Infrared Spectra of Acyclic Imides. I. Two Modifications of Diacetamide in the Crystalline State

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There have been two reports concerning the vibrational spectra of diacetamide. Kohlrausch et al.[1] have reported the Raman bands in the liquid state. Orr et al.[2] have measured the infrared spectrum as a solution in chloroform. However, the vibrational frequencies below 1600 cm^{-1} have not yet been assigned. Regarding the infrared spectra for the crystalline state, no literature has been available.

The purpose of this series is to determine and assign the characteristic bands of acyclic imides (R-CONHCO-R′) and to inquire into the relation between the structures and the characteristic bands of the -CONHCO- group. Since diacetamide is the first member of homologs which have the structure R-CONHCO-R′ (R, R′=alkyl), we have taken up the infrared spectra of this compound. In the course of

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[1] K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Ber.*, **66**, 1 (1933).

[2] S. F. D. Orr, P. Sims and D. Manson, *J. Chem. Soc.*, **1956**, 1338.

the measurements in the crystalline state, we have found that there are at least two modifications depending on the recrystallizing solvents. The infrared spectra of these two forms are markedly different from each other in the region 3600 to 400 cm^{-1} for each of the undeuterated and the *N*-deuterated species. A discussion will be made for the origin of the difference between the infrared spectra of these two forms of diacetamide.

Results and Discussion

Dimorphism of Diacetamide. — Crystals of diacetamide recrystallized from ethanol, ether, chloroform and carbon tetrachloride show an identical infrared spectrum with that of crystals from molten liquid. The recrystallization from water, however, gives another crystal form which shows a markedly different infrared spectrum from that of the former. Hereafter, the former and the latter will be called the form A and the form B respectively. The form B seems to be a metastable form, since a slow change to the form A often takes place when it is allowed to stand over several days at room temperature. Although the factors which affect this change are still uncertain, we have found that crystals obtained by the freeze-drying method from an aqueous solution always show the identical infrared spectrum with that of the form A. Owing to this fact, diacetamide-*d* in both the form A and the

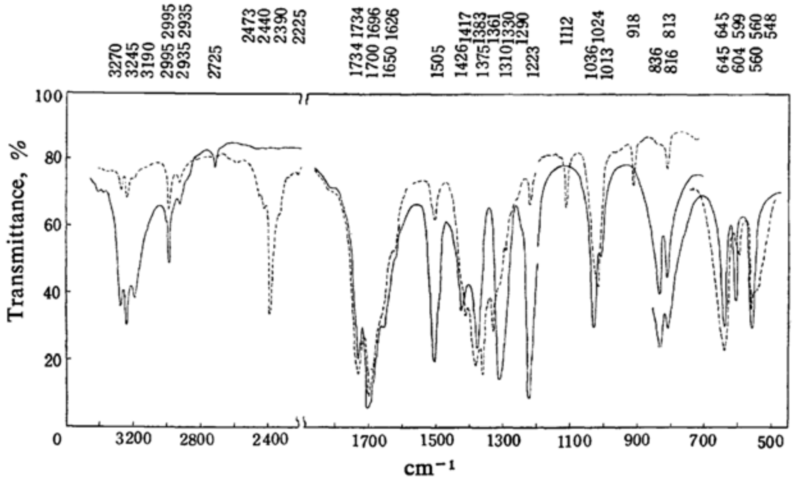

Fig. 1. Infrared spectra of diacetamide (solid line) and diacetamide-*d* (broken line) in the form A*.

