August, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2413—2423 (1972) 2413

Vibrational Spectra of *trans-trans* Diacetamide and Its C- and N-Deuterated Compounds

Yoshihiro Kuroda, Yutaka Saito, Katsunosuke Machida, and Toyozo Uno
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto,

(Received March 24, 1972)

The infrared spectra of $CH_3CONHCOCH_3$, $CD_3CONHCOCH_3$, $CD_3CONHCOCD_3$, and their N-deuterated compounds have been recorded for the unstable crystalline modification in which the molecules are in the *trans-trans* conformation (form B). The Raman spectra of $CH_3CONHCOCH_3$ in the form B crystal and in the complex with KI have also been recorded. Vibrational assignments have been given by referring to the characteristic group frequencies of related compounds, the infrared dichroic measurement for $CH_3CONHCOCH_3$ and the isotopic frequency shifts. The normal coordinates analysis has been made by assuning the planar *trans-trans* conformation of the –CONHCO– (–CONDCO–) group. The calculated frequencies fit to the observed satisfactorily.

The rotational isomerism of the imide (–CONHCO–) group has been found for diacetamide, the first member of the homologous series of aliphatic acyclic imides.[1,2] In the usually occuring crystalline modification, form A, and in the concentrated solutions in non-polar solvents, diacetamide takes the *trans-cis* conformation, in which one of the C=O bonds is at the *trans* position and the other at the *cis* position with respect to the central NH bond. The more symmetric *trans-trans* conformation is taken, on the other hand, by molecules in another crystalline modification, form B, which is unstable at room temperature. Previously, the in-plane normal frequencies of *trans-trans* diacetamide and the corresponding *N*-deuterated derivatives were calculated on a simplified model in which the methyl groups were taken as point masses.[3] However, more detailed investigations for both the *trans-trans* and the *trans-cis* conformations are necessary to discuss how the force constants of the –CONHCO– group are affected by the change of molecular environments on the interconversion of the conformation. In succession to the recently reported vibrational analysis of *trans-cis* diacetamide,[4,5] the present paper deals with the infrared and Raman spectra of *trans-trans* diacetamide and the infrared spectra of its C- and N-deuterated derivatives. Most of the fundamental frequencies have been assigned and the normal coordinate calculation has been made by assuming a Urey-Bradley force field supplemented by the general valence force constants for C–C and C–N torsions and the C=O and N–H out-of-plane deformations. The force constants have been refined by the least squares method to give the best agreement between the observed and the calculated frequencies. The C=O and C–N stretching force constants of the *trans-trans* and *trans-cis* molecules reflect well the difference in the type of hydrogen bonds between the form A and form B crystals.

Experimental

The preparation and N-deuteration of $CH_3CONHCOCH_3$ and $CD_3CONHCOCD_3$ were described in our preceding paper.[4] In the present work, $CD_3CONHCOCH_3$ was also synthesized from CH_3COND_2 and CD_3COCl by the same method that was used to synthesize $CD_3CONHCOCD_3$.[4] The NMR spectrum of the obtained specimen revealed that it contained a small amount of the CHD_2 and CH_2D species. However, this specimen exhibited no indication of infrared absorptions due to such isotopic impurities, and the infrared spectra of $CD_3CONHCOCH_3$ and $CD_3CONDCOCH_3$ were used as references for the interpretation of the vibrational spectra of diacetamide. The recrystallization from water, which is the previously described method to prepare the form B crystal,[1] resulted mostly in the formation of the form A crystal for the material used in this work. Instead, the slow crystallization from the melt in a sealed glass tube was found to lead effectively to the formation of the form B crystal. For Nujol mulls of the samples prepared as described above, the infrared spectra were measured on a Koken DS-301 infrared spectrophotometer (4000—700 cm^{-1}), on a Perkin-Elmer Model-521 grating spectrophotometer (900–250 cm^{-1}) and on a Hitachi FIS-3 grating spectrophotometer (400—33 cm^{-1}). In the region where the absorptions of Nujol appear, hexachlorobutadiene was used as the mulling medium for $CH_3CONHCOCH_3$ and $CH_3CONDCOCH_3$,

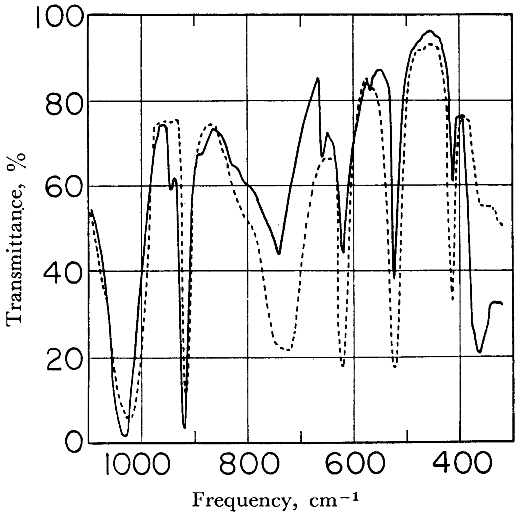

Fig. 1. Polarized infrared spectra of $CH_3CONHCOCH_3$ in the region between 1100 and 350 cm^{-1}.
Solid line: electric vector parallel to the direction of crystal growth.
Dotted line: electric vector perpendicular to the direction of crystal growth.

---

[1] T. Uno and K. Machida, This Bulletin, **34**, 545 (1961)
[2] T. Uno and K. Machida, *ibid.*, **35**, 1226 (1962)
[3] T. Uno and K. Machida, *ibid.*, **36**, 427 (1963)
[4] Y. Kuroda, Y. Saito, K. Machida, and T. Uno, *Spectrochim. Acta*, **27**, 1481 (1971).
[5] Y. Kuroda, Y. Saito, K. Machida, and T. Uno, *ibid.*, in press.

but hexachlorobutadiene could not be used for the C-deuterated compounds since the transition to the form A crystal took place very quickly in this medium. It was found previously that diacetamide mixed with NaBr, NaI, and KI shows similar infrared spectra to the form B crystal.[6] Recently, Roux *et al.* have confirmed by the X-ray analysis that diacetamide takes the *trans-trans* conformation on forming the complex with NaBr and KI.[7] Since the form B crystal of the C-deuterated compounds were found to be very unstable even in Nujol mulls, infrared spectra of the complex with KI were used to check the absorptions due to the *trans-cis* molecules. Occasionally, the form B crystal was obtained by the slow crystallization form the melt inserted between two KBr plates. One of these solid films of CH_3-

TABLE 1. OBSERVED FREQUENCIES OF $CH_3CONHCOCH_3$, $CH_3CONDCOCH_3$, $CD_3CONHCOCH_3$, $CD_3CONDCOCH_3$, $CD_3CONHCOCD_3$, AND $CD_3CONDCOCD_3$

$CH_3CONHCOCH_3$		CH_3CONH-$COCH_3$-KI	CH_3COND-$COCH_3$	CD_3CONH-$COCH_3$	CD_3COND-$COCH_3$	CD_3CONH-$COCD_3$	CD_3COND-$COCD_3$
Infrared	Raman	Raman	Infrared	Infrared	Infrared	Infrared	Infrared
3260 s		3245		3260 s		3260 s	
3180 s		3163		3180 s		3170 s	
3015 m		3001				3015 w	
2995 vw		2968	2995 vw	2995 vw	2995 vw		
2915 vw		2935	2915 vw	2915 vw	2915 vw		
		2920	2405 vs		2415 vs		2420 vw
1841 vw		1763		2230 vw	2230 vw	2230 vw	2230 vw
		1750		2110 vw	2110 vw	2110 vw	2110 vw
1730 vs	1734	1733	1730 vs	1728 vs	1726 vs	1720 vs	1720 vs
1695 sh		1705	1672 sh			1690 sh	1665 sh
		1523[a]					
1513 s		1488		1510 vs		1508 vs	
1428 w		1427	1428 w	1421 w	1421 w		
1369 m		1378	1369 s				1353 s
1327 vw			1327 sh	1324 vw		1324 w	1324 sh
		1250[a]				1260 vs	
1236 vs		1224		1243 vs		1175 sh	
			1120 vw		1110 sh	1122 vw	1120 m
1070 sh ($\perp$)[b]			1094 w	1079 m	1098 m	1087 w	1087 w
1030 s ($\parallel$)[b]	1033	1037	1028 m	1038 w	1037 w	1030 w	1030 sh
1027 s ($\perp$)				1018 m	1018 m		1011 m
945 vw ($\parallel$)	976[a]	979[a]	947 m	959 w	992 m	972 m	955 m
					924 m		
920 s ($\parallel$, $\perp$)	923	921	900 w	910 m	910 m	909 m	909 m
		836[a]		890 w	883 w	868 w	842 w
				805 vw	796 w	819 m	816 m
737 s ($\perp$)		751		737 s		734 m	734 m
661 vw ($\parallel$)	673	673					
		650[a]					
626 s ($\perp$)			626 s	627 vw	627 vw		
				603 m	605 w		550 sh
			546 s		546 s	542 m	540 s
526 s ($\perp$)	532	533	523 s	498 s	498 s	485 s	485 s
418 s ($\perp$)	420	420	412 w	408 w	402 w		379 vw
368 m ($\parallel$)	380	382	368 s	349 m	347 m	343 m	343 s
250 vw		227	240 vw				230 vw
160 vw		177	160 vw				
		120					
95 m	109		95 m				80 m
65 m	74		65 m				63 m
	55						
	38						

a) These frequencies may be due to the *trans-cis* diacetamide.
b) Infrared dichroism. $\perp$, $\parallel$: Electric vector perpendicular and parallel to the direction of crystal growth, respectively.

