Infrared Spectra of Acyclic Imides. II. The Characteristic Absorption Bands of Saturated Acyclic Imides in the Crystalline State

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The infrared spectra of four saturated aliphatic acyclic imides and their *N*-deuterated compounds in the crystalline state have been measured and compared with those of diacetamide and diacetamide-*d* reported previously[1]. The crystals of these higher homologs show the same characteristic absorption bands as those of the form B of diacetamide. This suggests that in the crystalline state, these higher homologs take a configuration similar to that in the form B of diacetamide. Vibrational assignments have been given to the characteristic bands in the sodium chloride region in analogy with the case of monosubstituted amides[2,3]. The influence of an adjacent carbonyl group on the characteristic frequencies of the –CONH– group has been discussed. The present result gives support to the trans-trans planar structure for the crystals of these higher homologs as well as for the form B of diacetamide.

Results and Discussion

The infrared spectra of these acyclic imides and their absorption frequencies are shown in Fig. 1 [4] and Table I[4]. As seen from Fig. 1, the infrared spectra of the crystals of those

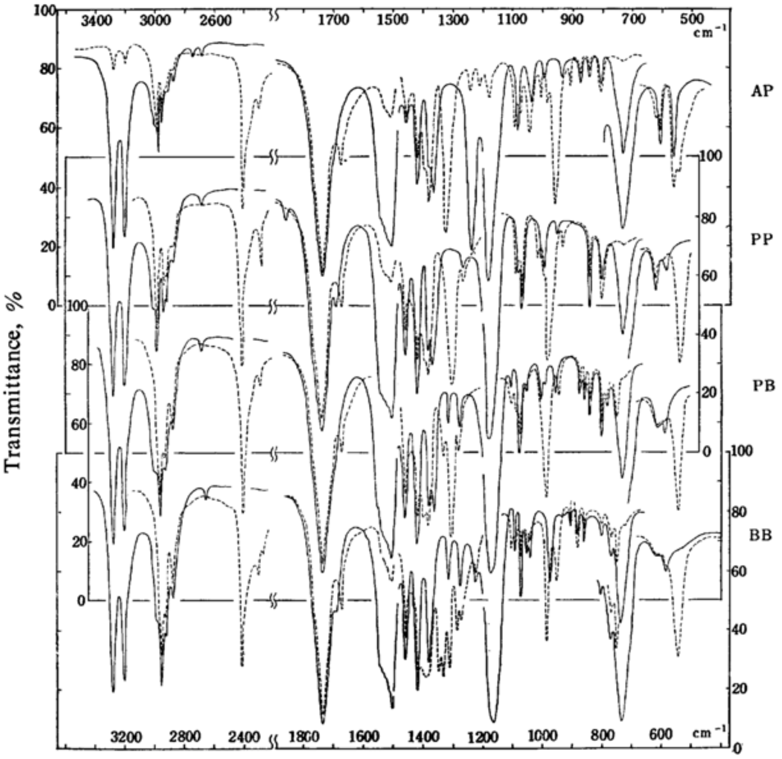

Fig. 1. Infrared spectra of higher homologs of diacetamide in the crystalline state.
Solid line: the undeuterated species, broken line: the *N*-deuterated species.
(3600∼2300 cm⁻¹ and 1480∼1200 cm⁻¹) hexachlorobutadiene pastes
(1900∼1480 cm⁻¹ and 1200∼400 cm⁻¹) Nujol pastes.

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[1] T. Uno and K. Machida, This Bulletin, 34, 545 (1961).

[2] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, 24, 408 (1956); ibid., 29, 611 (1958).

[3] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), 77, 171, 321, 526, 619 (1956).

[4] Abbreviations used in Fig. 1 and Tables I—IV are: AA: diacetamide, AP: *N*-acetylpropionamide, PP: dipropionamide, PB: *N*-propionyl-*n*-butyramide, BB: di-*n*-butyramide.

