five of those will give rise to bands outside of the rock salt region. They may be torsional, τ(N–N), τ(C_1–N)*2 and τ(C_2–N) (species A″), and deformation vibrations, δ(C_1–N–N) and δ(C_2–N–N) (species A′), because the τ(N–N) frequency of NH_2NH_2 is 377 cm^{-1} [5], and the δ(C–N–N) frequency of CH_3NHNH_2 is 433^{-1} [6]. In consequence, sixteen bands are expected to appear in the rock salt region.

The infrared absorption spectra of SDFH and SDFH-d are illustrated in Fig. 1. Let us first consider the frequencies related to the C–H bond, such as bond stretching ν(C–H), in-plane bending δ(C–H) and out-of-plane bending π(C–H). For diformylhydrazine Miyazawa[4] obtained a ν(C–H) frequency of 2900 cm^{-1} and a δ(C–H) frequency of 1368 cm^{-1}, while no π(C–H) frequency was found. SDFH has bands at 2870 and 1357 cm^{-1} and, accordingly, they are ascribed to ν(C–H) and δ(C–H) respectively. Bands corresponding to them are found at 2870 and 1354 cm^{-1} in the SDFH-d spectrum, respectively. For the ion $(HCONHNCOH)^-$ twe bands may be expected to appear as ν(C–H) or δ(C–H). However, only a single band due to ν(C–H) was observed on the background of absorption. On the other hand, a band appears at 1380 cm^{-1} in the SDFH spectrum which may be assigned to δ(C–H), while a band corresponding to it is seen at 1378 cm^{-1} for SDFH-d. SDFH has two bands at 1026 and 974 cm^{-1} which are easily ascribed to π(C–H), because bands corresponding to them were obtained at 1050 cm^{-1} for formamide[7], 1037 cm^{-1} for formamidoxime[8] and 1015 cm^{-1} for *N*-methyl formamide[9].

Other vibrational modes involving a hydrogen atom will be ν(N–H), δ(N–H) and π(N–H).

1) M. Mashima, This Bulletin, 35, 332 (1962).
2) G. Peillizzari, *Gazz. chim. ital.*, 39, I, 529 (1909).
3) R. Stolle, *J. prakt. chem.*, [2] 69, 145 (1904).
*1 The analyses of C, H and N were made by the Elementary Analysis Centre of Kyushu University, the analysis of Na, by Mr. H. Waki, Faculty of Science, Kyushu University.
4) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 76, 341 (1955), and see also T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, 24, 408 (1956).

*2 For C_1 and C_2 see Fig. 2.
5) A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, 31, 843 (1959).
6) D. W. E. Axford, G. J. Janz and K. E. Russell, ibid., 19, 704 (1951).
7) J. C. Evans, ibid., 22, 1228 (1954).
8) W. J. Oriville-Thomas and A. E. Parsons, *Trans. Faraday Soc.*, 54, 460 (1958).
9) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 77, 171 (1957).

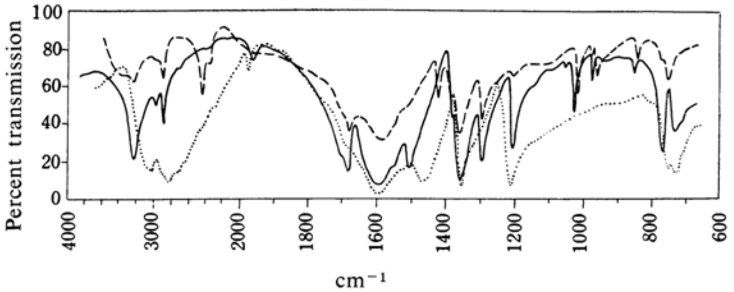

Fig. 1. Infrared absorption spectra of sodium diformylhydrazine (the solid curve), its *N*-deuterated derivative (the dashed curve) and diformylhydrazine (the dotted curve) in the solid state (KBr disk).

SDFH has a band at 3210 cm^{-1}, while a band at 2410 cm^{-1} corresponds to it in the spectrum of SDFH-d, the ratio ν_H/ν_D being 1.33. The band of 3210 cm^{-1} can, therefore, be easily assigned to ν(N-H). The identification of δ(N-H) will be considered later. The 785 cm^{-1} band of SDFH is not very different in frequency from the 770 cm^{-1} band of π(N-H) of diformylhydrazine[4], and, further no band corresponding to it is seen in the SDFH-d spectrum. It may, therefore, be taken as π(N-H).

