The Infrared Absorption Spectra of $(NH_2CONH–)_2$, $NH_2CONHNH_2$, $(NH_2CSNH–)_2$ and $NH_2CSNHNH_2$

By Mitsuo MASHIMA

(Received February 21, 1964)

The infrared absorption spectra of hydrazides containing the –CONHNHCO–[1] or $–CONHNH_2$[2] group have been investigated and the frequencies characteristic of those groups obtained by the present author. On the other hand, Suzuki[3,4] has discussed the frequency of the stretching vibration of the C=S bond adjacent to the C–N bond in thioamides in connection with the results of infrared measurements and normal vibration calculations. He has concluded that the band of thioformamide[3] at 843 cm^{-1} is associated with an almost pure C=S stretching vibration.

For the present study, the infrared spectra of hydrazine-*N*, *N′*-bis-carbonic acid amide, semicarbazide, hydrazine-*N*, *N′*-bis-thiocarbonic acid amide, thiosemicarbazide, acetyl-semicarbazide, formyl- and acetyl-thiosemicarbazide and the *N*-deuterated derivatives of these compounds were examined in the rock salt region. For the sake of comparison, semicarbazide hydrochloride and its *N*-deuterated derivative were examined spectroscopically. The frequencies obtained were tentatively assigned to the fundamental vibrational modes by comparing the spectra with those of related compounds.

Experimental

Hydrazine-*N*,*N′*-bis-carbonic Acid Amide (HCA): $(NH_2CONH–)_2$.—This compound was obtained by heating a mixture of urea (2 mol.) and hydrazine hydrate (1 mol.) in a sealed tube,[5] and it was purified by recrystallization from water (m. p. 267°C).

Semicarbazide (SC): $NH_2CONHNH_2$.—This compound was synthesized by heating the 1 : 1 (in mole) mixture of urea and hydrazine hydrate in a sealed tube,[6] and it was purified by recrystallization from ethanol (m. p. 96°C). Semicarbazide hydrochloride was prepared with hydrochloric acid and semicarbazide, and it was purified by recrystallization from water (m. p. 174°C). This hydrochloride was examined analytically.

Found: Cl, 30.4%. Calcd. for $NH_2CONHNH_2 \cdot HCl$: Cl, 31.8%.

Acetyl-semicarbazide (ASC): $CH_3CONHNH \cdot CONH_2$.—This compound was synthesized with acetic anhydride and semicarbazide,[7] and it was purified by recrystallization from ethanol (m. p. 165°C).

Hydrazine-*N*, *N′*-bis-thiocarbonic Acid Amide (HTCA): $(NH_2CSNH-)_2$.—This compound was synthesized with hydrazine sulfate and ammonium rhodanide[8] and was purified by recrystallization from water (m. p. 215°C).

Thiosememicarbazide (TSC): $NH_2CSNHNH_2$.—This compound was synthesized by the method presented by Freund and Imagat[9] and was purified by recrystallization from water (m. p. 180°C).

Formyl-thiosemicarbazide (FTSC): $HCONHNH \cdot CSNH_2$.—This compound was synthesized with thiosemicarbazide and formic acid[10] and was purified by recrystallization from water (m. p. 175°C).

Acetyl-thiosemicarbazide (ATSC): $CH_3CONH \cdot NHCSNH_2$.—This compound was synthesized with thiosemicarbazide and acetic anhydride[11] and was purified by recrystallization from water (m. p. 164°C).

The *N*-deuterated derivatives examined were prepared in a sealed tube in the presence of heavy water (99.8%). The excess of heavy water was evaporated in a vacuum.

The spectra of all of the compounds in the solid state were studied with KBr disks. A double-beam Hitachi infrared spectrophotometer, Type EPI-2, was used in the rock salt region.

Results and Discussion

The infrared spectra obtained are shown in Figs. 1 to 3.

The ν(C=O)[*1] Frequency.—SC and HCA are considered to show a strong band which is mainly associated with the ν(C=O) vibration because, for urea[12] and oxamide[13], corresponding band has been found at 1686 and 1656 cm^{-1} respectively. In ASC, FTSC and ATSC,

---

[1] M. Mashima, This Bulletin, **35**, 332, 338, 423 (1962).

[2] M. Mashima, ibid., **35**, 1882, 2020 (1962); **36**, 210 (1963).

[3] I. Suzuki, ibid., **35**, 1286 (1962).

[4] I. Suzuki, ibid., **35**, 1449 (1962).

[5] T. Curtius, *Ber.*, **26**, 405 (1893).

[6] T. Curtius and K. Heidenreich, ibid., **27**, 56 (1894).

[7] O. Widman and A. Cleve, ibid., **31**, 381 (1898).

[8] M. Freund and S. Wischewiansky, ibid. **26**, 2877 (1893).

[9] M. Freund and H. Imagat, ibid., **28**, 948 (1895).

[10] M. Freund and C. Meinecke, ibid., **29**, 2513 (1896).

[11] M. Freund and C. Meinecke, ibid., **29**, 1515 (1896).

[*1] In this paper the following notations are used: ν: bond stretching, β: bending, δ: deformation, r: rocking, w: wagging, t: twisting, π: out-of-plane deformation, τ: tortional, a: asymmetric and s: symmetric.

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

[13] T. A. Soctt, 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).

TABLE I. THE ν(C=O) AND AMIDE I BANDS IN cm^{-1}

$NH_2CONHNH_2$	1661	$ND_2CONDND_2$	1640
$NH_2CONHNH_3^+$	1687	$ND_2CONDND_3^+$	1642
$(NH_2CONH-)_2$	1687	$(ND_2COND-)_2$	1625
$CH_3CONHNHCONH_2$	1668	$CH_3CONDNDCOND_2$	1663
$HCONHNHCSNH_2$	1690	$HCONDNDCSND_2$	1684, 1661
$CH_3CONHNHCSNH_2$	1706	$CH_3CONDNDCSND_2$	1670

TABLE II. THE ν(C=S) FREQUENCY IN cm^{-1}

	$HCSNH_2$[a)]	$(NH_2CSNH-)_2$	$NH_2CSNHNH_2$	$HCONHNHCSNH_2$	$CH_3CONHNHCSNH_2$
ν(C=S)	830	831	803	858	837
	$HCSND_2$[a)]	$(ND_2CSND-)_2$	$ND_2CSNDND_2$	$HCONDNDCSND_2$	$CH_3CONDNDCSND_2$
ν(C=S)	996	901	928	908	910
$r(ND_2)$	752	735	700	726	743

a) See Ref. 3.