---

6) T. Uno and K. Machida, This Bulletin, **34**, 1448 (1961).

7) J. P. Roux and J. C. A. Boeyens, *Acta Crystallogr.*, **B25**, 1700, 2395 (1969)

CONHCOCH$_3$ was found to contain a small portion of the oriented crystal by the inspection under a polarization microscope. The infrared dichroic measurement for this sample has been made on a Perkin-Elmer Model-521 grating spectrophotometer with a wire-grid polarizer in the region between 1100 and 350 cm^{-1} (Fig. 1). All the wave numbers were calibrated by the standard absorptions of polystyrene, indene, ammonia, and 1, 2, 4-trichlorobenzene. The Raman spectrum of the form B crystal of CH$_3$CONHCOCH$_3$ obtained from the melt sealed in a capillary tube was recorded on a JEOL JRS-O1A laser Raman spectrophotometer. The exciting line (4880Å) was generated by an argon-ion laser at an approximate output power of 250 mW. The Raman spectrum of a mixed pellet of CH$_3$CONHCOCH$_3$ and KI was measured on a JRS-U1 laser Raman spectrophotometer with the excitation source of a 400 mW argon-ion laser (4880Å). The observed infrared and Raman frequencies are listed in Table 1.

Vibrational Assignment

On the assumption of the *trans-trans* planar conformation, the C-undeuterated and the fully C-deuterated diacetamides belong to the point group C_{2v}, and should contain 30 infrared active fundamental transitions, $12(a_1)+11(b_2)+7(b_1)$, while the remaining $6(a_2)$ normol modes are infrared inactive. All of the fundamental transitions of the half C-deuterated diacetamides, which have the C_s symmetry, should be infrared active. There is no Raman inactive transition for both the C_{2v} and the C_s molecules. The X-ray analysis by Roux and Boeyens[7] has revealed that the –CONHCO– group of diacetamide in the diactamide-KI (2 : 1) complex is only slightly distorted from the *trans-trans* planar conformation. Since the infrared spectrum of this complex and that of the form B crystal of diacetamide are almost identical with each other, it is reasonable to assume that diacetamide molecules in the form B crystal have essentially the same conformation as those in the KI complex.

The characteristic infrared absorptions of the *trans*-CONHCO-group observed in the region above 1150 cm^{-1} are the NH stretching doublet at 3260 and 3180 cm^{-1}, the imide I (a_1 C=O stretching) band at 1730 cm^{-1} and the imide II and III bands.[2] The last two bands arise from the coupled vibrations of the NH in-plane bending and CN stretching. All these bands were observed similarly for the C-deuterated compounds, and were used to check the formation of the form B crystal throughout this work. The diminishing of the imide II and III bands and the appearance of the imide II′ band (CN stretching) on the N-deuteration are clearly recognized for the fully C-deuterated compounds, for which no interference by the CH$_3$ absorptions is expected in the region between 1450 and 1350 cm^{-1} (see Fig. 2).

The assignment of infrared absorptions of *trans-trans* CH$_3$CONHCOCH$_3$ below 1150 cm^{-1} were much facilitated by the dichroism observed for the thick oriented specimen of the form B crystal described in the experimental section. By analogy with the X-ray analysis of dipropionamide, which takes the *trans-trans* conformation in the crystlline state,[8] *trans-trans* diacetamide is thought to form chain polymers by means of the bifurcated hydrogen bond, retaining the two-fold axis in the direction of chains along which the crystal grows. We may accordingly expect that the direction of crystal growth is parallel to the transition moment of a_1 vibrations but is perpendicular to those of b_1 and b_2 vibrations. The medium band at 1030 cm^{-1} of CH$_3$CONHCOCH$_3$ was assigned previously to the a_1, b_1, and b_2 CH$_3$ rocking vibrations.[3] In accord with this assignment, the dichroic measurement disclosed three components, one of which was observed at 1030 cm^{-1} for the parallel polarization of the incident radiation, while the others, a peak at 1027 cm^{-1} and a shoulder at 1070 cm^{-1}, for the perpendicular polarization. Since the initial calculation in the normal coordinate analysis gave the b_1 CH$_3$ rocking frequency about 50 cm^{-1} higher than the b_2 frequency, we assigned the shoulder near 1070 cm^{-1} and the peak at 1027 cm^{-1} to the b_1 and b_2 CH$_3$ rocking vibrations, respectively. On the N-deuteration, the intensity of the 1030 cm^{-1} band is reduced appreciably, and two weak bands

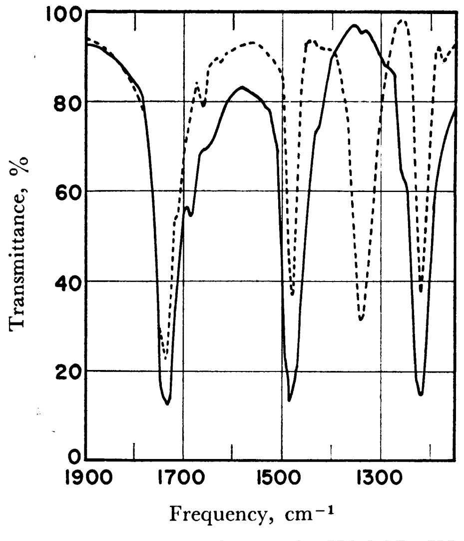

Fig. 2. Infrared spectra of CD$_3$CONHCOCD$_3$-KI complex (solid line) and CD$_3$CONDCOCD$_3$-KI complex (dotted line) in the region between 1900 and 1150 cm^{-1}.

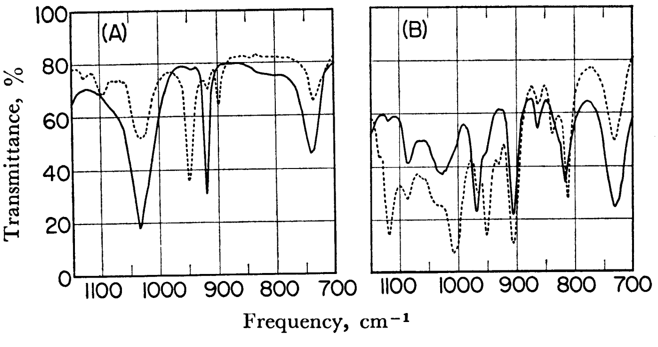

Fig. 3. (A) Infrared spectra of CH$_3$CONHCOCH$_3$ (solid line) and CH$_3$CONDCOCH$_3$ (dotted line) in the region between 1150 and 700 cm^{-1}. (B) Infrared spectra of CD$_3$CONHCOCD$_3$ (solid line) and CD$_3$CONDCOCD$_3$ (dotted line) in the region between 1150 and 700 cm^{-1}.

---

[8] T. Uechi, T. Watanabé, and K. Osaki, *Sci. Rep.* (*Osaka Univ.*) **15**, 1(1966)

appear nearly at 1094 and 947 cm^{-1}. This spectral change has been ascribed to the coupling between the b_2 CH_3 rocking and the ND in-plane deformation vibrations.[3] The b_1 CH_3 rocking absorption of CH_3-$CONDCOCH_3$ could not be identified (Fig. 3).