TABLE I. INFRARED ABSORPTION FREQUENCIES OF ACYCLIC IMIDES (in cm^{-1})

Undeuterated species				*N*-Deuterated species			
AP	PP	PB	BB	AP	PP	PB	BB
3280 vs	3280 vs	3280 vs	3280 vs	2978 m	2992 s	2960 s	2958 s
3205 vs	3200 vs	3205 vs	3200 vs	2960 w	2948 w	2939 m, sh.	2935 m, sh.
3000 w, sh.	3005 w, sh.	3000 w, sh.	2995 w, sh.	2920 w, sh.			
2978 m	2992 s	2960 s	2958 s	2875 w	2875 w, sh.	2875 w	2875 w
2960 w	2948 m	2939 m	2935 w, sh.	2410 s	2416 s	2415 s	2410 s
2920 w, sh.	2923 w			2300 w	2283 m	2290 w	2300 w
2875 w	2875 w	2875 w	2875 w				2283 w
2750 w				1734 vs	1736 vs	1737 vs	1733 vs
2690 w	2693 w	2695 w	2678 w	1674 w	1673 w	1674 w	1673 w
	1860 w			1458 w	1459 m	1460 m	1460 m
1734 vs	1736 vs	1737 vs	1733 vs	1419 m	1420 m	1423 m	1415 s
	1690 w		1695 w, sh.	1405 m, sh.	1395 m, sh.	1404 m, sh.	
1504 vs, br.	1504 vs, br.	1507 vs, br.	1503 vs, br.	1381 s	1380 s	1380 s	1385 s, br.
1458 w	1459 m	1460 m	1460 m				1348 m
1419 m	1420 s	1423 s	1415 s	1329 s		1334 w	1332 m
1380 m, sh.	1384 m	1380 m	1378 m		1304 s	1307 s	1314 m
1370 s	1367 s	1367 s				1284 w	1285 w
		1311 w	1306 w				1275 w
		1275 w	1272 w	1212 w	1263 w		1230 w
1240 vs, br.	1263 w		1230 w			1105 w	1112 w
1180 vs, br.	1180 vs, br.	1180 vs, br.	1167 vs, br.	1090 m	1088 w		1098 w
	1080 w, sh.	1105 w	1098 m	1073 w	1075 m	1075 m	1076 w
1081 m	1075 m	1075 m	1076 m	1048 m			1055 w
		1050 w	1055 w	1008 w	1016 w		1044 w
1035 w	1009 w	1007 w	1044 w	988 w	994 w, sh.		
994 w	994 w	994 w, sh.		969 m	986 m	987 m	985 m
	955 w	964 w	971 m		934 w	945 w	954 w
938 w			903 w	914 w			903 w
879 w		879 w	880 w	879 w		879 w	880 w
		861 w	862 w			861 w	862 w
845 w	843 m	842 w		845 w	843 w	842 w	
808 w	806 w	807 m	802 w	808 w	806 m	807 w	802 w
		787 w	770 w, sh.			787 w	770 w
734 m, br.	732 m, br.	733 m, br.	733 m, br.			752 w	750 w
609 w	614 w, br.	616 w	620 w, sh.	620 w			
559 m	590 w	590 w, br.	589 w, br.	609 w	612 w, br.	610 w, br.	620 w, sh.
				559 m	590 w, sh.	586 w, sh.	580 w, sh.
				541 m, sh.	540 m	542 m	542 m

vs: very strong, s: strong, m: medium, w: weak, sh.: shoulder, br.: broad

higher homologs of diacetamide measured in the present study are quite similar to that of the form **B** of diacetamide, so that these crystals will also be called form B hereafter. Since both acyclic imides R–CONHCO–R′ and monosubstituted amides R–CONH–R′ contain the –CONH– group, their infrared spectra are expected to be closely related with each other. In fact, these acyclic imides and *N*-deuterated acyclic imides exhibit a number of absorption bands whose frequencies and intensities correspond to those of the characteristic bands of monosubstituted amides and their *N*-deuterated compounds[2,3]. Thus, it appears that similar vibrational modes are responsible for the corresponding absorption bands of acyclic imides and monosubstituted amides. The characteristic frequencies and their vibrational assignments of these imides are shown in Table II[4] along with those of *N*-methylacetamide[2] for comparison. Detailed discussion for each characteristic frequency is as follows.