Next the amide bands will be considered. In the range 1700~1200 cm^{-1} SDFH has bands at 1683, 1592, 1507, 1295, and 1202 cm^{-1} (except for the bands at 1380 and 1357 cm^{-1} which have already been ascribed to δ(C-H)). Three of the five bands scarcely change in frequency on *N*-deuteration; i. e., bands at 1676, 1588, and 1288 cm^{-1} in the spectrum of SDFH-d correspond to the bands at 1683, 1592, and 1295 cm^{-1} of SDFH respectively. On the other hand, two bands at 1417 and 955 cm^{-1} of SDFH-d correspond to the two remaining bands at 1507 and 1202 cm^{-1} respectively. Therefore, these two bands can be assigned without difficulty. The 1507 cm^{-1} band can be taken as an amide II band, because it is close in frequency to the corresponding bands of secondary amides, which generally show frequencies within 1570~1515 cm^{-1} [10]. Moreover, the wave number ratio is 1.063. This is close in value to 1.106 for diformylhydrazine[4]. The 1202 cm^{-1} band can be ascribed to an amide III band, the ratio ν_H/ν_D being 1.258, which is close to 1.248 for diformylhydrazine[4]. In addition to the amide II and amide III bands due to the CONH group of the ionized group $CONHNCO^-$, an amide I band will be expected to appear. It can be identified with the 1683 cm^{-1} band because the value of frequency is very close to the upper limit of the range 1680~1630 cm^{-1} in which many secondary amides have amide I frequencies. In consequence, the amide bands I, II, and III due to the CONH group are located in their own characteristic regions. It may, therefore, be concluded that the vibrations relating to the CONH group are not much influenced by an electronic charge stored in another part of the $CONHNCO^-$ group, and hence the NCO^- group probably has its own absorption frequencies. It is reasonable to expect that in the ion $(RCONHNCOR')^-$ there is a resonance between the two structures as indicated in Fig. 2. Therefore, absorptions due to the NCO^- group will be somewhat similar to those of the ionized group COO^-. The antisymmetrical and symmetrical vibrations of the COO^- structure concern two bands within the ranges 1610~1550 cm^{-1} and 1420~1300 cm^{-1} respectively[10]. In the range 1700~1200 cm^{-1} of SDFH two bands at 1592 and 1295 cm^{-1} remain to be assigned. We may ascribe the bands at 1592 and 1295 cm^{-1} to $\nu'(NCO^-)$ and $\nu''(NCO^-)$ respectively. The modes of vibrations of $\nu'(NCO^-)$ and $\nu''(NCO^-)$ may be assumed to be similar to those of ν_{as} and ν_s of a COO^- group respectively.

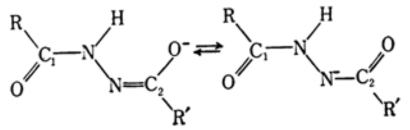

Fig. 2.

There remain three fundamentals unaccounted for, i. e., $\delta(O-C_1-N)$, $\delta(O-C_2-N)$, and ν(N-N). SDFH has a band at 731 cm^{-1} which can possibly be assigned to $\delta(O-C_1-N)$, because a band corresponding to it is observed at 753 cm^{-1} in the diformylhydrazine spectrum[4] and 746 cm^{-1} for SDFH-d. A ν(N-N) band was observed at 1100 cm^{-1} for HCONDNHCOH[4] and at 1165 cm^{-1} for $(CH_3CONH-)_2 \cdot H_2O$[11].

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

11) A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 880 (1958).

TABLE I. INFRARED FREQUENCIES OF Na·HCONHNCOH AND Na·HCONDNCOH IN THE ROCK SALT REGION (in cm^{-1})

Species	Mode	Na·HCONHNCOH	Na·HCONDNCOH	Wave number ratio ν_H/ν_D
A′	ν(N-H), ν(N-D)	3200	2410	1.336
	ν(C-H)	2870	2870	1.000
	Amide I	1683	1676	1.004
	$\nu'(NCO^-)$	1592	1588	1.003
	Amide II	1507	1417	1.092
	$\nu''(NCO^-)$	1295	1288	1.005
	Amide III	1202	955	1.259
	δ(C-H)	1380 1357	1378 1354	1.001 1.002
	ν(N-N)	(1000)	(1000)	
	$\delta(N-C_2-O)$	843	837	1.007
	$\delta(N-C_1-O)$	732	746	0.981
	$\delta(N-N-C_2)$			
	$\delta(N-N-C_1)$			
A′′	π(C-H)	1026 974	1012 973	1.014 1.001
	π(N-H)	767	—	
	$\tau(C_1-N)$			
	$\tau(C_2-N)$			
	τ(N-N)			

ν: stretching, δ: in-plane bending, π: out-of-plane bending, τ: torsional.
Values in parentheses are no exact ones.

