Infrared Spectra of Acyclic Imides. III. Infrared Dichroism of Dipropionamide and N-Acetylpropionamide Crystals

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In order to obtain information on the molecular structure of acyclic imides in the form B, infrared dichroic measurement has been made for dipropionamide and *N*-acetylpropionamide. These compounds were chosen as examples of the simplest acyclic imides being stable in the form B. Their oriented crystals were easily prepared on sodium chloride plates. Further evidences for the trans-trans planar structure[1] could be given to these molecules from the dichroic properties of the imide characteristic bands and some other bands. With the aid of these evidences, the splitting of the N-H stretching bands which is one of the important features in the infrared spectra of the form B, will be discussed in terms of the Fermi resonance.

Results and Discussion

Configurations of Imide Group and Molecular Symmetries.—Since the dichroic property of an infrared absorption band, if the molecule in question has any symmetry at all, depends on the symmetry of the vibrational mode from which the band arises, the interpretation of infrared dichroism should be closely related to molecular symmetry. In this connection, a brief survey of the relationship of molecular symmetry to the configurations of the -CONHCO- group will be presented here. In the trans-trans or the cis-cis configuration of this group, both the C=O bonds take an equivalent position with respect to the N-H bond. Consequently, as long as we are concerned with an isolated molecule, symmetrically substituted acyclic imides in the trans-trans configuration, as well as cyclic imides with polymethylene chains can be regarded to have the molecular symmetry C_{2v}. However, for actual molecules in the crystalline state, this is not always true exactly. For instance, although succinimide clearly takes the cis-cis configuration, those two C=O bonds in this molecule are not equivalent to each other regarding their nature in the crystalline state. The X-ray diffraction study[2] has shown that only one C=O bond for each molecule is involved in hydrogen bond, the other C=O bond not being so. Thus, just as in the case of diacetamide in the form A[3], every two molecules of succinimide form a ring dimer in the crystalline state. Furthermore, the five-membered ring of this molecule forms an oblique pentagon in which no two-fold axis exists. Speaking thus more strictly, the molecular symmetry of succinimide is not C_{2v} but C_s, in which only the plane of symmetry coinciding with the molecular plane remains. A similar situation may be seen for symmetrically substituted acyclic imides in the trans-trans configuration since they can exactly have the symmetry C_{2v} only if those two C=O bonds in the -CONHCO- group are equivalent to each other in their nature as well as in their configuration. Although we have shown that the infrared spectra of acyclic imides in the form B are reasonably interpreted in terms of the symmetry C_{2v}[1], it is not yet determined whether they exactly have the symmetry C_{2v} or whether the deviations from C_{2v} are too small to affect their infrared spectra. Under these situations,

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[1] T. Uno and K. Machida, This Bulletin, **34**, 545, 551 (1961).

[2] R. Mason, *Acta Cryst.*, **9**, 405 (1956).

[3] T. Watanabé and K. Osaki, unpulished.

the results of infrared dichroic measurements in the present study will be discussed on the basis of the approximation in which symmetrically substituted acyclic imides in the trans-trans configuration are regarded to have the symmetry C_{2v}. Discussions will also be made on the nature of the hydrogen bond in the form B which is closely related to whether those two C=O bonds in the -CONHCO- group are equivalent or not.

TABLE I. INFRARED DICHROISM OF DIPROPIONAMIDE

Frequency, cm^{-1}	Intensity[*1] //	⊥	Assignments (species)
3500	w	—	1736×2 (A_1)
3280	vs	—	N-H stretch. (A_1)
3200	vs	—	1690+1504 (A_1)
3005	sh	—	1504×2 (A_1)
2992	s	s	C-H stretch.
2948	—	sh	
2923[*2]	—	m	
2875	—	w	
2693	w	—	1504+1180 (A_1)
1860	vw	—	?
1736	vs	vw	sym. imide I (A_1)
1690	sh	w	antisym. imide I (B_1)
1504	—	vs	imide II (B_1)
1459	m	m	CH_3 asym. def. (//: A_1, ⊥: B_1 and B_2)
1420	s	w	CH_2 bend. (//: A_1, ⊥: B_1)
1384	m	sh	CH_3 sym. def. (//: A_1, ⊥: B_1)
1367	—	s	CH_2 wag., imide II and imide III (B_1)
1263	w	w	//: C-N-C sym. stretch., CH_2 wag. (A_1) ⊥: CH_2 twist. (B_2)
1180	w	vs	imide III (B_1)
1080	—	w	
1075	m	—	C-C stretch.
1009	—	w	(//: A_1, ⊥: B_1)
994	m	—	CH_3 rock.
955	w	w	(//: A_1, ⊥: B_1 or B_2)
843	—	w	CH_2 rock. (⊥: B_2)
806	—	w	
732	—	w	imide V (B_2)

[*1] vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

[*2] Probably due to the CH_2 out-of-phase stretch. (B_2) mode.