Imide I (Carbonyl Stretching) Band.—All the undeuterated and *N*-deuterated species of these acyclic imides show a strong band clearly due to the C=O stretching vibration near 1735 cm^{-1}.

TABLE II. THE CHARACTERISTIC FREQUENCIES OF ACYCLIC IMIDES (in cm^{-1})

Undeuterated species

	AA	AP	PP	PB	BB	MA*
Imide I						
(sym.)	1734	1734	1736	1737	1733	1653
(antisym.)	—	—	1690	—	1695	
Imide II	1505	1504	1504	1507	1503	1567
C–N–C sym. stretch.	1295	—	1263	—	1230	—
Imide III	1236	1240				1299
		1180	1180	1180	1167	
Imide V	739	734	732	733	733	725
Imide IV	625	609	614	616	620	627
	523	559	590	590	589	
Imide VI	(625)**	(609)				600

N-Deuterated species

	AA	AP	PP	PB	BB	MA
Imide I						
(sym.)	1734	1734	1736	1737	1733	1642
(antisym.)	1675	1674	1673	1674	1673	
Imide II′	1348				1348	
		1329		1334	1332	1475
			1304	1307	1314	
C–N–C sym. stretch.	1295	—	1263	—	1230	—
Imide III′	951	969	986	987	985	960
Imide V′	547	541	540	542	542	510
Imide IV	625	609	?	?	?	627
	523	559				
Imide VI′	640	620	?	?	?	(627)

* The corresponding amide characteristic frequencies of *N*-methylacetamide (liquid)[2].

** Parentheses indicate the overlapping frequencies.

TABLE III. THE C–H DEFORMATION FREQUENCIES OF ACYCLIC IMIDES (in cm^{-1})

	AA	AP	PP	PB	BB
$CH_3(\alpha)$* asym.	1425	1419			
$CH_3(\alpha)$ sym.	1372	1380			
$CH_2(\alpha)$ bend.		(1419)**	1420	1423	1415
$CH_2(\beta)$ bend.				1460	1460
$CH_3(\beta)$ or (γ) asym.		1458	1459	(1460)	(1460)
$CH_3(\beta)$ or (γ) sym.		(1380)	1384	1380	1378

* α, β and γ indicate the position of the methyl or the methylene group with respect to the carbonyl group.

** Parentheses indicate the overlapping frequencies.

Such high C=O frequencies have been reported[5-8] for a number of imides and explained as resulting from the appreciable double bond character of the imide C=O bond. To distinguish the C=O stretching bands of imides from the amide I band whose lower frequencies indicate the decreased double bond character of the amide C=O bond, we may call the former the imide I bands. In contrast with amides, imides may show two bands in the 6μ region as many other dicarbonyl compounds do. In fact, the duplication of the C=O stretching band of several diacyl derivatives of aromatic amines have been reported and attributed to a vibrational coupling between two C=O stretching modes[6]. In general, an acyclic imide can exhibit the symmetric and the antisymmetric imide I band if the molecule

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[5] B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, **74**, 3861 (1952).

[6] R. A. Abramovitch, *J. Chem. Soc.*, **1957**, 1413.

[7] J. F. Grove, P. W. Jeffs and D. W. Rustidge, ibid., **1956**, 1956.