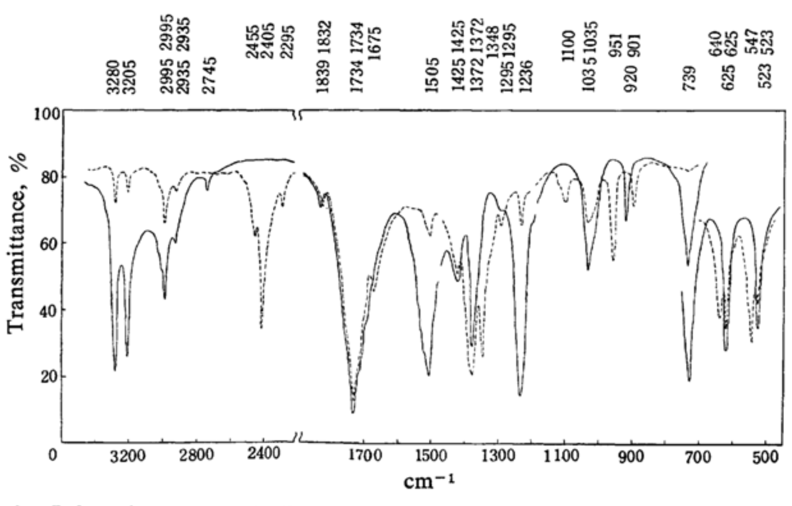

Fig. 2. Infrared spectra of diacetamide (solid line) and diacetamide-*d* (broken line) in the form B*.

* (3600∼2300 cm^{-1} and 1480∼1200 cm^{-1}): hexachlorobutadiene pastes.
(1900∼1480 cm^{-1} and 1200∼400 cm^{-1}): Nujol pastes.

form B has been obtained by the usual exchange reaction with deuterium oxide.

As shown in Figs. 1 and 2, many differences are observed between the infrared spectra of the form A and the form B. In the region 3300 to 3150 cm^{-1}, two sharp strong bands are observed for the undeuterated species in the form B while there is a medium triplet for that in the form A. As for the C=O stretching bands, the intensity of the band near 1734 cm^{-1} increases while the band near 1700 cm^{-1} almost disappears on going from the form A to the form B. Furthermore, there is no correspondence of absorption bands between these two forms below 1000 cm^{-1}. However, several correspondences of absorption bands are also observed between these two forms. Both the form A and the form B of the undeuterated species show a strong band near 1500 cm^{-1} which disappears on deuteration. A band near 1035 cm^{-1} is observed for each of these two forms of the undeuterated and the *N*-deuterated species.

To interpret these observations, the structural or the rotational isomerism must be considered since the difference only in crystal lattice can hardly give rise to such a remarkable spectral difference as is seen between the form A and the form B of diacetamide. Isoimide (R-C-(=NH)-O-CO-R′), a structural isomer of imide (R-CO-NH-CO-R′), has been proposed to correspond to an unstable isomer (m. p. 68~69°C) of *N*-butyrylbenzamide (m. p. 104°C) and a slow change of this unstable form to the stable one has been reported3). Another author4) has regarded it as an intermediate in the pyrolytic formation of acyclic imides from primary amides.

As for the unstable form of diacetamide (the form B), the C=O stretching frequency (1734 cm^{-1}) is as high as those of fatty acid esters. The strong band at 1236 cm^{-1} seems to correspond to the C-O-C antisymmetric stretching band of acetic acid esters. These features favor the isoimide structure which contains the group $-O-CO-CH_3$ for the form B. However, the disappearance of the band at 1236 cm^{-1} on deuteration cannot be explained by the assignment of this band to the C-O-C antisymmetric stretching vibration of the isoimide structure, because *N*-deuterated isoimide has also the group $-O-CO-CH_3$ and must show a similar strong band in this region. On the other hand, if the imide structure is assumed, the above fact can be reasonably explained in analogy with the case of the amide III band of monosubstituted amides since a considerable coupling between the C-N stretching modes and the N-H deformation mode is expected for the imide structure.

On the other hand, the imide structure of diacetamide in the form A has been proved by the X-ray diffraction study5), which has revealed that every two molecules of diacetamide form a ring dimer by means of a pair of the hydrogen-oxygen hydrogen bond. The oxygen atom not involved in the hydrogen bond is in the trans position with respect to the hydrogen atom as shown in Fig. 3. Thus, the isoimide structure has been ruled out from both of these two forms. These facts suggest that the difference in the infrared spectra between the form A and the form B of diacetamide is due to the rotational isomerism among imide structures.

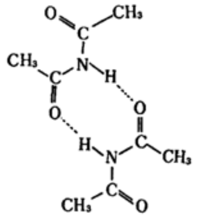

Fig. 3. Dimeric structure of diacetamide in the form A.