SDFH and SDFH-d also have a band near 1100 cm^{-1}, but the definite frequency can not be determined because of its broad absorption pattern. Now, only one fundamental, $\delta(O-C_2-N)$, remains to be located. The 843 cm^{-1} band not yet interpreted may be ascribed to $\delta(O-C_2-N)$, a corresponding band being at 837 cm^{-1} for SDFH-d. The observed frequencies and their assignments are summarized in Table I.

In order to check the validity of these assignments, the Teller-Redlich product rule[12] is applied to the frequencies of species A′. The structure of $(HCONHNCOH)^-$ is not definitely determined, but the dimensions used in calculating moments of inertia are assumed as follows; for the HCONH-N part[4] N–H 1.00 Å, C–N 1.32 Å, C–O 1.21 Å, C–H 1.07 Å, N–N 1.38 Å, ∠C–N–N– 116°, ∠H–N–C 122°, ∠N–N–H 122°, ∠O–C–N 124°, ∠H–C–O 118°, ∠N–C–H 118°, for the HCON–N part C–N 1.21 Å, C–O 1.27 Å, C–H 1.07 Å, ∠N–N–C 118°, ∠H–C–O 118°, ∠N–C–O 124°. For the HCON the C–O distance and N–C–O angle are assumed to be equal to the C–O distance and O–C–O angle of sodium formate[13], and the C–N distance and N–N–C angle are chosen as equal to the C–N distance and H–N–C angle of HNCO[14]. In applying the product rule, it is assumed that the ratio ν_H/ν_D is 1.024*3 for δ(C–N–N) due to the HCONH–N part and that the values of δ(C–N–N) related to the HCONH–N part and ν(N–N) of SDFH-d are the same as those of SDFH. The observed product ratio is 0.530, while the calculated ratio is 0.509. Although the agreement is not very good, a much better value could be calculated if more reasonable estimates of the ratios of δ(C–N–N) and ν(N–N) could be made.

Sodium Diacetylhydrazine (SDAH). — The infrared absorption spectra of SDAH and SDAH-d in the solid state are shown in Fig. 3, in which the spectrum of diacetylhydrazine is also given for comparison. Let us chiefly consider the location of bands due to vibrations relating to the ionized group $CONHNCO^-$. SDAH has a band at 3290 cm^{-1} which is easily assigned to ν(N–H), while a band corresponding to it is at 2390 cm^{-1} for SDAH-d, the ratio ν_H/ν_D being 1.34.

A complicated spectral pattern is seen in the region of 1650∼1250 cm^{-1}, and bands in that region will reflect vibrations relating to the $CONHNCO^-$ and CH_3 groups. There are bands at 1656, 1552*4, 1513, 1428, 1392, 1339,

12) G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York (1947), p. 232.
13) W. H. Zachariasen, *Phys. Rev.*, 53, 917 (1938).
14) L. H. Jones, J. N. Shooler, R. G. Shulman and D. M. Yost, *J. Chem. Phys.*, 18, 990 (1950).
*3 It was postulated by Miyazawa (Ref. 3).
*4 This is a mean value of the two peak frequencies at 1563 and 1541 cm^{-1}.

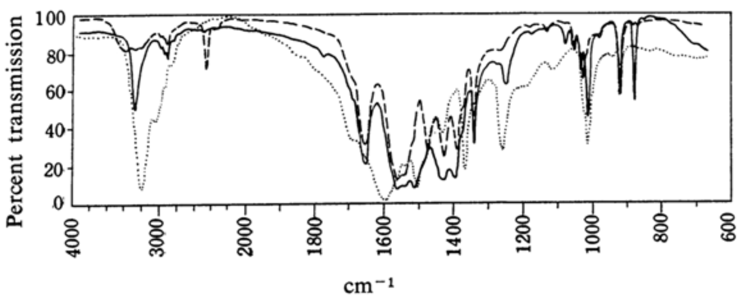

Fig. 3. Infrared absorption spectra of sodium diacetylhydrazine (the solid curve), its *N*-deuterated derivative (the dashed curve), and diacetylhydrazine (the dotted curve) in KBr disk.