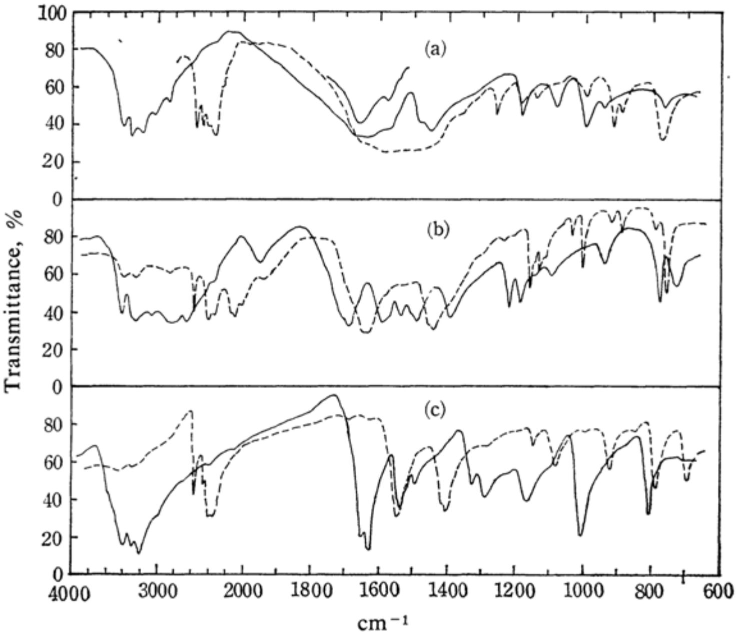

Fig. 1. Infrared spectra of SC (a), SC·HCl (b), and TSC (c) (solid lines) and their *N*-deuterated derivatives (broken lines) in the solid state.

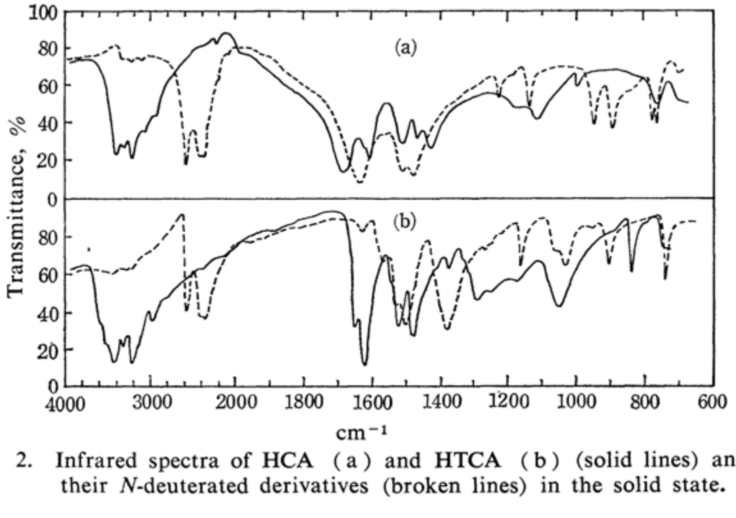

Fig. 2. Infrared spectra of HCA (a) and HTCA (b) (solid lines) and their *N*-deuterated derivatives (broken lines) in the solid state.

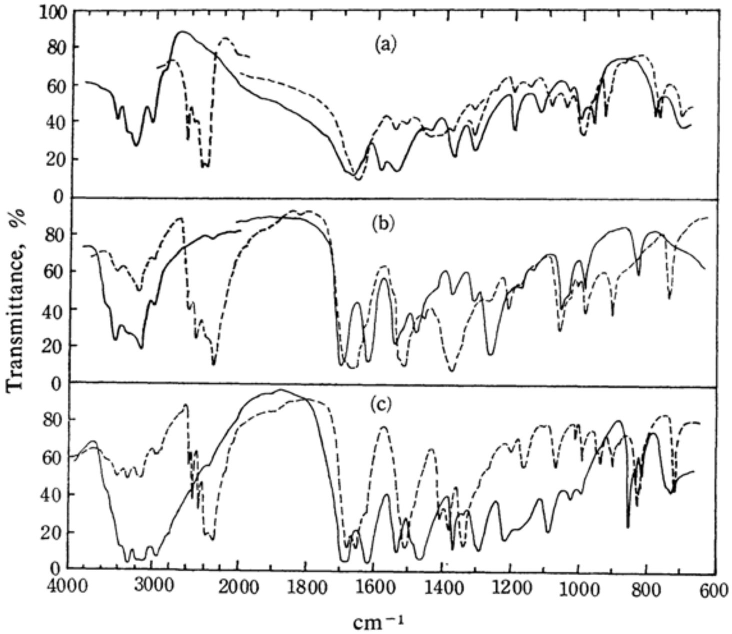

Fig. 3. Infrared spectra of ASC (a), ATSC (b), and FTSC (c) (solid lines) and their *N*-deuterated derivatives (broken lines) in the solid state.

the amide I band characteristic of monosubstituted amides is expected to appear. In fact, these bands are very easily identified in the spectra of those compounds. The ν(C=O) and amide I band are summarized in Table I.

The ν(C=S) Frequency.—This frequency has been found in the 1400~1150 cm^{-1} range in thioureas. This wide range has been ascribed to varying degrees of coupling with other vibrations.[14] Recently, Suzuki concluded that, judging from the normal vibration calculations, the ν(C=S) vibration in simple thioamides may couple with other vibrations; the band of thioformamide[3] at 830 cm^{-1} is associated with an almost pure ν(C=S) vibration, while the band of thioacetamide[4] at 718 cm^{-1} is due to a hybridized vibration mainly composed of the ν(C=S) motion. The spectra of HTCA, TSC, and ATSC are comparatively simple in the region 900~700 cm^{-1}, and they have only a moderately strong band near 830 cm^{-1}: 831 cm^{-1} of HTCA, 803 cm^{-1} of TSC, and 837 cm^{-1} of ATSC. In place of this band, their *N*-deuterated derivatives have two bands, near 910 and 730 cm^{-1}. It is of interest that the 830 $^{-1}$ band of thioformamide disappears on *N*-deuteration and that, in place of it, two bands appear, at 996 and 752 cm;[1-3] the latter two bands have been assigned to vibrations composed of the ν(C=S) and r(ND$_2$) vibrations. The bands corresponding to these two bands may very easily be identified with the bands at 901 and 735 cm^{-1} for HTCA-d$_6$ and 910 and 743 cm^{-1} for ATSC-d$_4$, because they have only those two bands in this region. On the other hand, TSC-d$_5$ has three moderately strong bands, at 928, 792 and 700 cm^{-1}; of these, the first and last bands are considered to correspond to the two bands mentioned above. In this region the spectrum of FTSC is rather complicated, and it is comparatively hard to find the corresponding bands, but the band at 858 cm^{-1} may be taken as the ν(C=S) band because, on *N*-deuteration, it is displaced by new bands at 908[*2] and 726 cm^{-1}.