Internal Rotation in the Imide Structure.—It has been well established that there are marked differences in the characteristic bands between the trans and the cis configurations for monosubstituted amides6,7). In the case of imides, the presence of two (O=C)-N links differentiates three configurations shown in Fig. 4 among the planar structure of the -CONHCO- group. However, possibility for several non-planar structures must not be neglected in this case since the C-N bond order of the (O=C)-N

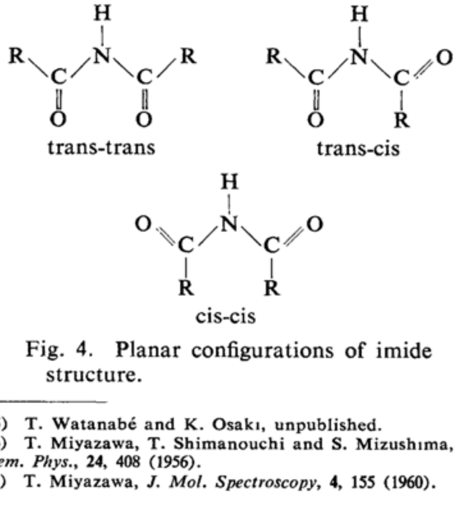

Fig. 4. Planar configurations of imide structure.

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3) P. Dunn, E. A. Parkes and J. B. Polya, *Rec. trav. chim.*, **71**, 680 (1952).

4) D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1066 (1956).

5) T. Watanabé and K. Osaki, unpublished.

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

7) T. Miyazawa, *J. Mol. Spectroscopy*, **4**, 155 (1960).

link may be less for imides than for amides. Since there is the close similarity between the amide and the imide structure, it is reasonably expected that the infrared spectra of those isomers whose differences are in the configuration of the -CONHCO- group may be presumably different from one another. Consequently, if acyclic imides take the configuration other than the cis-cis one which can be regarded approximately as the configuration of five- or six-membered cyclic imides, the infrared spectra of the former will be markedly different from those of the latter. Comparison of the infrared spectrum of succinimide[8,9] with those of the form A and the form B of diacetamide suggests that this is the case.

Monosubstituted amides with the trans -CONH- group show the amide II band in the region 1600 to 1450 cm^{-1} while those with the cis -CONH- group does not. This simple but well-known rule seems to be applicable to the -CONHCO- group in somewhat modified form. For instance, succinimide[8,9] and glutarimide[10], which are in the cis-cis configuration, exhibit no strong band in the region 1600 to 1450 cm^{-1} while the form A of diacetamide, which is in the trans-cis configuration, show a strong band which disappears on deuteration near 1500 cm^{-1}. Thus, it is seen that a distinguished band analogous to the amide II band of monosubstituted amides arises from the -CONHCO- group provided that the trans -CONH- group is contained in it. The form B of diacetamide also shows the band in question near 1500 cm^{-1} while that of diacetamide-*d* does not. Consequently, it seems quite probable that the trans -CONH- group is contained in the -CONHCO- group of diacetamide not only in the form A but also in the form B. The spectral difference between these two forms may be due to the difference in the configuration of the remaining C=O bond with respect to the N-H bond in the -CONHCO- group.

The Bands in the Potassium Bromide Region. —Another information concerned with the symmetry of a molecule can be obtained from the behavior of the absorption bands on deuteration in the potassium bromide region. From the analogy to monosubstituted amides, the band at 739 cm^{-1} observed for the form B is assigned to the N-H deformation mode perpendicular to the plane of the C-N-C link. This band shifts to 547 cm^{-1} on deuteration. The corresponding N-H deformation vibration in the form A is reasonably assigned to the broad doublet (836 and 816 cm^{-1}) which disappears on deuteration. The splitting of this band may result from Fermi resonance with an overtone or a combination tone of some lower fundamentals. For the *N*-deuterated species, the alternative N-D deformation band appears at 645 cm^{-1}, where the band splitting is not observed. Since these N-H (or N-D) deformation frequencies are within the region where the usual C=O deformation frequencies occur, the more or less coupling of the N-H or the N-D deformation mode in question with appropriate C=O deformation modes can be expected as long as the condition of the same symmetry is satisfied. However, if the molecule has a plane of symmetry or a two-fold axis along the N-H or the N-D bond, at least two C=O deformation modes are free from the possibility of such a coupling with the N-H or the N-D deformation mode. Thus, the number of the C=O deformation bands which undergo no frequency shift on deuteration may be used to estimate the symmetry of the molecule. The bands between 700 and 450 cm^{-1} observed for the undeuterated species should be attributed to the C=O deformation modes. Regarding the form A, three bands are observed at 645, 604 and 560 cm^{-1} for the undeuterated species. The change of these bands on deuteration is such that the band at 645 cm^{-1} is overlapped by the N-D deformation band without any apparent frequency shift, the band at 604 cm^{-1} shifts to 599 cm^{-1} and a shoulder not well resolved from the band at 560 cm^{-1} appears near 548 cm^{-1}. This fact may be taken as indicating that the band at 560 cm^{-1} observed for the undeuterated species is the overlap of two bands, one of which arises from a vibrational mode belonging to the same symmetry species as the N-H deformation mode and the other does not. Thus, except for the band at 645 cm^{-1} whose frequency shift on deuteration is uncertain owing to the overlap of the broad N-D deformation band, there is at least one band undergoing no frequency shift on deuteration. Therefore, a molecular structure with no symmetry is improbable for the form A. In fact, as an approximation, the planar structure (the presence of a plane of symmetry) has been shown by the X-ray diffraction study[5].