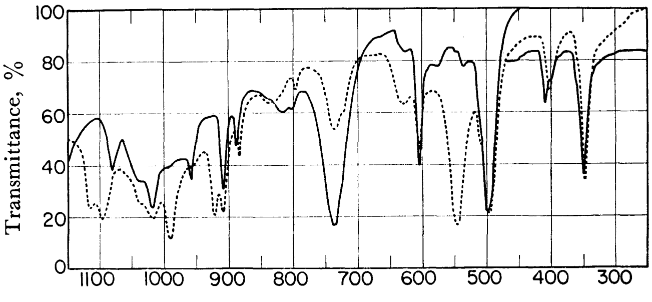

Fig. 4. Infrared spectra of $CD_3CONHCOCH_3$ (solid line) and $CD_3CONDCOCH_3$ (dotted line) in the region between 1150 and 250 cm^{-1}.

From analogy with the cases of CD_3CONH_2 and *trans-cis* $CD_3CONHCOCD_3$,[4,9] the infrared bands at 1087 and 1030 cm^{-1} of *trans-trans* $CD_3CONHCOCD_3$ are assigned to the CD_3 symmetric (a_1 and b_2) and asymmetric (a_1, b_1, and b_2) deformation vibrations, respectively. The *N*-deuteration gives rise to two additional bands at 1120 and 1011 cm^{-1}, which indicate that one of the b_2 CD_3 deformation vibrations couples with the ND in-plane deformation vibration. The half C-deuterated compound, $CD_3CONHCOCH_3$ shows two weak bands at 1079 and 1018 cm^{-1} and a shoulder band at 1038 cm^{-1} (see Fig. 4). According to the normal coordinated analysis, there is no appreciable coupling between the CH_3 and the CD_3 group vibrations, and the band at 1079 cm^{-1} and the shoulder at 1038 cm^{-1} are assigned respectively to the a' CD_3 symmetric and asymmetric deformation vibrations, while the band at 1018 cm^{-1} is assigned to both the a' CH_3 rocking and the a'' CD_3 asymmetric deformation vibrations. On the N-deuteration, the half *C*-deuterated compound shows a spectral change between 1150 and 950 cm^{-1} which is similar to that observed for the fully C-deuterated compound. The occurence of the coupling between the ND in-plane deformation vibration and the CH_3 or CD_3 deformation vibrations of $CH_3CONDCOCH_3$, $CD_3CONDCOCH_3$, and $CD_3CONDCOCD_3$ was confirmed by the normal coordinates analysis, and the assignments of the infrared absorptions of the N-deuterated compounds in this region were given reasonably by referring to the calculated frequencies.

Diaceamide has two C–C stretching vibrations, the intrinsic frequency of which is estimated to be near 900 cm^{-1} from analogy with acetamide[9] and *N*-methylacetamide.[10] So we assigned first the parallel and perpendicular components of the band at 920 cm^{-1} of $CH_3CONHCOCH_3$ to the a_1 and b_2 C–C strecthing vibrations, respectively. According to the mormal coordinates analysis, however, the a_1 mode responsible for this band is rather complex, consistimg of the CN stretching, the CH_3 rocking and the C–N–C deformation vibrations. The calculated a_1 and b_2 frequencies are very close to each other just as are observed. On the N-deuteration, the band at 920 cm^{-1} is replaced by a weak band at 900 cm^{-1}, which may be assigned to analogous vibrations. The infrared spectrum of CD_3CO-$NHCOCD_3$ between 1000 and 700 cm^{-1} is much more complicated than that of $CH_3CONHCOCH_3$, since the CD_3 rocking frequencies occur in this region. There are five bands in all, among which the bands at 972 and 868 cm^{-1} shift to 955 and 842 cm^{-1}, respectively, while those at 909 and 819 cm^{-1} shift hardly on the N-deuteration. By referring to the calculated frequencies, we assigned the 972 cm^{-1} band to the complicated a_1 vibration corresponding to that related to the 920 cm^{-1} band of $CH_3CONHCOCH_3$, and the 868 cm^{-1} band to the b_2 C–C stretching vibration. The N-deuteration insensitive bands at 909 and 819 cm^{-1} were assigned to the b_1 and b_2 CD_3 rocking vibrations, respectively. The remaining a_1 CD_3 rocking frequency was calculated to be 756 cm^{-1}. The corresponding absorption seems to be overlapped by the broad band at 734 cm^{-1} due to the NH out-of-plane deformation (imide V) vibration. For $CH_3CONHCOCH_3$, this imide V band shows the perpendicular dichroism just as expected for the b_1 species.

In the region between 700 and 300 cm^{-1}, *trans-trans* diacetamide is expected to have five infrared active fundamentals due to the a_1, b_1, and b_2 C=O deformations and the a_1 and b_2 C–C–N deformations, but the form B crystal of $CH_3CONHCOCH_3$ shows only four bands at 626, 526, 418, and 368 cm^{-1} for the unpolarized radiation. Previously, the band at 626 cm^{-1} was assigned to the a_1 and b_1 C=O deformation vibrations, based on the appearance of an additional band at 640 cm^{-1} on the N-deuteration.[1] The band at 640 cm^{-1} observed previously for the form B crystal of $CH_3CONDCOCH_3$ is missing, however, in the newly recorded spectra in this work, and is considered to be due to the contaminated *trans-cis* compound. Instead, the Raman spectra of the form B crystal and the KI-complex of $CH_3CONHCOCH_3$ recorded

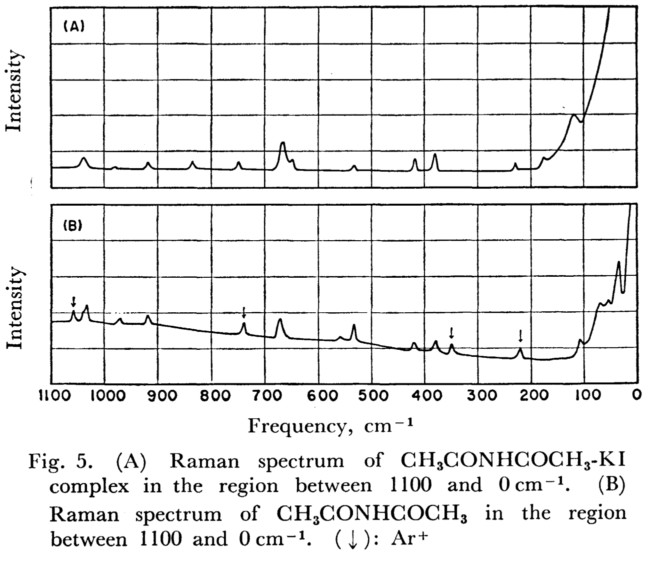

Fig. 5. (A) Raman spectrum of $CH_3CONHCOCH_3$-KI complex in the region between 1100 and 0 cm^{-1}. (B) Raman spectrum of $CH_3CONHCOCH_3$ in the region between 1100 and 0 cm^{-1}. (↓): Ar^+

---

[9] T. Uno, K. Machida, and Y. Saito, This Bulletin., **42**, 897 (1969).

[10] J. Jakes and B Schneider, *Collect. Czech. Chem. Commun.* **33**, 643 (1968).

in this work (Fig. 5) exhibited a very strong band near 673 cm^{-1} hardly assignable to non-totally symmetric fundamentals. Correspondingly, the infrared dichroic measurement revealed the presence of a weak band at 661 cm^{-1} appearing only for the parallel polarization of the incident radiation(Fig.1). The difference of 12 cm^{-1} between the Raman and infrared frequencies may be ascribed to a factor group splitting. Based on this result, the assignment of the a_1 C=O deformation (imide IV) frequency in the infrared spectrum should be revised from 626 cm^{-1} to 661 cm^{-1}. According to the normal coordinates analysis, the contribution of the C-C stretching vibration to this fundamental is also large, explaining well the prominent intensity of the Raman band at 673 cm^{-1}.