The ν(C=S) frequencies in thioformamide and the compounds examined here are summarized in Table II, which also contains the bands associated with the hybridized vibrations, mainly composed of the ν(C=S) and r(ND$_2$) vibrations. As may be seen in Table II, the ν(C=S) frequency in this class of compounds falls in the range of 860~800 cm^{-1}, which is rather lower than that of 1400~1150 cm^{-1} in thioureas and that in other classes of compounds containing the C=S bond.[14]

The β(NH$_2$)[*1] Frequency.—For TSC and HTCA this frequency will be easily found because no band, except for one associated with the β(NH$_2$) vibration, is considered to

---

14) L. J. Bellamy, "The Infrased Spectra of Complex Molecules," Methuen & Company, London (1958), p. 356.

[*2] FTSC shows several bands in the region where the band mentioned in the text is considered to appear. By comparing the value of this frequency with those of HTCA, TSC, and ATSC, this frequency was used for the band considered just now.

appear in the region from 1650 to 1600 cm^{-1}. In fact, these compounds have a strong band at 1626 and 1617 cm^{-1} respectively. Since they disappear on *N*-deuteration, we can safely take them as $\beta(NH_2)$ frequencies. The $\beta(ND_2)$ frequency is easily found at 1150 cm^{-1} for TSC-d_6 and 1158 cm^{-1} for HTCA-d_6.

The bands at 1624 cm^{-1} for FTSC and 1633 cm^{-1} for ATSC may also be safely taken as $\beta(NH_2)$ bands. This assignment is supported by the spectroscopic observations for these compounds in the acetonitrile solution. In changes of state, the 1624 cm^{-1} band of FTSC shifts to 1618 cm^{-1} and the 1633 cm^{-1} band of ATSC, to 1613 cm^{-1}. These frequency shifts are, in direction and value, in accordance with those obtained for the $\beta(NH_2)$ bands of thioformamide³⁾ and thioacetamide.⁴⁾ HCA has a band at 1604 cm^{-1} which is accompanied with a shoulder band at 1622 cm^{-1}. They disappear on *N*-deuteration. Accordingly, they are taken as $\beta(NH_2)$ frequencies. In the remaining compounds, SC and ASC, the location of the $\beta(NH_2)$ band is very difficult to ascertain. As has been indicated above, TSC-d_5 and HTCA-d_6 have the $\beta(ND_2)$ band at ca. 1150 $^{-1}$. The corresponding band has been obtained at 1118 $^{-1}$ for $HCOND_2$,¹⁵⁾ 1145 cm^{-1} for $HCSND_2$,³⁾ 1189 cm^{-1} for CH_3COND_2,¹⁶⁾ and 1160 cm^{-1} for $CH_3CSND_2$⁴⁾. Therefore, the $\beta(ND_2)$ band of the remaining five compounds is expected to appear near at 1150 cm^{-1}. It has been obtained as summarized in Table III.

Bands in the Region from 1590 to 1340 cm^{-1}. —In ASC, ATSC and FTSC, the amide II band is considered to appear in this region. Recently, Suzuki obtained amide II-like bands for *N*-methylthioamides: 1550 cm^{-1} of $HCSNH\cdot CH_3$ and 1564 cm^{-1} of $CH_3CSNHCH_3$.¹⁷⁾ On the other hand, the ν(C–N) vibration of the $CO(S)NH_2$ group is considered to give rise to a band in this region because the ν(C–N) frequency has been found at 1464 cm^{-1} for urea¹²⁾ and 1470 cm^{-1} for thiourea.¹⁸⁾

In this region the observed frequencies of ASC, ATSC and FTSC are collected in Table IV(a). ASC has two strong bands at 1587 and 1542 cm^{-1}, one of which may be taken as the amide II band and the other as the ν(C–N) band. On *N*-deuteration, the amide II band usually moves to lower frequencies and the so-called amide II′ band occurs; e.g., $CH_3\cdot CONHCH_3$¹⁹⁾ shows the 1567 (amide II) and 1475 (amide II′) cm^{-1} bands. ASC-d_4 shows a relatively weak band at 1552 cm^{-1} and two strong bands at 1445 and 1410 cm^{-1}. The amide II′ band of $CH_3CONHCH_3$ has been ascribed to the ν(C–N) vibration interacting with other vibrational modes.¹⁹⁾ In ASC-d_4, it is considered that the ν(C–N) vibration interacts with at least the $\delta_a(CH_3)$ vibration, and two strong bands are shown as has been indicated above. The bands at 1443 and 1372 cm^{-1} of ASC may be safely assigned to the $\delta_a(CH_3)$ and $\delta_s(CH_3)$ vibrations respectively, because the values of frequency lie in the normal ranges for those vibrations of the C–CH_3 group. The band of ASC-d_4 at 1380 cm^{-1} may safely be ascribed to the $\delta_s(CH_3)$ vibration.