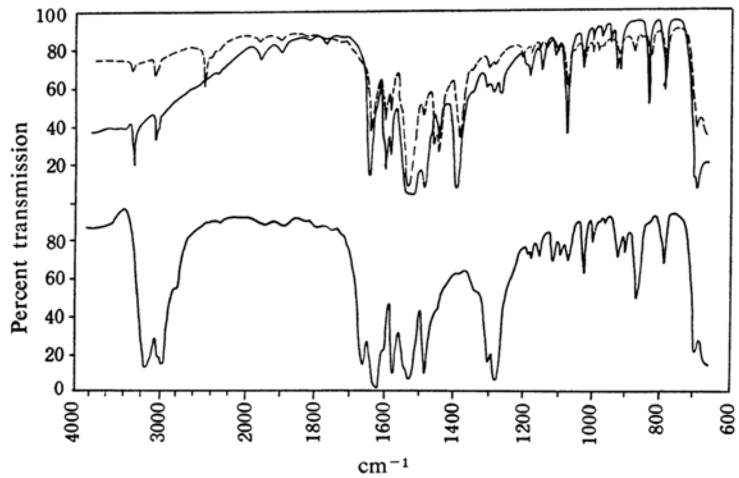

Fig. 4. Infrared absorption spectra of sodium dibenzoylhydrazine (the upper solid curve), its *N*-deuterated derivative (the dashed curve) and dibenzoylhydrazine (the lower solid curve) in KBr disk.

and 1249 cm^{-1} for SDAH. Of these seven bands the 1513 cm^{-1} band seems to correspond to a band at 1473 cm^{-1} of the SDAH-d spectrum, while the 1249 cm^{-1} band has no counterpart in the SDAH-d spectrum. The former is very close in frequency to the amide II band at 1506 cm^{-1} for diacetylhydrazine[11], and hence it may be taken as the amide II band relating to the CONH group of the ion $(CH_3CONHNCOCH_3)^-$. The latter may be taken as the amide III band of the CONH group because a band corresponding to it was found at 1260 cm^{-1} for diacetylhydrazine[11].

On the other hand, the five remaining bands of SDAH have respective counterparts of nearly the same frequencies in the SDAH-d spectrum. Their assignments can be made by comparison of the SDAH spectrum with that of SDFH. The rather weak band at 1656 cm^{-1} corresponds to the 1683 cm^{-1} band of SDFH and, accordingly, may be ascribed to the C=O vibration relating to the CONH group. Although the occurrence of two peaks as indicated in the footnote is not reasonably explained the 1552 cm^{-1} band corresponds in frequency and especially in intensity to the 1592 cm^{-1} band of SDFH. In consequence, it is probably ascribed to ν' as mentioned in the previous section. Further, two bands at 1428 and 1392 cm^{-1} can be assigned to the asymmetrical and symmetrical CH_3 deformation vibrations respectively; a detailed assignment will be given in a later section. Only the 1339 cm^{-1} band is not yet accounted for in the region 1650～1250 cm^{-1}. It can probably be ascribed to ν'' of the NCO^- group like the 1295 cm^{-1} band of SDFH. This assignment is corroborated by the fact that no corresponding band has been observed for diacetylhydrazine[11].

Sodium Dibenzoylhydrazine (SDBH).—The infrared absorption spectra of SDBH and SDBH-d are shown in Fig. 4, the solid spectrum of dibenzoylhydrazine (DBH) is also given for comparison.

In the 3000 cm^{-1} region, SDBH has a band at 3290 cm^{-1} and a relatively weak band at

3030 cm^{-1}. The former is within the normal range 3320~3270 cm^{-1} of secondary amides[10], and a band corresponding to it is found at 2480 cm^{-1} in the SDBH-d spectrum. Therefore, the 3290 cm^{-1} and 2480 cm^{-1} bands are ascribed to ν(N–H) and ν(N–D) respectively, the ratio ν_H/ν_D being 1.326. The 3030 cm^{-1} band can be attributed to the aromatic C–H stretching vibrations, because its corresponding band is seen at 3040 cm^{-1} in the SDBH-d spectrum. Since the ionized group $CONHCO^-$ has one N–H group, only a single N–H band is expected to appear. In fact, it is observed at 3290 cm^{-1}, as indicated above.