The infrared bands at 626, 526, and 418 cm^{-1} show the perpendicular dichroism and are assigned to the b_1 C=O deformation (imide VI), b_2 C=O deformation (imide IV) and the b_2 C–C–N deformation vibrations, respectively. The assignments of the bands at 526 and 418 cm^{-1} to b_2 fundamentals are supported by the appearance of a weak infrared band at 945 cm^{-1}, which shows the parallel dichroism and is assignable to the combination tone, 526+418. The remaining infrared band at 368 cm^{-1} shows the parallel dichroism and is assigned undoubtedly to the a_1 C–C–N deformation vibration. In the Raman spectra, three bands are observed near 530, 420, and 380 cm^{-1} corresponding to the infrared bands at 526, 418, and 368 cm^{-1}, but no Raman counterpart is observed for the infrared band at 626 cm^{-1}. This result is reasonable since out-of-plane fundamentals are usually weak in Raman spectra. It is difficult to explain why the infrared band at 626 cm^{-1} does not shift on the N-deuteration, whereas the normal coordinates analysis predicts a high-frequency shift of 10 cm^{-1} for the b_1 C=O deformation vibration. For the $CH_3CONHCOCH_3$-KI complex, the corresponding infrared band at 621 cm^{-1} shifts to 626 cm^{-1} on the N-deuteration, reflecting a small interaction between the ND and the C=O deformation vibrations in the b_1 species. The assignments of the infrared bands due to the skeletal deformation vibrations of the C- and N-deuterated diacetamide were made by referring to the result for $CH_3CONHCOCH_3$ and taking account of the isotope shifts. The infrared band due to the a_1 imide IV vibration of the C- and the N-deuterated compounds could not be identified probably because of its extreme weakness. In the infrared spectrum of the form B crystal of $CD_3CONHCOCD_3$ in Fig. 6, the bands at 587 and 523 cm^{-1} are due to the *trans-cis* molecules formed by the partial transition from the form B to the form A crystal. Similarly, the bands of *trans-cis* $CD_3CONDCOCD_3$ appear at 620, 587, and 521 cm^{-1} in Fig. 6.

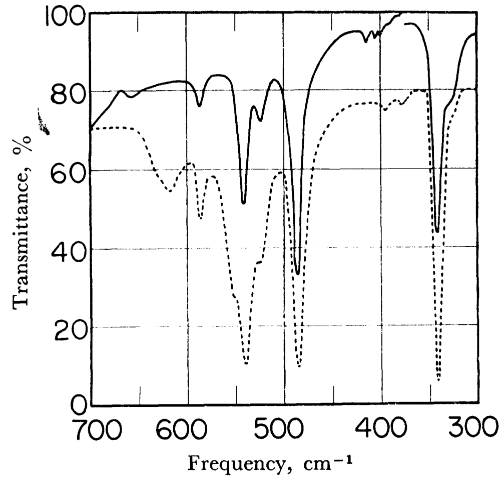

Fig. 6. Infrared spectra of $CD_3CONHCOCD_3$ (solid line) and $CD_3CONDCOCD_3$ (dotted line) in the region between 700 and 300 cm^{-1}.

In analogy with the case of *trans-cis* diacetamide, the infrared bands due to the C–N and the C–C torsional and C–N–C deformation vibrations are expected in the region below 300 cm^{-1}. We assigned the broad band centered at about 250 cm^{-1} and the very weak band at 160 cm^{-1} of the form B crystal of $CH_3CONHCOCH_3$ to the b_1 C–N torsional and the a_1 C–N–C deformation vibrations, respectively (Fig. 7). In consistent with the calculated isotope effect, the former band undergoes a low-frequency shift by about 10 cm^{-1}, while the latter remains unshifted on the *N*-deuteration. In the Raman spectrum of $CH_3CONHCOCH_3$-KI complex, the corresponding bands were observed at 227 and 177 cm^{-1}. For both $CH_3CONHCOCH_3$ and $CH_3CONDCOCH_3$, the infrared absorption due to the b_1 C–C torsional vibration is thought to overlap with a lattice absorption, giving rise to the peak at 95 cm^{-1}, since the form B crystal of CD_3COND-

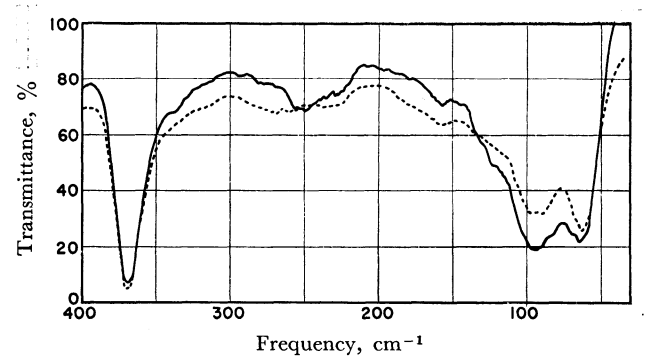

Fig. 7. Infrared spectra of $CH_3CONHCOCH_3$ (solid line) and $CH_3CONDCOCH_3$ (dotted line) in the region between 400 and 33 cm^{-1}.

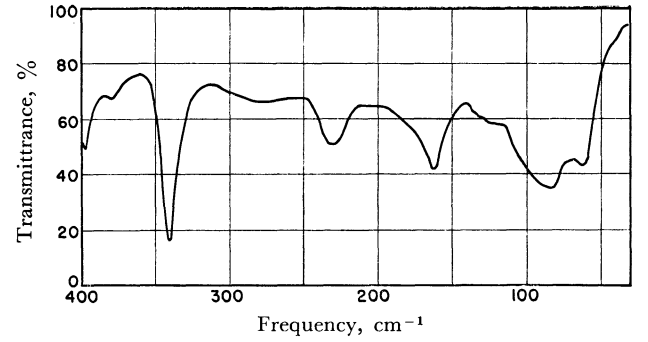

Fig. 8. Infrared spectrum of $CD_3CONDCOCD_3$ in the region between 400 and 33 cm^{-1}.

$COCD_3$ shows the corresponding peak at 80 cm^{-1} (Fig. 8). No isotope shift is observed for the infrared band at 65 cm^{-1} of the form B crystal. This band is missing in the spectra of the form A crystal, and is assigned undoubtedly to lattice vibrations. The infrared band due to the C–N torsional and the C–N–C deformation vibrations of the C-deuterated diacetamides in the *trans-trans* conformation could not be detected because of the interference of the bands due to the *trans-cis* molecules.

Normal Coordinates Analysis

In order to check the internal consistency of the present assignments of the fundamental frequencies of various isotopic molecules and to obtain a reliable set of force constants, the normal coordinates treatment has been made for *trans-trans* diacetamide and its C- and N-deuterated compounds. The internal symmetry coordinates were written down in the same way as the case of *trans-cis* diacetamide,[4,5] since we included the half C-deuterated molecules having the C_s symmetry in the calculation. The meanings of the symmetry coordinates are listed in Table 2. The secular equations were set up according to the GF matrix method.[11] We used a Urey-Bradley force field for the in-plane vibrations and the out-of-plane vibrations concerning the methyl groups and a valence force field for the remaining out-of-plane vibrations. The starting set of the Urey-Bradley force constants was the same as that used in the calculation for *trans-cis* diacetamide.[4] The diagonal valence force constants were transferred from acetamide[12] and *trans-cis* diacetamide,[5] while the off diagonal valence force constants were assumed to be zero first. The isotope shifts predicted by the initial calculation were useful to pick up some of the empirically unassignable fundamentals of the N- and the C-deuterated compounds. The force constants for the in-plane vibrations were refined in an analogous way to the case of *trans-cis* diacetamide,[4] until an overall

TABLE 2. THE MEANINGS OF THE INTERNAL SYMMETRY COORDINATES

	Description of modes			Description of modes			Description of modes	
S_1	CC str.	(νCC)	S_{13}	CH_3 rock.	(ρCH_3)	S_{25}	CH_3 asym. def.	($\delta_{as}CH_3$)
S_2	C=O str.	(νC=O)	S_{14}	C=O def.	(δC=O)	S_{26}	CH_3 rock.	(ρCH_3)
S_3	CN str.	(νCN)	S_{15}	CCN def.	(δCCN)	S_{27}	CH_3 asym. str.	($\nu_{as}CH_3$)
S_4	CN str.	(νCN)	S_{16}	CNC def.	(δCNC)	S_{28}	CH_3 asym. def.	($\delta_{as}CH_3$)
S_5	C=O str.	(νC=O)	S_{17}	C=O def.	(δC=O)	S_{29}	CH_3 rock.	(ρCH_3)
S_6	CC str.	(νCC)	S_{18}	CCN def.	(δCCN)	S_{30}	CH_3 torsion	(τCH_3)
S_7	CH_3 sym. def.	($\delta_s CH_3$)	S_{19}	NH str.	(νNH)	S_{31}	CH_3 torsion	(τCH_3)
S_8	CH_3 asym. def.	($\delta_{as}CH_3$)	S_{20}	CH_3 sym. str.	($\nu_s CH_3$)	S_{32}	CN torsion	(τCN)
S_9	CH_3 rock.	(ρCH_3)	S_{21}	CH_3 asym. str.	($\nu_{as}CH_3$)	S_{33}	CN torsion	(τCN)
S_{10}	NH def.	(δNH)	S_{22}	CH_3 sym. str.	($\nu_s CH_3$)	S_{34}	C=O def.	(πC=O)
S_{11}	CH_3 sym. def.	($\delta_s CH_3$)	S_{23}	CH_3 asym. str.	($\nu_{as}CH_3$)	S_{35}	C=O def.	(πC=O)
S_{12}	CH_3 asym. def.	($\delta_{as}CH_3$)	S_{24}	CH_3 asym. str.	($\nu_{as}CH_3$)	S_{36}	NH def.	(πNH)