Since the bands at 1545 cm^{-1} for ATSC and 1540 cm^{-1} for FTSC correspond in fueqency to the amide II band of *N*-methylthioamides,¹⁷⁾ these bands may be taken as amide II bands. Two strong bands, at 1513 and 1437 cm^{-1}, of $HCSNDCH_3$¹⁷⁾ have been ascribed to the hybridized vibrations composed of the ν(C–N) and $\delta_a(CH_3)$ vibrations, while in $CH_3CSND\cdot CH_3$¹⁷⁾ the coupling occurs among the ν(C–N), $\delta_a(CH_3)_N$ and $\delta_a(CH_3)_C$ vibrations and three bands have been observed at 1515, 1483 and 1442 cm^{-1}. ATSC-d_4 and FTSC-d_4 also have strong bands at 1517 and 1515 cm^{-1} respectively; their frequency-values are in good accordance with those of the bands at 1513 cm^{-1} for $HCSNDCH_3$ and 1515 cm^{-1} for $CH_3CSNDCH_3$. Therefore, they seem to be bands characteristic of the –CSND– group (amide II′). The band of ATSC at 1485 cm^{-1} is displaced by a strong band at 1380 cm^{-1} on *N*-deuteration. The former may be associated with the amide II band; the latter is suitable in frequency to the $\delta_s(CH_3)$ vibration, but it appears more strongly than that vibration. Probably, the 1380 cm^{-1} band will be the $\delta_s(CH_3)$ band overlapped with the amide II′ band come from the CH_3COND– group. The band of FTSC at 1472 cm^{-1} moves to 1346 cm^{-1} on *N*-deuteration; they may be taken as the amide II and II′ bands respectively. In ATSC two bands at 1430 and 1379 cm^{-1} are easily associated with the $\delta_a(CH_3)$ and $\delta_s(CH_3)$ vibrations respectively. The band at 1374 cm^{-1} of FTSC corresponds to the band at 1384 cm^{-1} of FTSC-d_4, and these may safely be assigned to the δ(C–H) vibration.

In this region HCA shows three bands at 1505, 1465, and 1426 cm^{-1} which are displaced by two strong bands at 1506, 1473 cm^{-1} and a weak band at 1221 cm^{-1} on *N*-deuteration. For SC, the corresponding bands are found at 1577, 1484 and 1452 cm^{-1}. In the spectrum of SC-d_5, the location of the bands corresponding

---

15) I. Suzuki, This Bulletin, **33**, 1359 (1960).

16) I. Suzuki, ibid., **35**, 1279 (1962).

17) I. Suzuki, ibid., **35**, 1456 (1962).

18) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lange, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

19) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

TABLE III. THE $\beta(NH_2)$ AND $\beta(ND_2)$ FREQUENCIES IN cm^{-1}

	$(NH_2CSNH\text{-})_2$	$NH_2CSNHNH_2$	$CH_3CONHNHCSNH_2$	$HCONHNHCSNH_2$	$(NH_2CONH\text{-})_2$	$NH_2CONHNH_2$	$CH_3CONHNHCONH_2$
$\beta(NH_2)$	1642 1617	1648 1626	1633	1624	1622 1604	—[a]	—[a]
	$(ND_2CSND\text{-})_2$	$ND_2CSNDND_2$	$CH_3CONDNDCSND_2$	$HCONDNDCSND_2$	$(ND_2COND\text{-})_2$	$ND_2CONDND_2$	$CH_3CONDNDCOND_2$
$\beta(ND_2)$	1158	1150	1142	1168	1130	1190 1142	1152

a) The corresponding bands were not located with certainty.

TABLE IV. THE OBSERVED FREQUENCIES IN THE REGION FROM 1590 TO 1340 cm^{-1}

(a) ABC, ATSC, and FTSC

	$CH_3CONHNHCONH_2$	$CH_3CONDNDCOND_2$	$CH_3CONHNHCSNH_2$	$CH_3CONDNDCSND_2$	$HCONHNHCSNH_2$	$HCONDNDCSND_2$
Amide II (II') and $\nu(C\text{-}N)$	1587(s) 1542(s)	1552(m) 1445(s)	1545(m) 1527(sh) 1485(m)	1532(sh) 1517(s)	1540(s) 1493(sh) 1472(s)	1515(s) 1413(m) 1346(s)
$\delta_a(CH_3)$	1443(w)	1410(s)	1430(w)	1458(w)		
$\delta_s(CH_3)$	1372(m)	1380(m)	1379(w)	1380(s)		
$\delta(CH)$					1374(m)	1384(m)

(b) HCA, SC, HTCA, and TSC

	$(NH_2CONH\text{-})_2$	$(ND_2COND\text{-})_2$	$NH_2CONHNH_2$	$ND_2CONDND_2$	$(NH_2CSNH\text{-})_2$	$(ND_2CSND\text{-})_2$	$NH_2CSNHNH_2$	$ND_2CSNDND_2$
Amide II (II') and $\nu(C\text{-}N)$	1505(s) 1465(m) 1426(s)	1506(s) 1473(s)	1577(s) 1484(m) 1452(s)	—[a] —[a]	1517(s) 1473(s) 1368(w)	1523(w) 1493(s) 1374(s)	1536(m) 1491(m) 1391(vw)	1550(s) 1418(sh) 1407(s)
		1221(w)		1259(w)				

a) It is difficult to locate the corresponding band.

TABLE V (a). THE OBSERVED FREQUENCIES OF HCA, SC, HTCA AND TSC IN THE REGION FROM 1340 TO 700 cm^{-1}

	$(NH_2CONH\text{-})_2$	$(ND_2COND\text{-})_2$	$NH_2CONHNH_2$	$ND_2CONDND_2$	$(NH_2CSNH\text{-})_2$	$(ND_2CSND\text{-})_2$	$NH_2CSNHNH_2$	$ND_2CSNDND_2$
Amide III					1287(m)		1322(m) 1287(m)	
$\delta(NH_2)$[a]			1182(m)					
$r(NH_2)$	1110(m)		1080(m)		1049(m)		1164(m)	
Amide III'						1028(m)		1086(m)
$\delta(NH_2)$[a]			996(m)				1001(s)	
$\delta(O{=}C\text{-}N)$	996(w)		946(w)					
$\delta(ND_2)$[a]				997(w)				
$r(ND_2)+\delta(O{=}C\text{-}N)$		943(m) 883(m)		917(m) 891(m)				
$\delta(ND_2)$[a]				834(vw)				792(w)
$\pi(O{=}C\text{-}N_2)$	759(w)	771(m) 758(m)	767(w)	772(m)				

a) It is of the hydrazine residue.