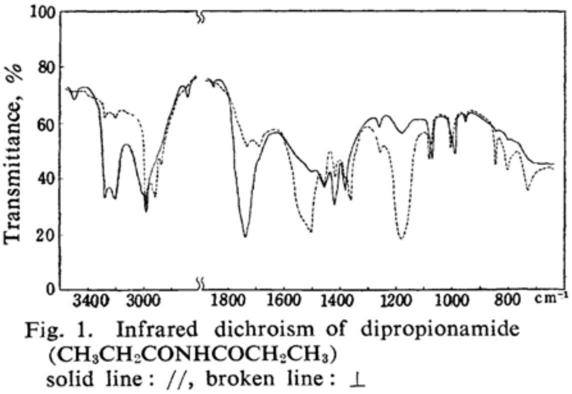

Fig. 1. Infrared dichroism of dipropionamide ($CH_3CH_2CONHCOCH_2CH_3$)
solid line: //, broken line: ⊥

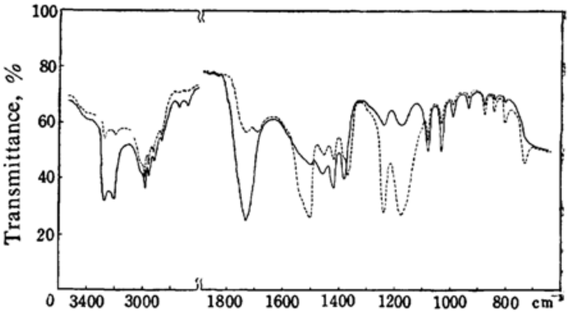

Fig. 2. Infrared dichroism of N-acetylpropionamide ($CH_3CH_2CONHCOCH_3$)
solid line: //, broken line: ⊥

TABLE II. INFRARED DICHROISM OF *N*-ACETYLPROPIONAMIDE

Frequency, cm^{-1}	Intensity //	⊥	Assignments (species)
3280	vs	w	N-H stretch. (A′)
3200	vs	w	1690+1504 (A′)
3000	sh	sh	1504×2 (A′)
2978	m	m	C-H stretch.
2960	m	m	
2920	w	w	
2875	w	w	
2750	w	—	1504+1240 (A′)
2690	w	—	1504+1180 (A′)
1734	vs	w	sym. imide I (A′)
1690	—	w	antisym. imide I (A′)
1504	vw	vs	imide II (A′)
1458	m	w	CH_3 (β) asym. def. (A′ or A″)
1419	m	w	CH_3 (α) asym. def. (A′ or A″), CH_2 bend. (A′)
1380	m	sh	CH_3 (α or β) sym. def. (A′)
1370	—	s	CH_2 wag., imide II and imide III (A′)
1240	w	vs	imide III (A′)
1180	w	vs	imide III (A′)
1081	m	w	C-C stretch. (A′) CH_3 rock. (A′ or A″) CH_2 rock. (A″)
1035	m	w	
994	w	vw	
938	w	vw	
879	w	w	
845	vw	w	
808	vw	w	
733	—	w	imide V (A″)

As shown in Figs. 1 and 2, dipropionamide and *N*-acetylpropionamide show marked infrared dichroism. Tables I and II show the dichroic properties of the absorption bands of these acyclic imides together with the assignments given to these bands. The symbols // and $\perp$ are used for the polarized light with the electric vector parallel and perpendicular, respectively, to the elongation direction of the crystal. Since the molecular symmetry of dipropionamide (C_{2v}) and that of *N*-acetylpropionamide (C_s) are different from each other with respect to their alkyl groups, discussions will be made separately for these two compounds.