Next we will consider amide bands. As pointed out previously[1], DBH has amide I bands at 1669 and 1636 cm^{-1}, while SDBH has a band at 1637 cm^{-1} and a band of the same frequency is found in the SDBH-d spectrum. All the bands lie within the normal range (1680~1630 cm^{-1}) of the amide I band of the secondary amides. In consequence, the 1637 cm^{-1} band should be taken as the amide I band due to the CONH group of $CONHCO^-$.

The amide III absorption has also been found as two bands at 1302 cm^{-1} and 1285 cm^{-1} in the DBH spectrum[1], while SDBH has a band at 1264 cm^{-1} (very weak) and no corresponding band is seen in the SDBH-d spectrum. Therefore, the 1264 cm^{-1} band is taken as the amide III band of the CONH part of the $CONHCO^-$ group.

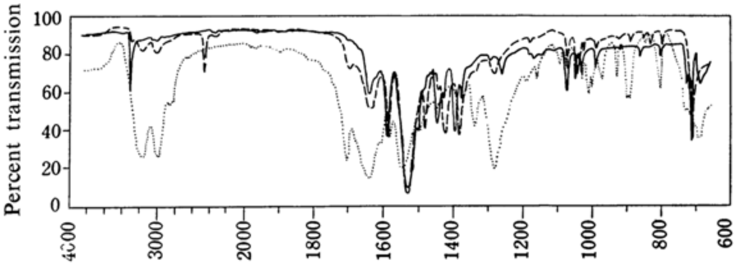

Fig. 5. Infrared absorption spectra of sodium acetylbenzoylhydrazine, its (solid curve), its *N*-deuterated derivative (dashed curve), and acetylbenzoylhydrazine (dotted curve) in KBr disk.

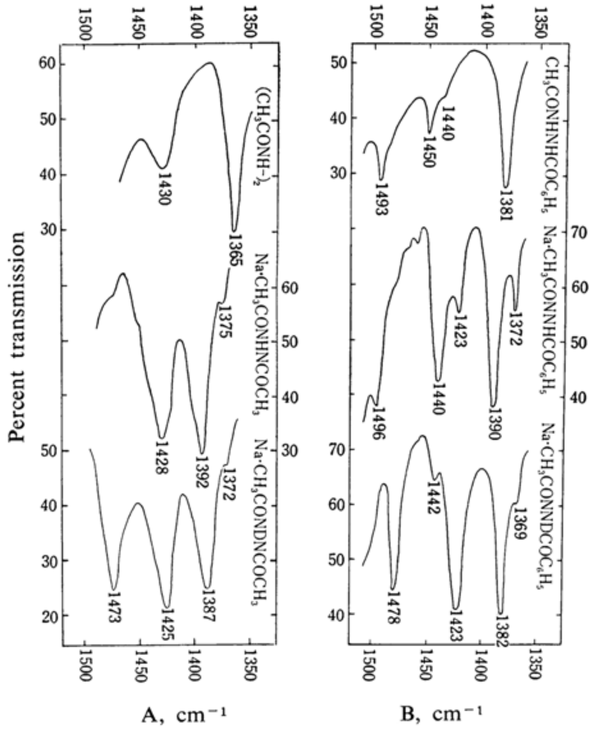

Fig. 6. Infrared spectra in the region of methyl bending vibrations.

The presence of the aromatic ring absorption in the 1600~1450 cm^{-1} region makes the spectrum much more complicated, but the amide bands in that region can be located without difficulty by comparison of the spectral patterns in Fig. 4 with each other. The 1535 cm^{-1} band of DBH[1] has been assigned to the amide II band. SDBH has a very strong absorption band at 1528 cm^{-1} and, further, a band at 1390 cm^{-1}, while SDBH-d has corresponding bands at 1527 and 1383 cm^{-1}. Moreover, a band at 1485 cm^{-1} of SDBH is too intense to be ascribed to an aromatic ring vibration of about 1500 cm^{-1} [10]. In the SDBH-d spectrum a relatively weak band at 1487 cm^{-1} may correspond to it, and in addition a band of 1442 cm^{-1} appears. Therefore, the 1485 cm^{-1} band of SDBH is ascribed to the amide II band of the CONH group. In consequence, both bands, at 1528 and 1390 cm^{-1} of SDBH, are ascribed to vibrations of the NCO^- group. They can probably be attributed to ν' and ν'', as indicated in the previous sections.