TABLE V (b). THE OBSERVED FREQUENCIES OF ASC, ATSC AND FTSC IN THE REGION FROM 1340 TO 700 cm^{-1}

	$CH_3CONHNHCONH_2$	$CH_3CONDNDCOND_2$	$CH_3CONHNHCSNH_2$	$CH_3CONDNDCSND_2$	$HCONHNHCSNH_2$	$HCONDNDCSND_2$
Skeletal	1313(m)	1315(m)	1318(m)	1213(m)		
Amide III	1197(m)		1265(s)		1298(s)	
					1223(m)	
Skeletal	1121(w)	1089(w)	1180(w)	1185(w)	1093(m)	1074(m)
$r(CH_3)$ and $\nu(C-C)$	1037(w)	1043(w)	1058(m)	1058(m)		
	1002(m)	998(m)	1045(m)	1034(w)		
	996(m)	931(w)	990(m)	992 983(m)		
$\pi(C-H)$					1029(w)	1019(w)
					1001(w)	
Amide III′						997(w)
						946(w)
Skeletal					840 823(w)	837 827(m)
$\pi(O=C-N_2)$	783(m)	774(m)				
Skeletal	700(m)	706(m)				

TABLE VI (a). THE OBSERVED FREQUENCIES OF HCA AND HTCA IN THE REGION FROM 3000 TO 2000 cm^{-1}

	$(NH_2CONH-)_2$	$(ND_2COND-)_2$	$(NH_2CSNH-)_2$	$(ND_2CSND-)_2$
$\nu_a(NH_2)$	3360(s)		3380(s)	
	3280(s)		3280(m)	
$\nu_s(NH_2)$ and $\nu(NH)$	3190(s, b)		3170(s)	
	3040(w)		3100(sh)	
	2920(w)		2940(m)	
$\nu_a(ND_2)$		2560(s)		2540(s)
$\nu_s(ND_2)$ and $\nu(ND)$		2390 2340(s)		2400 2320(s)
	2210(w)	2180(w)		

Table VI (b). The observed frequencies of SC and TSC in the region from 3000 to 2000 cm^{-1}

	$NH_2CONHNH_2$	$ND_2CONDND_2$	$NH_2CONHNH_3^+$	$ND_2CONDND_3^+$	$NH_2CSNHNH_2$	$ND_2CSNDND_2$
$\nu_a(NH_2)$	3410(s)		3410(s)		3370(s)	
$\nu(NH_2)$	3310(s)				3270(s)	
$\nu_s(NH_2)$ and $\nu(NH)$	3200(s) 3060(w) 2890(w)		3220(s) 3050(m)		3190(s) 2980(m)	
$\nu_a(NH_3^+)$			2850(s)			
$\nu_s(NH_3^+)$			2640(s)			
$\nu_a(ND_2)$		2850(m)		2570(m)		2560(m)
$\nu(ND_2)$		2470(m)				2470(m)
$\nu_s(ND_2)$ and $\nu(ND)$		2410 2330 (s)		2390 2320 (s)		2400 2330 (s)
$\nu_a(ND_3^+)$				2150(sh) 2090(s)		
$\nu_s(ND_3^+)$				2020(m)		

Table VI (c). The observed frequencies of ASC, ATSC and FTSC in the region from 3000 to 2000 cm^{-1}

	$CH_3CONHNHCONH_2$	$CH_3CONDNDCOND_2$	$CH_3CONHNHCSNH_2$	$CH_3CONDNDCSND_2$	$HCONHNHCSNH_2$	$HCONDNDCSND_2$
$\nu_a(NH_2)$	3440(m)		3440(s)		3390(w) 3295(s)	
$\nu(NH)$	3310(m)		3310(m)		3155(s)	
$\nu_s(NH_2)$ and $\nu(NH)$	3230(s) 3040(m) 2900(vw)		3170(s) 3000(m)		2970(s) 2830(w)	
$\nu_s(ND_2)$		2620(m)		2590(w)		2590(w)
$\nu(ND)$		2530(w)		2500(m)		2550(m) 2470(m)
$\nu_s(ND_2)$ and $\nu(ND)$		2440 2400 (s)	2340(vw)	2390 2310 (s)	2350(vw)	2390 2310 (s)

to the 1506 and 1473 cm^{-1} bands of HCA-d_6 is very difficult to determine because of the presence of strong back-ground absorptions, while the band corresponding to the 1221 cm^{-1} band is easily found at 1259 cm^{-1}. HTCA and TSC show absorptions a little different from those of HCA and SC: HTCA has only two strong bands at 1517 and 1473 cm^{-1} which are displaced by strong bands at 1493 and 1374 cm^{-1} on *N*-deuteration; TSC has also two moderately strong bands at 1536 and 1491 cm^{-1} and TSC-d_5, at 1550 and 1407 cm^{-1}. A detailed assignment is difficult from the present observations only, but these bands may be taken as the amide II and ν(C–N) bands.

The Bands in the Region from 1340 to 700 cm^{-1}.—The observed frequencies of HCA, SC, HTCA, and TSC are collected in Table V(a). The band of HCA at 759 cm^{-1} is displaced by a band with two peaks at 771 and 758 cm^{-1} on *N*-deuteration. SC has a band at 767 cm^{-1} which moves to 772 cm^{-1} on *N*-deuteration; ASC has also a corresponding band at 783 cm^{-1} and ASC-d_4, one at 774 cm^{-1}, as is indicated in Table V (b). A band of urea[12] at 776 cm^{-1}, which moves to 785 cm^{-1} on *N*-deuteration, has been assigned to the $\pi(OCN_2)$[*1] vibration. Therefore, the band near 770 cm^{-1} is considered to be one characteristic of these compounds and has been assigned to the $\pi(OCN_2)$ vibration.

HCA has, further, a moderately strong band at 1110 cm^{-1} and a weak band at 996 cm^{-1}; they are considered to be due to fundamental vibrational modes because they are displaced by two moderately strong bands, at 943 and 888 cm^{-1}, on *N*-deuteration. Urea[12] shows a band at 1150 cm^{-1} which has been assigned to the $r(NH_2)$ vibration of the A_1 and B_1 species: urea-d_4[12] has the $r(ND_2)$ bands at 1001 cm^{-1} (A_1) and 887 cm^{-1}(B_1). For oxamide,[13] the $r(NH_2)$ frequency has been obtained at 1103 cm^{-1} and the $r(ND_2)$ frequency at 927 cm^{-1}. The 1110 cm^{-1} band of HCA is determined to come from a vibration mainly due to the $r(NH_2)$ vibration by comparing the value of the frequency with those of the corresponding frequencies in urea and oxamide. In consequence, the 943 and 883 cm^{-1} bands of HCA-d_6 are considered to arise from the $r(ND_2)$ vibration strongly interacting with another vibration. Assuming the symmetry of C_{2h} for a molecule of HCA,[*3] of a total of thirty-six (3N-6) normal vibrations, eighteen are infrared active; six of these are of species A_u, and twelve of species B_u. Seven of them will give rise to bands outside the region examined here. They may be deformation N–N–C and N–C–N vibrations (species B_u) or torsional N–C and N–N vibrations, wagging and twisting NH_2 vibrations and out-of-plane N–H deformation vibrations (species A_u); the τ(N–N–)[*1] frequency of NH_2NH_2 is 377 cm^{-1},[20] the τ(C–N) frequency of $HCONHCH_3$[21] is 353 cm^{-1}, the δ(N–N–C) frequency of CH_3NHNH_2 is 433 cm^{-1},[22] and the δ(N–C–N) frequency of $NH_2 \cdot CONH_2$ is 556 cm^{-1}.[12] The π(N–H), $w(NH_2)$ and $t(NH_2)$[*1] frequencies are considered to be found in this region,[*4] but in the spectrum of HCA no band corresponding to them is observed. In consequence, eleven frequencies will be found for HCA in the region examined here. Of these only one has not yet been accounted for, the δ(O=C–N) frequency. Therefore, the 996 cm^{-1} band of HCA is considered to be due to that vibration, while the 943 and 888 cm^{-1} bands of HCA-d_6 may be ascribed to the hybridized vibrations composed of $r(ND_2)$ and δ(O=C–N) vibrations. The above assignment is supported by the fact that, for HTCA, no band corresponding to them is observed.