TABLE 3. FORCE CONSTANTS

(A) Urey-Bradley type force constants in mdyn/Å (*KAPPA* is given in mdyn·Å/(rad)^2)

	Force constant			Dispersion		Force constant			Dispersion
1.	*K*(CH)	4.53_7	(4.62)*	0.033	11.	*H*(CCH)	0.21_1	(0.358)	0.030
2.	*K*(NH)	5.42_0	(5.74)	0.074	12.	*H*(HCH)	0.40_6	(0.401)	0.007
3.	*K*(CO)	8.71_9	(9.8)	0.267	13.	*F*(NCO)	0.91_8	(1.20)	0.162
4.	*K*(CN)	3.77_9	(4.0)	0.161	14.	*F*(NCC)	0.41_2	(0.70)	0.177
5.	*K*(CC)	3.23_1	(3.2)	0.256	15.	*F*(CCO)	0.56_9	(0.50)	0.169
6.	*H*(NCO)	0.11_4	(0.2)	0.068	16.	*F*(HNC)	0.36_2	(0.35)	0.073
7.	*H*(NCC)	0.79_3	(0.3)	0.148	17.	*F*(CNC)	1.78_9	(1.70)	0.222
8.	*H*(CCO)	0.24_1	(0.25)	0.091	18.	*F*(CCH)	0.48_9	(0.372)	0.062
9.	*H*(HNC)	0.29_9	(0.31)	0.020	19.	*F*(HCH)	0.05_6	(0.083)	0.013
10.	*H*(CNC)	0.26_8	(0.50)	0.108	20.	*KAPPA*	-0.01_4	(−0.104)	0.018

* ( ); initial value

(B) Valence type force constants in mdyn·Å/(rad)^2

1. $f_{30,30}=f_{31,31}$	0.0033	4. $f_{36,36}$	0.087	7. $f_{32,36}=-f_{33,36}$	−0.019	10. $f_{26,34}=f_{29,35}$	−0.044
2. $f_{32,32}=f_{33,33}$	0.085	5. $f_{32,34}=f_{33,35}$	−0.018	8. $f_{34,35}$	−0.047		
3. $f_{34,34}=f_{35,35}$	0.417	6. $f_{32,35}=f_{33,34}$	0.004	9. $f_{34,36}=-f_{35,36}$	0.059		

---

[11] E. B. Wilson Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[12] T. Uno, K. Machida, and Y. Saito, *Spectrochim. Acta* **27**, 833 (1971).

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES OF $CH_3CONHCOCH_3$ IN cm^{-1}

(a) In-plane vibrations (a_1, b_2)

	Obsd.	Calcd.	Δ(%)[a]	P.E.D. (%)[b]	Assignment
ν_1 (a_1)	3215	3238	0.7	$S_{19}(100)$	νNH
ν_2 (a_1)	2995	2997	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CH_3$
ν_{13}(b_2)	2995	2997	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CH_3$
ν_3 (a_1)	2915	2922	0.3	$S_{20}(50), S_{22}(50)$	ν_sCH_3
ν_{14}(b_2)	2915	2922	0.3	$S_{20}(50), S_{22}(50)$	ν_sCH_3
ν_4 (a_1)	1730	1727	0.2	$S_2(35), S_5(35)$	Imide I
ν_{15}(b_2)	1695	1700	0.3	$S_2(34), S_5(34), S_{10}(17)$	Imide I
ν_{16}(b_2)	1513	1512	0.1	$S_3(19), S_4(19), S_{10}(69)$	Imide II
ν_5 (a_1)	1428	1428	0.0	$S_8(44), S_{12}(44)$	$\delta_{as}CH_3$
ν_{17}(b_2)	1428	1425	0.2	$S_8(44), S_{12}(44)$	$\delta_{as}CH_3$
ν_6 (a_1)	1369	1375	0.4	$S_7(50), S_{11}(50)$	δ_sCH_3
ν_{18}(b_2)	1369	1374	0.4	$S_7(52), S_{11}(52)$	δ_sCH_3
ν_7 (a_1)	1327	1326	0.1	$S_1(18), S_3(18), S_4(18), S_6(18)$	νCN
ν_{19}(b_2)	1236	1238	0.2	$S_1(17), S_3(31), S_4(31), S_6(17), S_{10}(12)$	Imide III
ν_8 (a_1)	1030	1015	1.4	$S_2(12), S_5(12), S_9(19), S_{13}(19)$	$\rho CH_3+\nu C{=}O$
ν_{20}(b_2)	1027	1005	2.2	$S_9(38), S_{13}(38)$	ρCH_3
ν_9 (a_1)	920	934	1.5	$S_3(10), S_4(10), S_9(22), S_{13}(22), S_{16}(17)$	$\rho CH_3+\delta CNC+\nu CN$
ν_{21}(b_2)	920	933	1.4	$S_1(27), S_3(12), S_4(12), S_6(27)$	νCC
ν_{10}(a_1)	661	661	0.0	$S_1(18), S_6(18), S_{14}(12), S_{16}(13), S_{17}(12)$	Imide IV
ν_{22}(b_2)	526	542	3.0	$S_{14}(12), S_{15}(30), S_{17}(12), S_{18}(30)$	Imide IV
ν_{23}(b_2)	418	407	2.6	$S_{14}(33), S_{15}(12), S_{17}(33), S_{18}(12)$	$\delta C{=}O+\delta CCN$
ν_{11}(a_1)	368	367	0.3	$S_{14}(18), S_{15}(17), S_{17}(18), S_{18}(17)$	$\delta C{=}O+\delta CCN$
ν_{12}(a_1)	177	184	3.9	$S_{14}(12), S_{15}(12), S_{16}(62), S_{17}(12), S_{18}(12)$	δCNC

(b) Out-of-plane vibrations (b_1)

	Obsd.	Calcd.	Δ(%)[a]	P.E.D. (%)[b]	Assignment
ν_{24}(b_1)	2995	2996	0.0	$S_{24}(50), S_{27}(50)$	$\nu_{as}CH_3$
ν_{25}(b_1)	1428	1427	0.1	$S_{25}(44), S_{28}(44)$	$\delta_{as}CH_3$
ν_{26}(b_1)	1070	1063	0.7	$S_{26}(38), S_{29}(38)$	ρCH_3
ν_{27}(b_1)	737	738	0.2	$S_{32}(32), S_{33}(32), S_{36}(63)$	$\pi NH+\tau CN$
ν_{28}(b_1)	626	613	2.1	$S_{34}(41), S_{35}(41), S_{36}(61)$	$\pi C{=}O+\pi NH$
ν_{29}(b_1)	250	255	1.8	$S_{32}(22), S_{33}(22)$	τCN
ν_{30}(b_1)	95	105	10.5	$S_{30}(49), S_{31}(49)$	τCH_3

a) $\Delta(\%)=|\nu_{obsd}-\nu_{calcd}|\times 100/\nu_{obsd}$

b) Those less than 10% are omitted.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES OF $CH_3CONDCOCH_3$ IN cm^{-1}

(a) In-plane vibrations (a_1, b_2)

	Obsd.	Calcd.	Δ(%)[a]	P.E.D. (%)[b]	Assignment
ν_1 (a_1)	2995	2997	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CH_3$
ν_{13}(b_2)	2995	2997	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CH_3$
ν_2 (a_1)	2915	2922	0.3	$S_{20}(50), S_{22}(50)$	ν_sCH_3
ν_{14}(b_2)	2915	2922	0.3	$S_{20}(50), S_{22}(50)$	ν_sCH_3
ν_3 (a_1)	2405	2373	1.3	$S_{19}(100)$	νND
ν_4 (a_1)	1730	1723	0.4	$S_2(36), S_5(36)$	Imide I′
ν_{15}(b_2)	1672	1677	0.3	$S_2(40), S_5(40)$	Imide I′
ν_{16}(b_2)	1428	1429	0.1	$S_8(42), S_{12}(42)$	$\delta_{as}CH_3$
ν_5 (a_1)	1428	1428	0.0	$S_8(44), S_{12}(44)$	$\delta_{as}CH_3$
ν_6 (a_1)	1369	1375	0.4	$S_7(50), S_{11}(50)$	δ_sCH_3
ν_{17}(b_2)	1369	1374	0.4	$S_7(51), S_{11}(50)$	δ_sCH_3
ν_{18}(b_2)	1353	1358	0.4	$S_3(44), S_4(44), S_{10}(26)$	Imide II′
ν_7 (a_1)	1327	1325	0.2	$S_1(18), S_3(18), S_4(18), S_6(18)$	$\nu CN+\nu CC$
ν_{19}(b_2)	1094	1076	1.6	$S_1(15), S_6(15), S_9(11), S_{10}(39), S_{13}(11)$	$\delta ND+\nu CC+\rho CH_3$
ν_8 (a_1)	1028	1010	1.8	$S_2(10), S_5(10), S_9(23), S_{13}(23)$	ρCH_3

