The Normal Vibrations of trans-trans Diacetamide

By Toyozo UNO and Katsunosuke MACHIDA

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In a previous report on the infrared spectra and structure of acyclic imides[1], it was concluded that diacetamide takes the trans-cis and the trans-trans configuration in the crystal in A and B forms respectively. With respect to form A, X-ray diffraction study was carried out and the trans-cis configuration was proven to be approximately valid[2]. Such a support from X-ray analysis, however, has not yet been given to form B, for which it is therefore of interest to determine the type of its hydrogen bond in connection with the molecular symmetry in the crystal[3].

The present work has been undertaken to see whether or not the observed infrared frequencies of diacetamide crystals in form B can be reproduced by a reasonable set of force constants based on the assumed trans-trans structure. For this purpose, we have carried out normal vibration calculations for the in-plane vibrations of diacetamide and diacetamide-d in the trans-trans configuration and have obtained satisfactory results, particularly for imide characteristic frequencies.

Calculation

The methyl group was treated as a point mass, and the resulting eight-body problem was treated by Wilson's ***GF*** matrix method[4]. A molecule of diacetamide in the trans-trans configuration has the C_{2v} symmetry. Besides the vibrations arising from the methyl group, there are thirteen inplane vibrations, which are classified into seven A_1 and six B_2 vibrations according to their symmetry[5]. The N–H stretching vibration belonging to the A_1 species was separated from the other A_1 vibrations[4,6], and secular equations of the sixth order were set up for both species A_1 and species B_2. The internal coordinates were defined as shown in Fig. 1, and the symmetry coordinates were constructed as shown in Table I. The bond lengths used in the present calculations are: $r(\text{C–N})=1.32\,\text{Å}$, $r(\text{C=O})=1.21\,\text{Å}$ and $r(\text{CH}_3\text{–C})=1.54\,\text{Å}$. All the bond angles were assumed to be 120°. These bond lengths and bond angles are the same as those used in the calculations for *N*-methylacetamide by Miyazawa et al.[7]

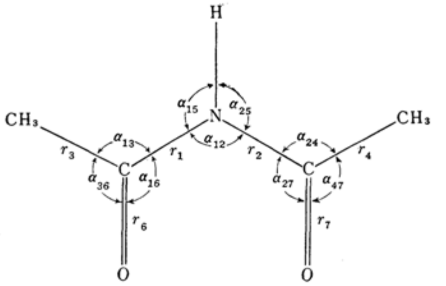

Fig. 1. Internal coordinates of diacetamide.

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

2) K. Osaki, H. Koizumi and T. Watanabé, Symposium on Molecular Structure, Sapporo, 1960.

3) T. Uno and K. Machida, This Bulletin, 34, 821 (1961).

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

5) The present description of the symmetry species is based on Reports on Notation for the Spectra of Polyatomic Molecules, *J. Chem. Phys.*, 23, 1997 (1955). The B_2 species in the present work should be compared with the B_1 species of the previous papers[1,3].

6) B. L. Crawford, Jr. and J. T. Edsall, *J. Chem. Phys.*, 7, 223 (1939).

7) T. Miyazawa, T. Shimanouchi and S. Mizushima, ibid., 29, 611 (1958).