Sodium Acetylbenzoylhydrazine (SABH).— The infrared absorption spectra of SABH and SABH-d are illustrated in Fig. 5. The spectrum of acetylbenzoylhydrazine is also shown for comparison.

SABH has an isolated absorption band at 3300 cm^{-1} which can easily be assigned to ν(N–H). A corresponding band is located at 2460 cm^{-1} for *N*-deuterated SABH, the ratio ν_H/ν_D being 1.34.

The 1637 cm^{-1} band of SABH is in good accordance in frequency and in relative intensity with the 1637 cm^{-1} of SDBH assigned to the amide I. A corresponding band is found at 1638 cm^{-1} for SABH-d. Therefore, both bands are ascribed to the amide I band.

Acetylbenzoylhydrazine[1] has an amide III band at 1281 cm^{-1}. A corresponding band is seen at 1256 cm^{-1} in the spectrum of SABH, but it is very weak in intensity. In the SABH-d spectrum a band at 1046 cm^{-1} may correspond to it. Therefore, the 1256 cm^{-1} band of SABH is taken as the amide III absorption.

SABH shows the most intense band at 1527 cm^{-1} among its spectral bands. It is in good accordance with the 1528 cm^{-1} band of SDBH in frequency, and a band of the same frequency is seen for SABH-d similar to that of SDBH-d. Hence, it is ascribed to $\nu'(NCO^-)$ like the 1528 cm^{-1} band of SDBH. On the other hand, it is difficult to fix a band due to $\nu''(NCO^-)$. Since SABH has a methyl group, deformation vibrations of the methyl group give rise to bands generally in the region of 1500~1350 cm^{-1}, and, moreover, SABH may also have bands of $\nu''(NCO^-)$ and aromatic ring frequencies in that region. The infrared spectra in the region of methyl bending vibrations of diacetylhydrazine, SDAH, and SDAH-d are illustrated in Fig. 6A, while those of acetylbenzoylhydrazine, SABH, and SABH-d are given in Fig. 6B. Acetylbenzoylhydrazine[1] has a band at 1381 cm^{-1} which is undoubtedly due to $\delta_s(CH_3)$. However, SABH has bands corresponding to it at 1390 and 1372 cm^{-1}, and SABH-d has them at 1382 and 1369 cm^{-1}. Similar bands are also observed in the spectra of diacetylhydrazine and its sodium salt, as is shown in Fig. 6A. Diacetylhydrazine shows a band due to $\delta_s(CH_3)$ at 1365 cm^{-1}. Bands corresponding to it are observed at 1392 and 1375 cm^{-1} in the spectrum of SDAH and at 1387 and 1372 cm^{-1} of SDAH-d. In general, the bands due to $\delta_s(CH_3)$ appear at nearly the same position. In the spectrum of SABH appearances of two bands due to $\delta_s(CH_3)$ can not be interpreted with confidence. However, these two bands can probably be ascribed to $\delta_s(CH_3)$, since they are in good agreement in frequency and relative intensity with those of the spectra SABH, SABH-d, SDAH, and SDAH-d. The compounds containing a methyl group generally show another absorption band near 1460 cm^{-1} arising from the asymmetrical deformation $\delta_{as}(CH_3)$. Diacetylhydrazine shows a corresponding band at 1430 cm^{-1}. SDAH also has an absorption band at 1428 cm^{-1}, and SDAH-d, at 1425 cm^{-1}. On the other hand, it is difficult to locate a band of $\delta_{as}(CH_3)$ in the spectra of SABH and of SABH-d, because aromatic ring vibrations also give rise to bands near 1450 cm^{-1}. In the spectrum of acetylbenzoylhydrazine, a band which appeared as a shoulder of the 1450 cm^{-1} band was ascribed to $\delta_{as}(CH_3)$ in the previous paper[1]. However, SABH shows two bands at 1423 and 1440 cm^{-1} (relatively strong), and, also, SABH-d has bands at 1423 (more intense) and 1442 cm^{-1}. These two bands of SABH are in good agreement with the corresponding bands of SABH-d in frequency but in an inverse intensity ratio. As mentioned above, diacetylhydrazine and its salt show a single band each assigned to $\delta_{as}(CH_3)$, i. e., 1430 and 1428 cm^{-1} respectively, while acetylbenzoylhydrazine has a single band at 1440 cm^{-1}. On the other hand, it can be expected that in SABH and SABH-d the absorption due to $\delta_{as}(CH_3)$ is overlapped by the absorption due to the aromatic ring vibrations and further $\nu''(NCO^-)$ vibrations. In consequence, it is impossible to locate these three vibrations definitely. The 1478 cm^{-1} band of SABH-d is not yet accounted for. No corresponding band is observed in the spectrum of SABH and also of acetylbenzoylhydrazine.