TABLE 5. Continued

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_{20}(b_2)$	947	984	3.9	$S_9(29), S_{13}(29)$	ρCH_3
$\nu_9\ (a_1)$	900	920	2.3	$S_3(11), S_4(11), S_9(18), S_{13}(18), S_{16}(18)$	$\rho CH_3+\nu CC+\delta CNC$
$\nu_{21}(b_2)$	900	892	0.9	$S_1(12), S_3(18), S_4(18), S_6(12), S_{10}(21)$	$\delta ND+\nu CN+\nu CC$
$\nu_{10}(a_1)$		658		$S_1(18), S_6(18), S_{14}(13), S_{16}(14), S_{17}(13)$	Imide IV′
$\nu_{22}(b_2)$	523	534	2.1	$S_{14}(12), S_{15}(29), S_{17}(12), S_{18}(29)$	Imide IV′
$\nu_{23}(b_2)$	412	407	1.2	$S_{14}(33), S_{15}(12), S_{17}(33), S_{18}(12)$	$\delta C{=}O+\delta CCN$
$\nu_{11}(a_1)$	368	367	0.4	$S_{14}(19), S_{15}(17), S_{17}(19), S_{18}(17)$	$\delta C{=}O+\delta CCN$
$\nu_{12}(a_1)$	160	183	14.4	$S_{14}(12), S_{15}(12), S_{16}(62), S_{17}(12), S_{18}(12)$	δCNC

(b) Out-of-plane vibrations (b_1)

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_{24}(b_1)$	2995	2996	0.0	$S_{24}(50), S_{27}(50)$	$\nu_{as}CH_3$
$\nu_{25}(b_1)$	1428	1427	0.1	$S_{25}(44), S_{28}(44)$	$\delta_{as}CH_3$
$\nu_{26}(b_1)$		1063		$S_{26}(38), S_{29}(38)$	ρCH_3
$\nu_{27}(b_1)$	626	623	0.5	$S_{34}(39), S_{35}(39), S_{36}(11)$	$\pi C{=}O+\pi ND$
$\nu_{28}(b_1)$	546	547	0.2	$S_{32}(18), S_{33}(18), S_{36}(117)$	$\pi ND+\tau CN$
$\nu_{29}(b_1)$	240	243	1.4	$S_{32}(28), S_{33}(28)$	τCN
$\nu_{30}(b_1)$	95	105	10.5	$S_{30}(49), S_{31}(49)$	τCH_3

a) $\Delta(\%)=|\nu_{obsd}-\nu_{calcd}|\times 100/\nu_{obsd}$

b) Those less than 10% are omitted.

TABLE 6. OBSERVED AND CALCULATED FREQUENCIES OF $CD_3CONHCOCH_3$ IN cm^{-1}

(a) In-plane vibrations (a')

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_1\ (a')$	3215	3238	0.7	$S_{19}(100)$	νNH
$\nu_2\ (a')$	2995	2997	0.1	$S_{23}(100)$	$\nu_{as}CH_3$
$\nu_3\ (a')$	2915	2922	0.3	$S_{22}(100)$	$\nu_s CH_3$
$\nu_4\ (a')$	2230	2228	0.1	$S_{21}(100)$	$\nu_{as}CD_3$
$\nu_5\ (a')$	2110	2099	0.5	$S_{20}(99)$	$\nu_s CD_3$
$\nu_6\ (a')$	1728	1725	0.2	$S_2(30), S_5(41), S_{18}(10)$	Imide I
$\nu_7\ (a')$		1698		$S_2(40), S_5(28), S_{10}(17)$	Imide I
$\nu_8\ (a')$	1510	1511	0.0	$S_3(19), S_4(20), S_{10}(70)$	Imide II
$\nu_9\ (a')$	1421	1427	0.4	$S_{12}(88)$	$\delta_{as}CH_3$
$\nu_{10}(a')$		1375		$S_6(11), S_{11}(102)$	$\delta_s CH_3$
$\nu_{11}(a')$	1324	1326	0.1	$S_1(25), S_3(19), S_4(18), S_6(18)$	νCN
$\nu_{12}(a')$	1243	1239	0.3	$S_1(21), S_3(30), S_4(31), S_6(17), S_{10}(12)$	Imide III
$\nu_{13}(a')$	1079	1081	0.1	$S_1(13), S_3(13), S_7(74)$	$\delta_s CD_3$
$\nu_{14}(a')$	1038	1030	0.8	$S_8(87)$	$\delta_{as}CD_3$
$\nu_{15}(a')$	1018	1006	1.2	$S_5(14), S_{13}(50)$	ρCH_3
$\nu_{16}(a')$	959	958	0.2	$S_4(19), S_{13}(26), S_{15}(11), S_{16}(15)$	$\rho CH_3+\nu CN$
$\nu_{17}(a')$	890	895	0.6	$S_1(14), S_3(10), S_6(24), S_7(16)$	νCC
$\nu_{18}(a')$	805	785	2.5	$S_9(71)$	ρCD_3
$\nu_{19}(a')$	627	632	0.8	$S_1(19), S_6(15), S_{16}(11), S_{17}(17)$	Imide IV
$\nu_{20}(a')$	498	510	2.4	$S_9(13), S_{14}(10), S_{15}(18), S_{17}(14), S_{18}(32)$	Imide IV
$\nu_{21}(a')$	408	401	1.7	$S_{14}(39), S_{17}(25), S_{18}(15)$	$\delta C{=}O+\delta CCN$
$\nu_{22}(a')$	349	348	0.4	$S_{14}(17), S_{15}(23), S_{17}(21)$	$\delta C{=}O+\delta CCN$
$\nu_{23}(a')$		180		$S_{14}(11), S_{15}(14), S_{16}(61), S_{17}(11), S_{18}(12)$	δCNC

(b) Out-of-plane vibrations (a'')

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_{24}(a'')$	2995	2996	0.0	$S_{27}(100)$	$\nu_{as}CH_3$
$\nu_{25}(a'')$	2230	2223	0.3	$S_{24}(100)$	$\nu_{as}CD_3$
$\nu_{26}(a'')$	1421	1427	0.4	$S_{28}(89), S_{29}(10)$	$\delta_{as}CH_3$
$\nu_{27}(a'')$	1038	1061	2.2	$S_{28}(10), S_{29}(78)$	ρCH_3

TABLE 6. Continued

	Obsd	Calcd	Δ(%)[a]	P.E.D. (%)[b]	Assignment
$\nu_{28}(a'')$	1018	1023	0.5	$S_{25}(92)$	$\delta_{as}CD_3$
$\nu_{29}(a'')$	910	886	2.7	$S_{26}(61), S_{34}(27)$	$\rho CD_3+\pi C{=}O$
$\nu_{30}(a'')$	737	733	0.5	$S_{32}(31), S_{33}(30), S_{36}(73)$	$\pi NH+\tau CN$
$\nu_{31}(a'')$	603	596	1.2	$S_{34}(13), S_{35}(66), S_{36}(48)$	$\pi C{=}O+\pi NH$
$\nu_{32}(a'')$	498	502	0.8	$S_{26}(22), S_{34}(61), S_{35}(28)$	$\pi C{=}O+\rho CD_3$
$\nu_{33}(a'')$		247		$S_{32}(20), S_{33}(24), S_{34}(10)$	$\tau CN+\pi C{=}O$
$\nu_{34}(a'')$		114		$S_{31}(28), S_{32}(34), S_{33}(36)$	$\tau CN+\tau CH_3$
$\nu_{35}(a'')$		101		$S_{31}(70), S_{32}(17), S_{33}(11)$	$\tau CH_3+\tau CN$
$\nu_{36}(a'')$		74		$S_{30}(96)$	τCD_3

a) $\Delta(\%)=|\nu_{obsd}-\nu_{calcd}|\times 100/\nu_{obsd}$
b) Those less than 10% are omitted.