Dipropionamide.—As shown in Table I, the dichroic properties of the characteristic bands of dipropionamide in the sodium chloride region, previously assigned on the basis of the trans-trans configuration of the -CONHCO- group, are closely related to the symmetry species of these bands. That is to say, the bands belonging to A_1 species show parallel dichroism while the bands belonging to B_1 or B_2 species show perpendicular dichroism. In order to explain these facts, the following structure may be proposed for the crystal preparations. In this structure, the two-fold axis of each molecule is parallel to the elongation direction of crystal while there are molecules whose molecular planes are not perpendicular to the incident light. The latter situation may be realized by the uniaxial orientation of the crystallites even in a case where the unit cell consists only from molecules whose molecular planes are parallel to one another. It will now be shown that the consistency between the dichroic properties of individual characteristic bands and the proposed structure is quite sufficient. The marked parallel dichroism of the bands at 3280 and 3200 cm^{-1}, whose origin will be discussed later, may be taken as indicating that the direction of the N-H bond involved in hydrogen bond (i. e. the direction of the two-fold axis) is parallel to the elongation direction of the crystal. The strong band at 1736 cm^{-1} also shows marked parallel dichroism supporting the assignment to the C=O symmetric stretching mode (A_1) as well as the trans-trans configuration of the -CONHCO- group, in which all the N-H and the C=O bonds are nearly parallel to one another. The weak band at 1690 cm^{-1}, which has been assigned to the C=O antisymmetric stretching mode (B_1), seems to show perpendicular dichroism although this is not so obvious owing to the broadness of the adjacent strong band at 1736 cm^{-1}. On the other hand, the marked perpendicular dichroism of the imide II (1504 cm^{-1}) and the imide III (1180 cm^{-1}) band is consistent with the assignment to B_1 fundamentals whose vibrational transition moments are perpendicular to the plane of symmetry bisecting the angle C-N-C. The imide V band at 732 cm^{-1}, to which the N-H out-of-plane deformation vibration mainly contributes, shows perpendicular dichroism. If all the molecular planes in the crystal are perpendicular to the incident radiation, the band due to an out-of-plane vibration will not be observed, regardless of polarization. The proposed structure, however, may afford reasonable elucidation to the dichroic property of this band. The weak band at 1263 cm^{-1} shows no dichroism. This fact may be taken as indicating that the band showing parallel dichroism resulting from the C-N-C symmetric stretching vibration (A_1) is overlapped by a band due to B_1 or B_2 vibration. This is probable since the B_2 CH_2 twisting band may occur in this region.

Further evidences for the proposed structure are obtained from the dichroic properties of the bands due to the vibrations of the C-H bonds. In the region where the C-H stretching bands occur, no band shows appreciable dichroism except for the band at 2923 cm^{-1}, which shows perpendicular dichroism and may be assigned to the CH_2 out-of-phase stretching mode. If the C_{2v} trans-trans configuration is assumed for dipropionamide, each of the C-H stretching vibrations will belong to the following symmetry species shown in parentheses: the CH_3 symmetric (A_1, B_1), the CH_3 asymmetric (A_1, B_1, A_2, B_2), the CH_2 in-phase (A_1, B_1) and the CH_2 out-of-phase (A_2, B_2). Thus, the dichroic properties of the C-H stretching bands are consistent with the proposed structure. A similar situation is seen for the C-H deformation bands at 1459, 1420 and 1384 cm^{-1}, each of which occurs for the polarized light with the electric vector along the elongation direction of the crystal as well as for the light polarized perpendicular to this direction. However, the dichroic ratio $I_{//}/I_{\perp}$ of the band at 1420 cm^{-1}, which is due to the CH_2 bending vibrations, is appreciably greater than unity, indicating that the magnitude of the vibrational transition moment of the A_1 mode is greater than that of the B_1 mode. This fact is consistent with the proposed structure where a molecule of dipropionamide has two equivalent CH_2 groups. With respect to the bending vibration of the CH_2 group at either side of the N-H bond, the component of the vibrational transition moment parallel to the N-H bond (the two-fold axis) is greater than the perpendicular component. Thus, the interaction between this vibration and the same vibration of the other CH_2 group results in a greater change of dipole moment for the in-phase (A_1) vibration than for the out-of-phase (B_1) vibration. The band at 1367 cm^{-1}, which disappears on deuteration, shows marked perpendicular dichroism. Possible vibrations which contribute to this band may be the B_1 CH_2 wagging, the N–H in-plane deformation, and the C–N–C antisymmetric stretching mode. Thus, we may notice that the coupling between the imide characteristic vibrations (the imide II and the imide III mode) and the C–H deformation vibrations takes place to some extent.