[8] S. F. D. Orr, P. Sims and D. Manson, ibid., **1956**, 1338.

has a symmetry operation permuting those two C=O bonds. Furthermore, if the transition moment of the stretching vibration of each C=O bond is nearly parallel to the bond itself, the intensity ratio of the antisymmetric imide I band to the symmetric one will increase with the angle between those two equivalent C=O bonds. In the present study, besides the above mentioned strong band near 1735 cm^{-1}, the undeuterated species of some imides show a weak band near 1700 cm^{-1}, which disappears on deuteration. On the other hand, a weak band near 1675 cm^{-1} is observed for all the *N*-deuterated acyclic imides in form B regardless of the presence of the band near 1700 cm^{-1} for the corresponding undeuterated species. Weak as it is, the band near 1675 cm^{-1} must be a fundamental one because it is unlikely to expect a constant overtone or combination frequency in this region throughout all the *N*-deuterated species of these acyclic imides. Thus, a similar fundamental frequency for the undeuterated species can be expected and it is quite probable that the band near 1700 cm^{-1} actually exists for all the undeuterated species of these acyclic imides although in some cases this band is covered with the shoulder of the strong band near 1735 cm^{-1}. These considerations lead to a reasonable assignment of the above bands to the symmetric and the antisymmetric C=O stretching vibration on the basis of the trans-trans planar structure proposed for the form B in the preceding paper[1]. Thus, the antisymmetric imide I band (near 1700 cm^{-1}) is expected to be weak, just as is observed, since in this configuration two C=O bonds are nearly parallel to each other. The low-frequency shift of this weak band on deuteration may be due to some contribution of the N-H deformation mode, whereas the strong symmetric imide I band (near 1735 cm^{-1}) does not shift on deuteration because there is no coupling between the C=O symmetric stretching and the N-H in-plane deformation mode. As will be discussed later, the antisymmetric imide I band near 1700 cm^{-1} is considered to combine with the band near 1500 cm^{-1} and to give rise to a combination band near 3200 cm^{-1}.

Imide II and II′ Bands.—Detailed discussions have been given to the band near 1500 cm^{-1} observed for the form A and the form B of diacetamide[1]. All higher homologs of diacetamide in the present study show a similar band near 1505 cm^{-1} which disappears on deuteration. On the basis of the trans-trans planar structure, this band is assigned to the vibration in which the coupling between the C-N-C antisymmetric stretching and the N-H in-plane deformation mode is considerable, and will be called the imide II band hereafter. As seen from the frequency difference between the imide I and the amide I bands, the double bond character of the C=O bond is greater for acyclic imides than for monosubstituted amides. Consequently, the C-N bond order of acyclic imides should be less than that of monosubstituted amides, and it is quite reasonable that the imide II frequency of acyclic imides in the trans-trans configuration is lower than the amide II frequency of monosubstituted amides in the trans configuration, since the C-N stretching force constant is one of the important factors which determine the imide II and the amide II frequency. Further studies such as normal vibration calculations are necessary for a more detailed elucidation of the nature of the imide II band since the structural differences between the -CONH- and the -CONHCO- group must be taken into account.

As is the case of the C=O stretching vibrations, the trans-trans configuration of the -CONHCO- group must exhibit the C-N-C symmetric stretching vibration as well as the antisymmetric one. Since there is no possibility of remarkable vibrational coupling, which would give rise to the high imide II frequency for the antisymmetric vibration, the C-N-C symmetric stretching frequency is expected to be considerably lower than the imide II frequency. In fact, diacetamide, dipropionamide and di-*n*-butyramide show a weak band due probably to the C-N-C symmetric stretching mode at 1295, 1263 and 1230 cm^{-1} respectively. These bands do not shift on deuteration. Since the angle between two C-N bonds in the imide group is nearly 120°, the vibrational transition moment of the C-N-C symmetric stretching mode is expected to be so small as to result in these weak bands.

The form B of diacetamide-*d* shows a band at 1348 cm^{-1}, which clearly corresponds to the amide II′ band of *N*-deuterated monosubstituted amides. This band, which may be called the imide II′ band, is assigned to the C-N-C antisymmetric stretching mode. It is obvious that the difference in the C-N bond order between imides and amides contributes to the frequency difference between the imide II′ and the amide II′ bands. As for the *N*-deuterated species of the higher homologs of diacetamide, the imide II′ band appears in the region 1350 to 1300 cm^{-1}, taking somewhat complicated features. In this case, there are several vibrational modes belonging to B_2 species in this region and they may contribute to the imide II′ band in various ways. This effect results in the splitting of the imide II′ band in the case of di-*n*-butyramide-*d*. The antisymmetric CH_2 wagging modes may be examples of such participating vibrational modes.