TABLE 7. OBSERVED AND CALCULATED FREQUENCIES OF $CD_3CONDCOCH_3$ IN cm^{-1}

(a) In-plane vibrations (a')

	Obsd	Calcd	Δ(%)[a]	P.E.D. (%)[b]	Assignment
$\nu_1\ (a')$	2995	2997	0.1	$S_{23}(100)$	$\nu_{as}CH_3$
$\nu_2\ (a')$	2915	2922	0.3	$S_{22}(100)$	ν_sCH_3
$\nu_3\ (a')$	2415	2373	1.7	$S_{19}(99)$	νND
$\nu_4\ (\alpha')$	2230	2228	0.1	$S_{21}(100)$	$\nu_{as}CD_3$
$\nu_5\ (a')$	2110	2099	0.5	$S_{20}(99)$	ν_sCD_3
$\nu_6\ (a')$	1726	1721	0.3	$S_2(32), S_5(40)$	Imide I′
$\nu_7\ (a')$		1675		$S_2(45), S_5(36)$	Imide I′
$\nu_8\ (a')$	1421	1429	0.5	$S_{12}(86)$	$\delta_{as}CH_3$
$\nu_9\ (a')$		1375		$S_6(10), S_{11}(101)$	δ_sCH_3
$\nu_{10}(a')$		1359		$S_3(45), S_4(47), S_{10}(27)$	Imide II′
$\nu_{11}(a')$		1325		$S_1(26), S_3(19), S_4(17), S_6(18)$	νCN
$\nu_{12}(a')$	1110	1110	0.0	$S_1(29), S_3(10), S_7(49), S_{10}(17)$	$\delta_sCD_3+\delta ND+\nu CC$
$\nu_{13}(a')$	1037	1030	0.7	$S_7(11), S_8(60), S_{10}(10)$	$\delta_{as}CD_3$
$\nu_{14}(a')$	1018	1027	0.8	$S_7(24), S_8(30), S_{10}(19), S_{13}(10)$	$\delta_{as}CD_3+\delta_sCD_3+\delta ND$
$\nu_{15}(a')$	992	999	0.7	$S_5(13), S_6(13), S_{13}(42)$	ρCH_3
$\nu_{16}(a')$	924	934	1.1	$S_4(15), S_{13}(21), S_{15}(10), S_{16}(17)$	$\rho CH_3+\delta CNC$
$\nu_{17}(a')$	883	870	1.4	$S_1(10), S_3(11), S_4(15), S_6(17), S_{10}(12)$	νCC
$\nu_{18}(a')$	796	779	2.1	$S_9(71)$	ρCD_3
$\nu_{19}(a')$	627	630	0.4	$S_1(18), S_6(15), S_{16}(11), S_{17}(17)$	Imide IV′
$\nu_{20}(a')$	498	504	1.2	$S_9(12), S_{14}(10), S_{15}(18), S_{17}(14), S_{18}(32)$	Imide IV′
$\nu_{21}(a')$	402	401	0.3	$S_{14}(39), S_{17}(25), S_{18}(16)$	$\delta C{=}O+\delta CCN$
$\nu_{22}(a')$	347	347	0.0	$S_{14}(17), S_{15}(24), S_{17}(21)$	$\delta C{=}O+\delta CCN$
$\nu_{23}(a')$		179		$S_{14}(11), S_{15}(14), S_{16}(62), S_{17}(11), S_{18}(12)$	δCNC

(b) Out-of-plane vibrations (a'')

	Obsd	Calcd	Δ(%)[a]	P.E.D. (%)[b]	Assignment
$\nu_{24}(a'')$	2995	2996	0.0	$S_{27}(100)$	$\nu_{as}CH_3$
$\nu_{25}(a'')$	2230	2223	0.3	$S_{24}(100)$	$\nu_{as}CD_3$
$\nu_{26}(a'')$	1421	1427	0.4	$S_{28}(89), S_{29}(10)$	$\delta_{as}CH_3$
$\nu_{27}(a'')$	1037	1060	2.2	$S_{28}(10), S_{29}(78)$	ρCH_3
$\nu_{28}(a'')$	1018	1023	0.5	$S_{25}(92)$	$\delta_{as}CD_3$
$\nu_{29}(a'')$	910	883	2.9	$S_{26}(62), S_{34}(27)$	$\rho CD_3+\pi C{=}O$
$\nu_{30}(a'')$	605	602	0.5	$S_{29}(10), S_{32}(10), S_{34}(12), S_{35}(62)$	$\pi C{=}O$
$\nu_{31}(a'')$	546	547	0.2	$S_{32}(18), S_{33}(18), S_{36}(117)$	$\pi ND+\tau CN$
$\nu_{32}(a'')$	498	502	0.8	$S_{26}(22), S_{34}(61), S_{35}(29)$	$\pi C{=}O+\rho CD_3$
$\nu_{33}(a'')$		236		$S_{32}(25), S_{33}(29)$	τCN
$\nu_{34}(a'')$		114		$S_{31}(28), S_{32}(34), S_{33}(36)$	$\tau CN+\tau CH_3$
$\nu_{35}(a'')$		101		$S_{31}(70), S_{32}(17), S_{33}(11)$	$\tau CH_3+\tau CN$
$\nu_{36}(a'')$		74		$S_{30}(96)$	τCD_3

a) $\Delta(\%)=|\nu_{obsd}-\nu_{calcd}|\times 100/\nu_{obsd}$
b) Those less than 10% are omitted.

TABLE 8. OBSERVED AND CALCULATED FREQUENCIES OF $CD_3CONHCOCD_3$ IN cm^{-1}

(a) In-plane vibrations (a_1, b_2)

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
ν_1 (a_1)	3200	3238	1.2	$S_{19}(100)$	νNH
ν_2 (a_1)	2230	2228	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CD_3$
$\nu_{13}(b_2)$	2230	2228	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CD_3$
ν_3 (a_1)	2110	2099	0.5	$S_{20}(50), S_{22}(50)$	$\nu_{s}CD_3$
$\nu_{14}(b_2)$	2110	2099	0.5	$S_{20}(50), S_{22}(50)$	$\nu_{s}CD_3$
ν_4 (a_1)	1720	1722	0.1	$S_2(36), S_5(36)$	Imide I
$\nu_{15}(b_2)$	1690	1696	0.4	$S_2(34), S_5(34), S_{10}(17)$	Imide I
$\nu_{16}(b_2)$	1508	1509	0.1	$S_3(20), S_4(20), S_{10}(70)$	Imide II
ν_5 (a_1)	1324	1326	0.1	$S_1(25), S_3(19), S_4(19), S_6(25)$	νCN
$\nu_{17}(b_2)$	1260	1240	1.6	$S_1(21), S_3(30), S_4(30), S_6(21), S_{10}(11)$	Imide III
$\nu_{18}(b_2)$	1087	1089	0.2	$S_7(36), S_{11}(36)$	$\delta_{s}CD_3$
ν_6 (a_1)	1087	1069	1.6	$S_7(39), S_{11}(39)$	$\delta_{s}CD_3$
ν_7 (a_1)	1030	1030	0.0	$S_8(43), S_{12}(43)$	$\delta_{as}CD_3$
$\nu_{19}(b_2)$	1030	1027	0.3	$S_8(47), S_{12}(47)$	$\delta_{as}CD_3$
ν_8 (a_1)	972	964	0.8	$S_2(11), S_5(11), S_{16}(22)$	δCNC+νC=O
$\nu_{20}(b_2)$	868	865	0.4	$S_1(16), S_3(10), S_4(10), S_6(16), S_7(12), S_{11}(12)$	νCC
$\nu_{21}(b_2)$	819	815	0.5	$S_9(34), S_{13}(34)$	ρCD_3
ν_9 (a_1)	734	756	3.1	$S_9(39), S_{13}(39)$	ρCD_3
$\nu_{10}(a_1)$		605		$S_1(16), S_6(16), S_{14}(10), S_{17}(10)$	Imide IV
$\nu_{22}(b_2)$	485	479	1.2	$S_9(11), S_{13}(11), S_{14}(14), S_{15}(21), S_{17}(14), S_{18}(21)$	Imide IV
$\nu_{23}(b_2)$		393		$S_{14}(29), S_{15}(14), S_{17}(29), S_{18}(14)$	δC=O+δCCN
$\nu_{11}(a_1)$	343	334	2.6	$S_{14}(20), S_{15}(14), S_{17}(20), S_{18}(14)$	δC=O+δCCN
$\nu_{12}(a_1)$		175		$S_{14}(10), S_{15}(10), S_{16}(61), S_{17}(10), S_{18}(14)$	δCNC

(b) Out-of-plane vibrations (b_1)

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_{24}(b_1)$	2230	2223	0.3	$S_{24}(50), S_{27}(50)$	$\nu_{as}CD_3$
$\nu_{25}(b_1)$	1030	1024	0.6	$S_{25}(46), S_{28}(46)$	$\delta_{as}CD_3$
$\nu_{26}(b_1)$	909	895	1.6	$S_{26}(28), S_{29}(28)$	ρCD_3+πC=O
$\nu_{27}(b_1)$	734	729	0.7	$S_{32}(29), S_{33}(29), S_{36}(83)$	πNH+τCN
$\nu_{28}(b_1)$	542	565	4.2	$S_{26}(16), S_{29}(16), S_{34}(31), S_{35}(31), S_{36}(42)$	πC=O+πNH
$\nu_{29}(b_1)$		240		$S_{32}(21), S_{33}(21)$	τCN
$\nu_{30}(b_1)$		75		$S_{30}(49), S_{31}(49)$	τCD_3

a) $\Delta(\%)=|\nu_{obsd}-\nu_{calcd}|\times 100/\nu_{obsd}$

b) Those less than 10% are omitted.