On the other hand, two bands are observed at 625 and 523 cm^{-1} for the undeuterated species of the form B, both of which undergo no frequency shift on deuteration. The *N*-deuterated species shows, besides these bands, a broad band near 640 cm^{-1}. Namely, the high-frequency shift of one component of the overlapped band at 625 cm^{-1} for the undeuteurated species takes place on deuteration. Thus, there are two bands which do not shift

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[8] J. Chouteau, *Bull. soc. chim. France*, (5) **20**, 1149 (1953).

[9] A. W. Baker, *J. Phys. Chem.*, **61**, 453 (1957).

[10] R. L. Frank and J. B. McPherson, Jr., *J. Am. Chem. Soc.*, **71**, 1389 (1949).

TABLE I. DEFORMATION FREQUENCIES IN THE KBr REGION OF THE FORM A AND THE FORM B OF DIACETAMIDE

Crystal form	Absorption frequencies (in cm^{-1})		Assignments	Symmetry species
	Undeuterated species	*N*-deuterated species		
A	836 816 } m**		N-H out-of-plane	A''
		645 m	N-D out-of-plane	A''
	645 m 560 m	(645)* 560 m	C=O in-plane	A'
	604 w (560)	599 w 548 w, sh.	C=O out-of-plane	A''
B	739 m		N-H out-of-plane	B_2
		547 m	N-D out-of-plane	B_2
	625 m 523 m	625 m 523 m	C=O in-plane	A_1 or B_1
	(625)	640 w, sh.	C=O out-of-plane	B_2

* Parentheses indicate the overlapping frequencies.

** m : medium, w : weak, sh. : shoulder

on deuteration and a plane of symmetry or a two-fold axis is necessarily required for this form. As suggested in the previous section, if the configuration of a C=O bond with respect to the N-H bond is not far from the trans one, the other C=O bond must also take the trans configuration with respect to the same N-H bond. Any other configuration with a trans -CONH- group has no symmetry except for the trans-cis one which has already been given to the form A. The fact that only one band shifts on deuteration is consistent with the trans-trans planar structure which has the symmetry C_{2v}, where only one C=O deformation mode belongs to the same symmetry species (B_2) as the N-H out-of-plane deformation mode.

These considerations made it possible to assign all the bands observed in the potassium bromide region to appropriate C=O and N-H (or N-D) deformation modes for both the form A and the form B of diacetamide and diacetamide-*d*. These results were summarized in Table I. Thus, it seems reasonable at least qualitatively that the configurations of the -CONHCO- group in the form A and the form B are not far from the trans-cis and the trans-trans ones respectively. This conclusion may be confirmed by the application of the product rule for the isotopic molecules.