TABLE II. OBSERVED FREQUENCIES AND THEIR ASSIGNMENTS (in cm^{-1})

Group	Assignment	DFH	SDF	DAFH	SDAH	DBH	SDBH	ABH	SABH
	Amide I	1610	1683	1598	1656	1669 1636	1637	1707 1646	1637
CONH	Amide II	1480	1507	1506	1513	1535	1485	1527	1510
	Amide III	1229	1202	1260	1249	1285 1305	1264	1281 1337	1256
NCO^-	ν'		1592		1552		1528		1528
	ν''		1295		1339		1390		—

Furthermore, its frequency value is too low to be ascribed to aromatic ring vibrations whose bands generally appear near 1500 cm^{-1}. The ring vibrations were observed at 1493 cm^{-1} and 1497 cm^{-1} for acetylbenzoylhydrazine and its *N*-deuterated derivative respectively. SABH also shows a band at 1496 cm^{-1}. Thus, the 1478 cm^{-1} band of **SABH-d** can be ascribed to the amide II′ absorption relating to the COND part of the ionized group $CONDNCO^-$. A corresponding band for SABH can be taken as a poorly defined shoulder (near 1510 cm^{-1}) which is accompanied by the 1528 cm^{-1} band.

Characteristic Frequencies.—In the solid state the sodium hydrazides can be expected to exist in a form $Na^+RCONHNCOR'^-$. The amide bands will, therefore, be shown by the group CONH in their infrared spectra. In addition to them, absorption bands due to the ionized group NCO^- will also be observed.

The observed frequencies and their assignments are summarized in Table II. For comparison the amide frequencies of the hydrazides are also represented in that table.

Secondary amides[10] in the solid state have the amide I and amide II bands in the ranges 1680～1630 cm^{-1} and 1570～1515 cm^{-1} respectively, and the amide III band near 1290 cm^{-1}. The hydrazides of aliphatic acids[15] have bands shifted towards lower frequencies. However, SDFH and SDAH show amide frequencies somewhat different from those of the corresponding hydrazides, i. e., the amide I band increased distinctly in frequency but decreased a little in intensity, the amide II band increased a little in frequency, and the amide III band decreased in frequency.

On the other hand, the hydrazides of aromatic acids[1] in the solid state showed the amide I band within the range of secondary amides but split into two bands, which bands are attributable to coupling between two C=O vibrations. Further, the amide II and amide III bands are seen within the normal ranges of secondary amides, but the latter splits into two bands. As for SDBH and SABH, their amide I bands are in good agreement in frequency each other, and they can be ascribed to the C=O group adjacent to the benzene ring. Further, these salts show that the amide II band has decreased in frequency, while the amide III bands of SDBH and SABH are nearly equal in frequency. Therefore, it may be understood that the amide bands due to the CONH group of the ions $(RCONHNCOR')^-$ appear generally in the normal range of secondary amides, so that the vibrations relating to CONH group are little affected by an electronic charge stored in the NCO^- group. In the NCO^- group resonance will be possible between the C–N and C–O bonds. In consequence, the NCO^- structure gives rise to two bands similar to those of the COO^- group as represented in Table II.

Furthermore, it is noteworthy that an N–H stretching vibration concerns a band near 3300 cm^{-1} in the spectra of the sodium hydrazides. The value of frequency lies in the normal range 3320～3270 cm^{-1} of the secondary amides[10].

15) To be published elsewhere.

Summary

The infrared absorption spectra of $HCONH \cdot NCOH \cdot Na$, $CH_3CONHNCOCH_3 \cdot Na$, $CH_3CON \cdot HNCOC_6H_5 \cdot Na$, and $C_6H_5CONHNCOC_6H_5 \cdot Na$ and their *N*-deuterated derivatives have been examined in the rock salt region. The characteristic frequencies of the ions $(RCON \cdot HNCOR')^-$ have been obtained, and the influence of an electronic charge on the amide frequencies has been discussed.

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