TABLE 9. OBSERVED AND CALCULATED FREQUENCIES OF $CD_3CONDCOCD_3$ IN cm^{-1}

(a) In-plane vibrations (a_1, b_2)

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
ν_1 (a_1)	2420	2373	1.9	$S_{19}(99)$	νND
ν_2 (a_1)	2230	2228	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CD_3$
$\nu_{13}(b_2)$	2230	2228	0.1	$S_{21}(50), S_{23}(50)$	$\nu_{as}CD_3$
ν_3 (a_1)	2110	2099	0.5	$S_{20}(50), S_{22}(50)$	$\nu_{s}CD_3$
$\nu_{14}(b_2)$	2110	2099	0.5	$S_{20}(50), S_{22}(50)$	$\nu_{s}CD_3$
ν_4 (a_1)	1720	1718	0.1	$S_2(36), S_5(36)$	Imide I'
$\nu_{15}(b_2)$	1665	1672	0.4	$S_2(40), S_5(40)$	Imide I'
$\nu_{16}(b_2)$	1353	1360	0.5	$S_3(48), S_4(48), S_{10}(28)$	Imide II'
ν_5 (a_1)	1324	1325	0.1	$S_1(25), S_3(19), S_4(19), S_6(25)$	νCN
$\nu_{17}(b_2)$	1120	1124	0.4	$S_1(24), S_6(24), S_7(28), S_{10}(15), S_{11}(28)$	$\delta_{s}CD_3$+νCC+δND
ν_6 (a_1)	1087	1068	1.8	$S_7(41), S_{11}(41)$	$\delta_{s}CD_3$
ν_7 (a_1)	1030	1030	0.0	$S_8(45), S_{12}(45)$	$\delta_{as}CD_3$
$\nu_{18}(b_2)$	1030	1027	0.3	$S_8(47), S_{12}(47)$	$\delta_{as}CD_3$
$\nu_{19}(b_2)$	1011	1007	0.4	$S_7(14), S_{10}(44), S_{11}(14)$	δND+$\delta_{s}CD_3$

TABLE 9. Continued

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_8\ (a_1)$	955	949	0.6	$S_2(11), S_5(11), S_{15}(10), S_{16}(21), S_{18}(10)$	δCNC+νC=O
$\nu_{20}(b_2)$	842	845	0.4	$S_1(14), S_3(10), S_4(10), S_6(14)$	νCC+νCN
$\nu_{21}(b_2)$	816	807	1.2	$S_9(34), S_{13}(34)$	ρCD_3
$\nu_9\ (a_1)$	734	753	2.6	$S_9(39), S_{13}(39)$	ρCD_3
$\nu_{10}(a_1)$		603		$S_1(16), S_6(16), S_{14}(10), S_{17}(10)$	Imide IV′
$\nu_{22}(b_2)$	485	474	2.3	$S_9(11), S_{13}(11), S_{14}(14), S_{15}(21), S_{17}(14), S_{18}(21)$	Imide IV′
$\nu_{23}(b_2)$	379	393	3.7	$S_{14}(28), S_{15}(15), S_{17}(28), S_{18}(15)$	δC=O+δCCN
$\nu_{11}(a_1)$	343	334	2.6	$S_{14}(20), S_{15}(14), S_{17}(20), S_{18}(14)$	δC=O+δCCN
$\nu_{12}(a_1)$		175		$S_{14}(10), S_{15}(14), S_{16}(61), S_{17}(10), S_{18}(14)$	δCNC

(b) Out-of-plane vibrations (b_1)

	Obsd	Calcd	$\Delta(\%)^{a)}$	P.E.D. $(\%)^{b)}$	Assignment
$\nu_{24}(b_1)$	2230	2223	0.3	$S_{24}(50), S_{27}(50)$	$\nu_{as}CD_3$
$\nu_{25}(b_1)$	1030	1024	0.6	$S_{25}(46), S_{28}(46)$	$\delta_{as}CD_3$
$\nu_{26}(b_1)$	909	891	2.0	$S_{32}(29), S_{29}(29)$	$\rho CD_3+\pi$C=O
$\nu_{27}(b_1)$	550	568	3.3	$S_{26}(16), S_{29}(16), S_{32}(13), S_{33}(13), S_{34}(27), S_{35}(27)$	πC=O+ρCD_3
$\nu_{28}(b_1)$	540	547	1.3	$S_{32}(15), S_{33}(15), S_{36}(123)$	πND+τCN
$\nu_{29}(b_1)$	230	229	0.4	$S_{32}(26), S_{33}(26)$	τCN
$\nu_{30}(b_1)$	80	75	6·7	$S_{30}(49), S_{31}(49)$	τCD_3

a) $\Delta(\%)=|\nu_{obsd}-\nu_{calcd}|\times 100/\nu_{obsd}$
b) Those less than 10% are omitted.

convergence of force constants was attained. On the refinement of the out-of-plane force constants, the Urey-Bradley force constants for the methyl groups were fixed to the converged values in the in-plane calculation, and the valence force constants were adjusted by referring to the Jacobian matrix and repeating the least squares method by parts. The final values of force constants are given in Table 3, and the calculated frequencies are listed in Tables 4—9 together with the dominant terms in the potential energy distribution and the assignments. The reliability of the presently obtained force constants may be ascertained from the agreement between the observed and the calculated frequencies. The potential energy distributions in Tables 4—9 show that the coupling among the skeletal deformation vibrations is considerable. For the C-deuterated compounds, the CD_3 rocking vibrations also participate in this coupling, explaining well the fact that the C-deuteration gives rise to much larger shifts of the skeletal deformation frequencies than the N-deuteration. In Table 10, the stretching force constants obtained in the present work are compared with those of the *trans-cis* diacetamide reported before (Calculation II in Ref. 4). In the form A crystal, only the *cis*-CONH- group of *trans-cis* diacetamide is involved in the hydrogen bonds, and accordingly K(CO)(*trans*) is larger than K(CO)(*cis*) and K(CN)(*trans*) is smaller than K(CN)(*cis*). The presently obtained values of K(CO) and K(CN) of *trans-trans* diacetamide fall between the values of the corresponding *trans-* and *cis-* constants of *trans-cis* diacetamide. This result is reasonable since the C=O and the C–N bonds involved in the bifurcated hydrogen bonds of the form B crystal are expected to have intermediate bond orders between the unassociated and the normally hydrogen-bonded cases.

TABLE 10. STRETCHING FORCE CONSTANTS OF *trans-cis* AND *tans-trans* DIACETAMIDES (mdyn/Å)

	trans-cis	*trans-trans*
K(CH)	4.40	4.54
K(NH)	5.46	5.42
K(CO)	8.92 (*trans*) 8.09 (*cis*)	8.72
K(CN)	3.50 (*trans*) 4.12 (*cis*)	3.78
K(CC)	3.36	3.23

The authors wish to express their thanks to Prof. T. Takenaka of Kyoto University for the use of Perkin-Elmer 521 and Hitachi FIS-3 grating infrared spectrophotometers. Thanks are also due to Prof. T. Miyazawa and Dr.H.Sugeta of Osaka University, Dr. T. Kajiura of Japan Electron Optics Laboratory Co., Ltd. for the measurements of laser Raman spectra and to the staff of the Kyoto University Computer Center for use of the FACOM 230-60 computer.