The Product Rule.—The product rule for the out-of-plane vibrations for each of the trans-cis and the trans-trans planar structure is represented by the equations

$$\frac{\Pi\nu(A'')}{\Pi\nu'(A'')}=\left(\frac{m_D M I_x I_z}{m_H M' I'_x I'_z}\right)^{1/2} \qquad (1)$$

and

$$\frac{\Pi\nu(B_2)}{\Pi\nu'(B_2)}=\left(\frac{m_D M I_x}{m_H M' I'_x}\right)^{1/2} \qquad (2)$$

respectively[11], where the primes indicate the *N*-deuterated species, ν's are the observed frequencies, the multiple products are taken over those belonging to the symmetry species indicated in the parentheses, m_H and m_D are the masses of hydrogen and deuterium atoms respectively, M is the total mass of the molecule, I_x and I_z are the moments of inertia with respect to the principal axes in the molecular plane. As for the trans-trans planar structure, Eq. 2 shows that the principal moment of inertia with respect to the two-fold axis (I_z) is not related to the B_2 species. In calculation of the moments of inertia, the bond lengths were assumed to be the same as those used in the normal vibration calculation of *N*-methylacetamide[12], and all the bond angles were assumed to be 120°. The observed and the theoretical values are shown in Table II, where the out-of-plane frequencies other than those shown in Table I were assumed to be unchanged on deuteration. As the N-H out-of-plane deformation frequency of the form A, the mean value (826 cm^{-1}) of the listed frequencies was used. As seen from Table II, the agreement between the observed and the theoretical values is rather reasonable, since the uncertainly in frequencies due to the broadening and the

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[11] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York (1955), p. 183.

[12] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, 29, 612 (1958).

TABLE II. PRODUCT RULE FOR THE OUT-OF-PLANE FREQUENCIES OF DIACETAMIDE

Crystal form	Configuration of the -CONHCO- group	Symmetry species	Product rule ratio (undeuterated species / N-deuterated species) theoretical	observed
A	trans-cis	A″	1.38	1.34
B	trans-trans	B_2	1.38	1.32

overlapping of bands may result in deviations up to 4%. These results give supports to the assignments of the bands in the potassium bromide region as well as the planar structures of the form A and the form B of diacetamide in the crystalline state. On the basis of these structures, the bands in the sodium chloride region will be discussed in successive papers.

Experimental

Materials. — Diacetamide was prepared by the acetylation of acetamide with acetic anhydride in the presence of ammonium chloride[13], distilled in vacuo and recrystallized twice from ether. Then each of two crystal forms was obtained as follows. The form A was crystallized from ether. M. p. 81°C. (Found: C, 47.43; H, 7.217; N, 13.56. Calcd. for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.86%). Recrystallization from water, at 30∼35°C under the reduced pressure (5∼10 mmHg) produces the form B. M. p. 81°C. (Found: C, 47.43; H, 7.08; N, 13.86%). The form B was identified before and after the elementary analyses by the infrared spectra.

Diacetamide-*d* was prepared by the exchange reaction with deuterium oxide. The form A was obtained when deuterium oxide was removed by the freeze-drying method with the mixture of acetone and dry ice at 1∼2 mmHg. The form B was obtained when deuterium oxide was removed under the same conditions as those applied to obtain the form B of the undeuterated species.

Measurements. — The Koken DS-301 infrared spectrophotometer was used with sodium chloride (3600 to 600 cm^{-1}) or potassium bromide (900 to 400 cm^{-1}) prisms. Ammonia and polystyrene were used for the frequency calibration. The errors were within 5 cm^{-1} in 3600∼2000 cm^{-1}, 2 cm^{-1} in 2000∼1200 cm^{-1} and 1 cm^{-1} in 1200∼400 cm^{-1}. The measurements of infrared spectra were carried out for hexachlorobutadiene (3600 to 1200 cm^{-1}) or Nujol (2300 to 400 cm^{-1}) pastes. A current of dry nitrogen gas was introduced into the spectrophotometer in order to exclude the effect of CO_2 absorption from the bands in the region 2400 to 2300 cm^{-1} for the *N*-deuterated species.

Summary

Two crystal forms have been found for diacetamide (the form A and the form B). Infrared spectra of these two forms of diacetamide and diacetamide-*d* have been measured in the region 3600 to 400 cm^{-1} and many differences of absorption bands have been observed. It has been shown that these differences of absorption bands can be explained to result from rotational isomerism. The trans-trans planar structure of the -CONHCO- group has been proposed to correspond approximately to the molecular structure of the unstable form (the form B) of diacetamide. The frequency shifts of absorption bands on deuteration in the potassium bromide region has been discussed to give support to this interpretation. An assignment has been given to each absorption band in the potassium bromide region for the form A and the form B of diacetamide and diacetamide-*d*.

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[13] D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1068 (1956).