SC has four bands, not yet accounted for, at 1182, 1080, 996 and 946 cm^{-1}. In order to explain these bands, the spectrum of SC was compared with that of SC·HCl. Of the four, only the third band has no band corresponding in frequency to it in the spectrum of SC·HCl, and it moves to 834 cm^{-1} on *N*-deuteration. Therefore, it may be ascribed to a $\delta(NH_2)$ vibration of the hydrazine residue[*5] contained in SC. The second and fourth bands are considered to correspond to the 1110 and 996 cm^{-1} bands of HCA, and they may be taken as the $r(NH_2)$ and δ(O=C–N) bands respectively. Since they are displaced by two bands at 917 and 891 cm^{-1} on *N*-deuteration, we can apply the same explanation to

---

[*3] Since the infrared spectrum of diformylhydrazine has been reasonably explained with a model of the trans-planar configuration of the -CONHNHCO- group (T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956); T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 341 (1955)), that group contained in HCA may be assumed to have a similar structure. On the other hand, the spectrum of urea has been interpreted by means of a model of the planar structure of a molecule (see Ref. 12) and part of the $-NHCONH_2$ of a molecule of HCA is considered to have a planar configuration. In that case, HCA has the symmetry of C_{2h}.

20) A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **31**, 843 (1959).

21) I. Suzuki, This Bulletin, **35**, 540 (1962).

22) D. W. E. Axford, G. J. Janz and K. E. Russel, *J. Chem. Phys.*, **19**, 704 (1951).

[*4] The π(N-H) frequencncy has been obtained at 720 cm^{-1} for *N*-methylformamide (see Ref. 21); the $w(NH_2)$ and $t(NH_2)$ frequencies have been found at 792 and 678 cm^{-1} for oxamide (see Ref. 13) and at 719 and 500 cm^{-1} for urea (see Ref. 12).

[*5] In SC·HCl, HCl is considered to attach itself to the hydrazine residue because the NH_2 group of this residue is considered to be more basic in nature than that group of $-CONH_2$.

the latter two bands as was applied to the 943 and 888 cm^{-1} bands of HCA-d_6. The first band also has a partner band at 1180 cm^{-1} in the spectrum of SC·HCl and moves to 997 cm^{-1} on *N*-deuteration; it may be ascribed to a $\delta(NH_2)$ vibration of the hydrazine residue. This assignment will be considered further later in this paper.

HTCA has a moderately strong band at 1049 cm^{-1} which is disappears on *N*-deuteration; its frequency-value is suitable for it to be assigned to the $r(NH_2)$ vibration. The $r(ND_2)$ frequency of HTCA-d_6 has been considered previously (see Table II). The band at 1287 cm^{-1} of this compound shifts to 1028 cm^{-1} on *N*-deuteration and corresponds in frequency to the amide III band of HCSNH·CH_3[17] at 1297 cm^{-1}. Therefore, we can take it as the amide III band characteristic of the –CSNH– group.

TSC has four bands, at 1332, 1287, 1164 and 1001 cm^{-1}, all of which are displaced on *N*-deuteration. In this compound an $r(NH_2)$ vibration in the –$CSNH_2$ plane[*6] and NH_2 deformation vibrations of the hydrazine residue will give rise to bands in the region just considered. Of the above four, the 1164 and 1001 cm^{-1} bands seem to be suitable in frequency for the $r(NH_2)$ and the NH_2 deformation vibrations respectively. In TSC-d_5 the 928 and 700 cm^{-1} bands have been assigned to the hybridized vibrations composed of the $r(ND_2)$ and $\nu(C{=}S)$ vibrations (see Table II). TSC-d_5 has a further band at 792 cm^{-1} which may be assigned to the ND_2 deformation vibration of the hydrazine residue. One of the 1322 and 1287 cm^{-1} bands of TSC is considered to correspond to the band at 1086 cm^{-1} of TSC-d_5 and may be taken as the amide III band.