Imide III and III′ Bands. — As previously reported[1], the form B of diacetamide shows a strong band at 1236 cm^{-1}. *N*-Acetylpropionamide also shows an analogous band at 1240 cm^{-1} together with another strong band at 1180 cm^{-1}. The other three higher homologs containing no acetyl group show only one strong band near 1180 cm^{-1}. All these bands disappear on deuteration and an alternative medium band appears in the region 990 to 950 cm^{-1} for each of these *N*-deuterated acyclic imides. In analogy with the case of monosubstituted amides, these bands of the undeuterated species of acyclic imides in the region 1250 to 1150 cm^{-1} may be assigned to the vibration to which both the C–N–C antisymmetric stretching and the N–H in-plane deformation mode mainly contribute and the medium band of the *N*-deuterated species in the region 990 to 950 cm^{-1} to the vibration to which the N–D in-plane deformation mode mainly contributes. Thus, these bands are considered to be characteristic of the -CONHCO- or the -CONDCO- group. Hereafter, the former and the latter bands will be called the imide III and the imide III′ bands of acyclic imides respectively. To explain the appearance of two strong imide III bands for *N*-acetylpropionamide, somewhat different fashions of vibrational coupling between the N–H in-plane deformation and the C–N streching vibrations must be considered. Because the C–N bond order of acyclic imides is less than that of monosubstituted amides, the imide III frequencies are lower than the amide III frequencies. On the other hand, it is noticed that there is no appreciable difference between the imide III′ and the amide III′ frequencies. Since there are many factors affecting such deformation frequencies, estimation of the difference in the deformation force constant of the angle C–N–H between monosubstituted amides and acyclic imides is not so simple as that in the stretching force constants. These problems will be discussed later with the aid of the normal vibration calculation for diacetamide.

Imide V and V′ Bands.—There is a medium band near 735 cm^{-1} for the undeuterated species while there is a somewhat weaker band near 540 cm^{-1} for the *N*-deuterated species of each higher homolog of diacetamide in the present study. The presence of these bands clearly indicates that the crystal form of higher homologs corresponds rather to the form B than to the form A of diacetamide. These two bands correspond to the amide V and the amide V′ band of monosubstituted amides and their *N*-deuterated compounds respectively. The N–H or the N–D out-of-plane deformation mode is considered to contribute mainly to these bands. Hereafter, the band of the undeuterated species near 735 cm^{-1} and the band of the *N*-deuterated species near 540 cm^{-1} will be called the imide V and the imide V′ band, respectively, of acyclic imides. A discussion concerning these bands has already been made in the preceding paper on diacetamide[1]. There are few differences between the imide V and the the amide V frequency and between the imide V′ and the amide V′ frequency. Namely, together with the case of the imide III′ and the amide III′ frequencies, it can be said that no appreciable frequency difference is observed between the bands of trans monosubstituted amides and those of trans-trans acyclic imides as far as nearly pure N–H deformation modes are concerned.

Imide IV, VI and VI′ Bands.—The other bands in the potassium bromide region observed for diacetamide and diacetamide-*d* were assigned before[1]. The correspondence between these bands and the amide IV, VI and VI′ bands of monosubstituted amides is obvious. In analogy with the case of monosubstituted amides, the C=O in-plane and the C=O out-of-plane deformation bands of the undeuterated species will be called the imide IV and the imide VI bands respectively, and the C=O out-of-plane deformation bands of the *N*-deuterated species will be called the imide VI′ bands. The imide IV bands which do not shift on deuteration are observed at 609 and 559 cm^{-1} for *N*-acetylpropionamide and the weak imide VI′ band appears at 620 cm^{-1} for *N*-acetylpropionamide-*d*. For the other three acyclic imides containing no acetyl group, two weak bands are observed near 610 and 590 cm^{-1} for the undeuterated species. They are probably due to some C=O deformation modes. However, because of ambiguous spectral change on deuteration in this region, the assignment of these bands is still uncertain.