Generally speaking, for the bands which exhibit distinguished dichroism in the region 1800 to 900 cm^{-1}, there is a simple relation between the dichroic property and the behavior on deuteration. In other words, the bands showing perpendicular dichroism (1504, 1367, 1180, 1080 and 1009 cm^{-1}) shift, while the bands showing parallel dichroism (1736, 1075 and 994 cm^{-1}) do not shift on deuteration. This fact means that two propionyl groups in a molecule take an equivalent configuration with respect to the central N–H bond. There are three cases which satisfy this condition, namely, the symmetry C_2 with the two-fold axis coinciding with the N–H bond, the symmetry C_s with the plane of symmetry bisecting the angle C–N–C, and the symmetry C_{2v} with both of these symmetry elements. However, the first two are not likely since an appreciable angle between two C=O bonds in the –CONHCO– group is inconsistent with the weakness of the C=O antisymmetric stretching band at 1690 cm^{-1}.

As discussed in the previous section, the study only on the infrared spectra seems to be insufficient to estimate the deviation from the exact equivalence of these two C=O bonds. Furthermore, since the imide hydrogen atom is clearly involved in the hydrogen bond, the exact equivalence of the proton acceptors can not be attained without the presence of the so-called bifurcated hydrogen bond, whose existence, however, has been reported for few molecules[4]. Although more detailed investigations such as the X-ray diffraction study must be carried out to decide the exact feature of this hydrogen bond, it is here pointed out that molecular structures where both the bonded and the free C=O bond exist can hardly elucidate the experimental results up to the present study; for instance, the occurrence of only one strong C=O stretching band with comparatively high frequency (1736 cm^{-1}) and its parallel dichroism. The bands in the 3 μ region observed for these acyclic imides are very sharp in contrast with other cases where the bonded N–H stretching bands are very broad. Furthermore, the imide II band, which is partly due to the N–H in-plane deformation mode, is remarkably broad. It is suggested that these features may be closely related to the nature of hydrogen bonds in these acyclic imides in the form B.

***N*-Acetylpropionamide.** — The dichroic properties of the imide characteristic bands of *N*-acetylpropionamide are quite similar to those of the corresponding bands of dipropionamide. It is noticed here that both of the two imide III bands (1240 and 1180 cm^{-1}) of *N*-acetylpropionamide show the same perpendicular dichroism. Although this molecule has no two-fold axis, the vibrational transition moments of these bands are considered to be almost perpendicular to the N–H bond owing to the large amplitude of the N–H in-plane deformation vibration contributing to the vibrational modes of these bands. The weak antisymmetric imide I band, which has not been resolved from the strong symmetric imide I band at 1734 cm^{-1} in the spectrum of non-oriented sample, appears at 1690 cm^{-1} with the light with electric vector perpendicular to the elongation direction of the crystal. On the other hand, the clear-cut relation between the behavior on deuteration and the dichroic property which is seen for all the bands showing remarkable dichroism in the region 1800 to 900 cm^{-1} of dipropionamide, does not hold well for the bands in the region 1100 to 900 cm^{-1} of *N*-acetylpropionamide. That is to say, all the bands showing parallel dichroism (1081, 1035, 994 and 938 cm^{-1}), which may be due to the vibrations of alkyl groups, shift or split on deuteration. These results are consistent with the trans-trans configuration of the –CONHCO– group since *N*-acetylpropionamide in this configuration can be regarded to have the symmetry C_{2v} only in the approximation where the difference between the CH_3 and the CH_3CH_2 groups is neglected.

Fermi Resonance in the 3 μ Region.—On the basis of the planar trans-trans configuration, the origin of the splitting of the N–H stretching bands of these acyclic imides in the form B will now be discussed. From the spectral features of the *N*-deuterated species in the region 2500 to 2300 cm^{-1}, where no more than one strong band appears, it is obvious that the situation giving rise to this splitting must be what vanishes on deuteration. From this point of view, the band near 3280 cm^{-1} is assigned to the N–H stretching mode and the band near 3200 cm^{-1} to a combination band of some lower fundamentals enhanced by Fermi resonance with the N–H stretching mode. Other possible reasons for the splitting of the band

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[4] For instance, see R. Marsh, *Acta Cryst.*, **11**, 662 (1958).