The observed frequencies of ASC, FTSC and ATSC in this region are collected in Table V (b), except for the $\nu(C{=}S)$ frequency accounted for already. All of these compounds are considered to show the amide III band characteristic of the –CONH– group; ASC and ATSC show the bands due to the $r(CH_3)$ and $\nu(C{-}C)$ vibrations, and FTSC, the band due to the $\pi(C{-}H)$ vibration. The bands at 1298 cm^{-1} of FTSC and 1265 cm^{-1} of ATSC may safely be taken as amide III bands because they disappear on *N*-deuteration, and their frequency-values are considered to be suitable for amide III bands. In ASC a band at 1197 cm^{-1} disappears on *N*-deuteration; we can take this as the amide III band. In the region where the $r(CH_3)$ and $\nu(C{-}C)$ vibrations will give rise to bands, three bands are found, at 1037, 1002 and 996 cm^{-1} for ASC and at 1058, 1045 and 990 cm^{-1} for ATSC. They may be ascribed to the $r(CH_3)$ and $\nu(C{-}C)$ vibrations or to the hybridized vibrations composed of those and the $r(NH_2)$, skeletal stretching vibrations. In ASC the above three bands are displaced by bands at 1043, 998 (relatively broad) and 931 cm^{-1}; those of ATSC are displaced by two bands, at 1058 and 1034 cm^{-1}, and a band with two peaks at 992 and 983 cm^{-1}. The 998 cm^{-1} band of ASC-d_4 and the doublet band of ATSC-d_4 may be regarded as the amide III′ band overlapping with a band arising from one of the hybridized vibrations indicated above. Now, ASC has three bands not yet accounted for, at 1313, 1121 and 700 cm^{-1}; the first and last bands are scarcely changed in frequency on *N*-deuteration, and, accordingly, they may be considered to come from skeletal stretching vibrations; the second shifts to 1089 cm^{-1}, but this is also due to a skeletal vibration. ATSC has two bands at 1318 and 1180 cm^{-1}; the latter is hardly changed on *N*-deuteration, while the former shifts to 1213 cm^{-1}. A detailed assignment of the two bands is not easy, but they are considered to come from skeletal vibrations. In the spectrum of FTSC, bands at 1093, 840 and 823 cm^{-1} are hardly changed on *N*-deuteration. Therefore, they may be ascribed to skeletal vibrations. In this compound the $\pi(C{-}H)$ and $r(NH_2)$ vibrations will give rise to bands in this region. They may be associated with the relatively weak bands at 1029 and 1001 cm^{-1}. In FTSC-d_4 the band at 1019 cm^{-1} may be assigned to the $\pi(C{-}H)$ vibration. A moderately strong band at 1223 cm^{-1} may be taken as the amide III band because it disappears on *N*-deuteration. In FTSC-d_4 the bands at 997 and 946 cm^{-1} are suitable in frequency for the amide III′ bands characteristic of the –COND– and –CSND– groups. The band at 733 cm^{-1} also disappears on *N*-deuteration and may be associated with the wagging or twisting NH_2 vibration.

The $\nu(NH_2)$ and $\nu(NH)$ Frequencies.—The frequencies observed above 2000 cm^{-1} and a tentative assignment of them are given in Tables VI (a), (b) and (c). As may be seen from Table VI (a), HCA and HTCA have two strong bands, near 3370 and 3190 cm^{-1}. They correspond in frequency to the $\nu_a(NH_2)$ band of 3335 cm^{-1} and the $\nu_s(NH_2)$ band of 3145 cm^{-1} for thioformamide[3] respectively. For formamide[15] the $\nu_a(NH_2)$ frequency has been found at 3330 cm^{-1} and the $\nu_s(NH_2)$ frequency, at 3190 cm^{-1}. Therefore, the bands near 3370 and 3190 cm^{-1} may safely be assigned to the $\nu_a(NH_2)$ and $\nu_s(NH)_2$ vibrations respectively.

[*6] It may be assumed that this group is planar because the infrared spectrum of $HCSNH_2$ has been reasonably explained with a planar model of the molecule (see Ref. 3).

TABLE VII. THE OBSERVED FREQUENCIES OF SC·HCl IN THE REGION FROM 1600 TO 700 cm^{-1}

	$NH_2CONHNH_3^+$	$ND_2CONDND_3^+$
$\delta_a(NH_3^+)$	1586(s)	
$\delta_s(NH_3^+)$	1529(m)	
Skeletal	1486(s) 1387(s)	1459(s) 1441(s) 1391(sh)
$r(NH_3^+)$	1215(m) 1180(m)	
$\delta_a(ND_3^+)$		1160(m) 1146(vw)
$\delta_s(ND_3)^+$		1130(m) 1112(vw)
$r(NH_2)$	1088(w)	
$r(ND_3^+)$		1036(w) 1005(m)
$\delta(O{=}C{-}N)$	933(w)	
$r(ND_2)$, $\delta(O{=}C{-}N)$		918(w) 892(w)
$\pi(O{=}CN_2)$	768(m)	761(m)
$w(NH_2)$ or $t(NH_2)$	717(m)	

As has been mentioned already, it is assumed that a molecule of HCA has the point symmetry C_{2h}, so that only the $\nu(NH)$ vibration is infrared-active. The hydrazides[1] containing the –CONHNHCO– group show a band about 3200 cm^{-1} which has been associated with the $\nu(NH)$ vibration. On *N*-deuteration, the 3360 cm^{-1} band of HCA moves to 2565 cm^{-1}, while the 3190 cm^{-1} band is displaced by a doublet band with two peaks at 2390 and 2340 cm^{-1}. Therefore, it seems possible that the 3190 cm^{-1} band is the $\nu_s(NH_2)$ band overlapping with the $\nu(NH)$ band. Such a doublet band, which has two peaks at 2400 and 2320 cm^{-1}, is also found for HTCA-d_6.

SC and TSC are considered to show rather complicated absorption bands associated with the $\nu(NH_2)$ and $\nu(NH)$ vibrations because of the less symmetrical structure of their molecules. In fact, SC shows three strong bands at 3410, 3310 and 3200 cm^{-1} and TSC, at 3370, 3270 and 3190 cm^{-1} (see Table VI(b)). On *N*-deuteration, the SC 3410 cm^{-1} band of SC moves to 2580 cm^{-1}, and the 3370 cm^{-1} band of TSC, to 2560 cm^{-1}. SC·HCl also has a band at 3410 cm^{-1} which is displaced by a band at 2570 cm^{-1} on *N*-deuteration. Therefore, the band about 3400 cm^{-1} may be assigned to the $\nu_a(NH_2)$ vibration of the $-CONH_2$ group. On the other hand, no band corresponding to the band near 3300 cm^{-1} is observed in SC·HCl; therefore, this band may be associated with the $\nu(NH_2)$ vibration of the $-NHNH_2$ group. This assignment is supported by the fact that the hydrazides[2] contaning the $-CONHNH_2$ group show a band ca. 3300 cm^{-1}. The 3200 cm^{-1} band of SC is displaced by a doublet band with two peaks at 2410 and 2330 cm^{-1} on *N*-deuteration. This band corresponds in frequency to, and behaves on *N*-deuteration like, the 3190 cm^{-1} band of HCA; therefore, it may be the $\nu_s(NH_2)$ band of the $-CONH_2$ group overlapping with the $\nu(NH)$ band. TSC also has the corresponding band at 3190 cm^{-1} which is displaced by a doublet band, 2400 and 2330 cm^{-1}, on *N*-deuteration. The band of SC·HCl at 3220 cm^{-1} may be similarly explained because it is displaced by a doublet band, 2390 and 2320 cm^{-1}, on *N*-deuteration. SC·HCl further shows two strong bands at 2850 and 2640 cm^{-1} which are displaced by two bands at 2090 and 2020 cm^{-1} on *N*-deuteration; therefore, they may be associated with the NH_3^+ stretching vibrations.