N–H and N–D Stretching Bands.—Two strong bands near 3280 and 3200 cm^{-1} are observed for the undeuterated species of these acyclic imides in the form B. These bands are related to the N–H stretching vibration, and their frequencies clearly show the presence of hydrogen bonds. Their distinguished sharpness, however, together with the high C=O stretching frequencies previously mentioned, suggests that the nature of hydrogen bonds involved in the form B is markedly different from those known for monosubstituted amides and related compounds. As for the N–D stretching vibration, except for the band near 2410 cm^{-1}, *N*-deuterated acycilc imides in the form B show no strong band in the region 2500 to 2300 cm^{-1}. Thus, it is seen that the remarkable band splitting observed for the undeuterated species vanishes

TABLE IV. ANALYTICAL DATA AND MELTING POINTS OF ACYCLIC IMIDES

	Calcd., %			Found., %			M. p., °C	
	C	H	N	C	H	N	Exp.	Lit.
AP	52.16	7.88	12.17	52.31	7.86	12.08	86	86[11]
PP	55.79	8.58	10.85	56.03	8.70	10.61	154	154[12]
PB	58.72	9.15	9.28	58.47	8.95	9.90	116	109[13]
BB	61.12	9.62	8.91	60.82	9.67	9.17	115	111[9]

on deuteration. This situation will be discussed in the next paper, where the dichroic properties of those two bands of the undeuterated species will also be treated.

C–H Deformation Bands.—Two or three bands are observed for each of the undeuterated species of these acyclic imides in the region 1460 to 1370 cm^{-1}. These bands are assigned to the CH_3 or the CH_2 deformation modes in analogy with the case of other compounds containing acyl groups. The results are summarized in Table III[4], where it is noticed that acyclic imides which contain the ethyl or the *n*-propyl group, show a sharp and strong band due to the bending vibrations of the α-methylene group near 1420 cm^{-1}. For the molecules containing the structure $-C-CH_2-CONHCO-CH_2-C-$, this band is the strongest among the C–H deformation bands in this region. Changes in features and intensities of these C–H deformation bands also take place on deuteration. In general, the intensity of the band near 1420 cm^{-1} decreases while that of the band near 1380 cm^{-1} increases. This fact shows that, in connection with the complicated features of the imide II′ bands of these higher homologs, certain C–H deformation vibrations may be involved in the couplings which give rise to the imide characteristic bands in this region.

Conclusion

On the basis of the trans-trans planar structure of the –CONHCO– group, almost all the assignments as well as the interpretation of the frequencies and the intensities have been given to the characteristic bands of those saturated acyclic imides in the form B. These results give support to the internal rotation mechanism for the dimorphism of diacetamide by confirming the configuration of the –CONHCO– group in the form B. There are few deviations in the imide I, II, V and V′ frequencies of these acyclic imides while the difference in the alkyl residues affects the imide II′, III and III′ frequencies as well as their band features. Further evidences of the trans-trans planar structure for form B will be given in the next paper which deals with the infrared dichroism of some acyclic imides.

Experimental

The four acyclic imides in the present paper were prepared by the acylation of primary amides with the mixture of acid chlorides and acid anhydrides according to Polya's method[9]. In the preparation of asymmetric acyclic imides, the smaller acyl groups were chosen to be in primary amides. These acyclic imides were recrystallized two or three times from petroleum ether[10]. Table IV[4] shows the analytical data for these preparations and their melting points together with those in the literatures. The *N*-deuterated species of these acyclic imides were prepared by the exchange reaction with deuterium oxide[10]. These preparations were subjected to measurements with the same instrument and technique as those described in the preceding paper[1].

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