TABLE III. THE COMBINATION FREQUENCIES OF THE *N*-DEUTERATED SPECIES OF SATURATED ACYCLIC IMIDES NEAR 2300 cm^{-1}

Compound	Frequency cm^{-1}	Intensity	Imide II′ frequency cm^{-1}	Imide III′ frequency cm^{-1}
Diacetamide-*d*	2295	w	1348	951
N-Acetylpropionamide-*d*	2300	w	1329	961
Dipropionamide-*d*	2283	m	1304	986
N-Propionyl-*n*-butyramide-*d*	2290	w	1307	987
Di-*n*-butyramide-*d*	2300	w	1332	985
Di-*n*-butyramide-*d*	2283	w	1314	985

in the 3 μ region, such as the intermolecular interaction in the unit cell, or the presence of two species of hydrogen bonds, must hold equally well for the undeuterated and the *N*-deuterated species to give rise to the splitting of the N–D stretching band of the latter. It is also difficult to explain the same parallel dichroism of these two bands near 3280 and 3200 cm^{-1} from these reasons. On the other hand, regarding whether appropriate fundamentals giving rise to an overtone or a combination tone in the regions in question exist or not, the situation for the undeuterated species is obviously different from that for the *N*-deuterated species. As the fundamentals which combine to give rise to the band near 3200 cm^{-1}, the antisymmetric imide I band (near 1700 cm^{-1}) and the imide II band (near 1500 cm^{-1}) are the most reasonable ones. In the C_{2v} approximation for the planar trans-trans configuration, these two bands belong to the B_1 species. Thus, it may be expected that the N–H stretching vibration (A_1) is involved in Fermi resonance with the combination tone of these two frequencies to give rise to two bands showing parallel dichroism in the 3 μ region just as has been observed. The constant frequencies of these lower fundamentals (near 1700 and 1500 cm^{-1}) throughout all of these acyclic imides result in a practically identical feature of the bands near 3280 and 3200 cm^{-1}. Similar Fermi resonance has already been reported for both the trans and the cis configuration of monosubstituted amides[5,6]. For the *N*-deuterated species of these acyclic imides in the form B, one or two weak bands sometimes appear near 2300 cm^{-1}. In contrast with the band near 3200 cm^{-1} for the undeuterated species, appreciable differences in frequencies and intensities of these weak bands are observed among the *N*-deuterated species of these acyclic imides. These bands may be assigned to the combination tones of the imide II′ and the imide III′ bands which also belong to the B_1 species. The imide II′ and the imide III′ frequencies of the *N*-deuterated species of these acyclic imides in the form B are appreciably different from one another and give rise to their combination bands in a somewhat different manner regarding both the frequencies and the intensities. These combination frequencies are shown in Table III, where good correspondences of these frequencies to the sums of the imide II′ and the imide III′ frequencies are observed.

Conclusion

By the examination of infrared dichroism of dipropionamide and *N*-acetylpropionamide, not only the assignments previously given to the characteristic and the C–H deformation bands have been confirmed, but further information concerning some other bands has also been obtained on the basis of the trans-trans configuration of the –CONHCO– group. Although some of the assignments proposed in the present study may be tentative, it seems significant that nearly all the infrared active vibrations in the sodium chloride region for the structure in question could have been attributed to the bands observed in this region.

The origin of the splitting of the N–H stretching band has been made clear in terms of Fermi resonance from the dichroic properties and the behavior on deuteration of these bands although there remains an interesting problem in regard to the nature of the hydrogen bond in which the N–H and the C=O bonds may be involved.

Experimental

Materials.—Oriented crystallites of *N*-acetylpropionamide and those of dipropionamide from molten liquid were prepared on sodium chloride plates with the application of temperature gradient. Their infrared spectra were confirmed to be identical with those of the crystals from petroleum ether in the paste method.

Dichroic Measurement.—The Hitachi EPI-2 infrared spectrophotometer with the sodium chloride prism, the IM-2P infrared microilluminator and the silver chloride transmission polarizer were used.

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5) R. M. Badger and A. D. E. Pullin, *J. Chem. Phys.*, **22**, 1142 (1954); M. Beer, H. B. Kessler and G. B. B. M. Sutherland, ibid., **29**, 1097 (1958).

6) T. Miyazawa, *J. Mol. Spectroscopy*, **4**, 168 (1960).

The measurements were carried out in the region 4000 to 650 cm^{-1}. The 1 m. gas cell was inserted in the path of the reference beam. The application of the radiations polarized parallel and perpendicular to the elongation direction of the crystal was attained with the rotation of the polarizer by 90°. The 100% line was adjusted by the attenuator for each radiation. Other conditions were similar to those described in the preceding papers[1].

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