ASC shows strong or moderately strong bands at 3440, 3310 and 3230 cm^{-1}; ATSC has corresponding bands at 3440, 3310, 3170 cm^{-1}. Of these three, the former two move to about 2600 and 2500 cm^{-1} on *N*-deuteration, while the third band corresponds in frequency to, and behaves on *N*-deuteration like, the bands about 3200 cm^{-1} of the compounds in Tables VI(a) and (b). Therefore, the band about 3200 cm^{-1} of ASC and ATSC may also be taken as the $\nu_s(NH_2)$ band overlapping with the $\nu(NH)$ band. On the other hand, the 3440 and 3310 cm^{-1} bands are considered to arise from the $\nu_s(NH_2)$ and $\nu(NH)$ vibrations respectively. For FTSC the corresponding bands are found at 3295, 3155 and 2970 cm^{-1}.

The Bands of SC·HCl.—The observed frequencies of this compounds have partly been accounted for in previous sections. Let us now consider the frequencies charateristic of the NH_3^+ structure. A number of investigations have been made of the infrared spectra of amino acids and their hydrochlorides. These compounds usually show two characteristic bands in the 1600∼1500 cm^{-1} region which are associated with the NH_3^+ deformation vibrations; many amino acids have a further band near 1300 cm^{-1} and their hydrochlorides, a band near 2000 cm^{-1}.[23] Mizushima and Nakagawa[24] have obtained the 1650∼1560 cm^{-1} range for the $\delta_a(NH_3)$ frequency, the 1350∼1150 cm^{-1} range for the $\delta_s(NH_3)$ frequency, and the 950∼650 cm^{-1} range for the $r(NH_3)$ frequency in ammine complex salts. On the other hand, the corresponding frequencies of the NH_3^+ structure have been found at 1613, 1504, 1133 and 1109 cm^{-1} for glycine[25] and 1620, 1515 and 1497, and 1185 and 1112 cm^{-1} for *C*-deuterated glycine.[26]

The observed frequencies of SC·HCl in the region from 1600 to 700 cm^{-1} and their assignments are summarized in Table VII. In the range for the $\delta_a(NH_3)$ frequency indicated above, SC·HCl has only a strong band at 1586 cm^{-1}; this disappears on *N*-deuteration and so may be associated with the $\delta({}_aNH_3^+)$ frequency. The band at 1529 cm^{-1} also disappears on *N*-deuteration and corresponds in frequency to the $\delta_s(NH_3^+)$ band of glycine. Therefore, it may be ascribed to the $\delta_s(NH_3^+)$ vibration. This hydrochloride shows two bands at 1215 and 1180 cm^{-1} in place of the 1182 cm^{-1} band of SC, and on *N*-deuteration those two bands shift to 1036 and 1005 cm^{-1} respectively. Their frequency-values are a little high, but they may be taken as $r(NH_3^+)$ frequencies. This assignment is consistent with the fact that these two bands appear in place of the 1882 cm^{-1} band of SC which has been ascribed to a $\delta(NH_2)$ vibration of the hydrazine residue. In SC·HCl-d_6 the two bands at 1160 and 1130 cm^{-1} are considered to arise from the $\delta_a(ND_3^+)$ and $\delta_s(ND_3^+)$ vibrations respectively.

Since three bands, at 1088, 933, and 768 cm^{-1} of SC·HCl and 918, 892 and 761 cm^{-1} of SC·HCl-d_6, have their partner bands in the spectra of SC and SC-d_5 respectively, these bands may be explained in the same way as those partner bands have been. It is especially interesting to see that the 1088 and 933 cm^{-1} bands of SC·HCl are displaced by two bands at 918 and 892 cm^{-1} on *N*-deuteration. In consequence, this observation supports the assignment presented already (see Table V(a)); i.e., the 1080 and 946 cm^{-1} bands of SC are associated with the $r(NH_2)$ and δ(O=C–N) vibrations of the $-CONH_2$ group, and the 917 and 891 cm^{-1} bands of SC-d_5, with the hybridized vibrations composed of the $r(ND_2)$ and δ(O=C–N) vibrations. The two bands at 1486 and 1387 cm^{-1} are displaced by bands at 1459 and 1441 cm^{-1} on *N*-deuteration, and these may be ascribed to skeletal stretching vibrations. A moderately strong band at 717 cm^{-1} disappears on *N*-deuteration and may be associated with a $w(NH_2)$ or $r(NH_2)$ vibration.

The weak band of SC·HCl at 1926 cm^{-1} seems to be one characteristic of the NH_3^+ structure, but it may be ascribed to a combination or overtone band because it is scarcely changed in frequency on *N*-deuteration.

Conclusions

(1) For HTCA, TSC, ATSC, and FTSC a ν(C=S) frequency has been obtained in the 860∼800 cm^{-1} range which is rather lower than that obtained in other classes of compounds containing the C=S bond. In *N*-deuterated species, the ν(C=S) vibration interacts with the $r(ND_2)$ vibration and two bands which may be regarded as characteristic of the $-CSND_2$ group appear. In consequence, the conclusion obtained for thioamides[15,16] has been confirmed by the present observations.

(2) The spectra of HCA and SC are rather more like that of urea than those of hydrazides containing a –CONHNHCO– or $-CONH\cdot NH_2$ group; the observed frequencies have tentatively been explained by comparing the spectra with the spectrum of urea.

(3) In ASC, ATSC, and FTSC the amide I, II, and III bands characteristic of the –CONH– group have without ambiguity been located. HTCA, TSC, ATSC, and FTSC show amide II- and III-like bands; these two bands are regarded as characteristic of the –CSNH– group, as previously been found for monosubstituted thioamides.[17]

(4) For SC·HCl the frequencies characteristic of the NH_3^+ structure have without much difficulty been obtained. By comparing the spectrum of SC·HCl with that of SC, the $r(NH_2)$ and δ(O=C–N) frequencies of the $-CONH_2$ group and two frequencies due to hybridized vibrations composed of the $r(ND_2)$ and δ(O=C=N) vibrations have been obtained.

The author is grateful to Professor Yoshiya Kanda of Kyushu University for the use of the spectrophotometer. He is also indebted to the Ministry of Education for its financial support.

Department of Literature and Science
Saga University
Saga

---

[23] See Ref. 14, pp. 234-244.

[24] S. Mizushima and I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 124 (1959).

[25] M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **12**, 253 (1958).

[26] K. Nakamura, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 118 (1959).