TABLE I. SYMMETRY COORDINATES

Symmetry species	Symmetry coordinates	Description
	$S_1=(1/2)^{1/2}\Delta(r_1+r_2)$	C-N stretching
	$S_2=(1/2)^{1/2}\Delta(r_3+r_4)$	C-C stretching
	$S_3=(1/2)^{1/2}\Delta(r_6+r_7)$	C=O stretching
A_1	$S_4=(1/6)^{1/2}\Delta(2\alpha_{12}-\alpha_{15}-\alpha_{25})$	C-N-C bending
	$S_5=(1/12)^{1/2}\Delta(2\alpha_{36}-\alpha_{13}-\alpha_{16}+2\alpha_{47}-\alpha_{24}-\alpha_{27})$	CH_3-C=O bending
	$S_6=(1/2)\Delta(\alpha_{13}-\alpha_{16}+\alpha_{24}-\alpha_{27})$	CH_3-C=O rocking
	$S_7=(1/2)^{1/2}\Delta(r_1-r_2)$	C-N stretching
	$S_8=(1/2)^{1/2}\Delta(r_3-r_4)$	C-C stretching
	$S_9=(1/2)^{1/2}\Delta(r_6-r_7)$	C=O stretching
B_2	$S_{10}=(1/2)^{1/2}\Delta(\alpha_{15}-\alpha_{25})$	N-H(N-D) in-plane deformation
	$S_{11}=(1/12)^{1/2}\Delta(2\alpha_{36}-\alpha_{13}-\alpha_{16}-2\alpha_{47}+\alpha_{24}+\alpha_{27})$	CH_3-C=O bending
	$S_{12}=(1/2)\Delta(\alpha_{13}-\alpha_{16}-\alpha_{24}+\alpha_{27})$	CH_3-C=O rocking

TABLE II. FORCE CONSTANTS (md./Å)

	Initial set	Final set
K_{C-N}	5.50	4.00
$K_{C=O}$	8.50	9.80
K_{C-CH_3}	3.40	3.20
H_{H-N-C}	0.35	0.31
H_{C-N-C}	0.20	0.50
H_{N-C-CH_3}	0.30	0.30
$H_{N-C=O}$	0.35	0.20
$H_{CH_3-C=O}$	0.30	0.25
$F_{H\cdots C}$	0.50	0.35
$F_{C\cdots C}$	0.40	1.70
$F_{N\cdots CH_3}$	0.50	0.70
$F_{N\cdots O}$	1.50	1.20
$F_{CH_3\cdots O}$	0.50	0.50

Force Constants. — The Urey-Bradley type potential function[8].

$$2V=\sum_{i} K_i(\Delta r_i)^2+\sum_{i\neq j}\{H_{ij}r_i^0r_j^0(\Delta\alpha_{ij})^2+F_{ij}(\Delta q_{ij})^2\}+\text{linear terms}$$

was assumed. Here, three bond-stretching (K_i), five bond-angle-deformation (H_{ij}), and five non-bonded repulsion (F_{ij}) force constants are necessary. These force constants may be transferred from *N*-methylacetamide[7], which includes all the five pairs of adjacent bonds (H-N-C, C-N-C, C-C-N, O=C-N and C-C=O) included in diacetamide. Diacetamide differs from *N*-methylacetamide, however, in containing a carbonyl carbon atom instead of the methyl carbon atom attached to the nitrogen atom in the latter. This may leave a question about the transferability of the force constants related to the C-N-C linkage. There has been no report, however, on the C-N-C bond angle deformation and the C···C repulsion force constants for the O=C-N-C=O linkage. The calculations were, therefore, started with the initial set of the force constants transferred from *N*-methylacetamide[7,9]. They are listed in the first column of Table II. The refinement of the force constants was made by a comparison of the observed and the calculated frequencies with reference to the Jacobian matrix[10]. Since there are two A_1 and one B_2 skeletal deformation frequencies which have not yet been observed, it was impossible to adjust the related force constant directly from these frequencies. On the other hand, except for the imide I, II and III frequencies[11], the observed frequencies were found to be not far from the frequencies calculated on the basis of the initial set of the force constants. Considering these facts, adjustment was made particularly with respect to the force constants related mainly to the imide I, II and III frequencies. In the course of this procedure it was found that the difference in the bond orders of C=O and C-N bonds between amides and imides should be taken into account in the refinement of $K_{C=O}$, K_{C-N} and H_{H-N-C}. The conceivable canonical forms in the resonance hybridization of an imide molecule are shown in Fig. 2, from which it may easily be understood that the C=O bond order increases but the C-N bond order decreases with an increase in the contribution of the non-polar form b. The trans-trans configuration may be advantageous for form b since the other two forms should give rise to a strong repulsion between the adjacent oxygen atoms. Thus, it is quite reasonable that

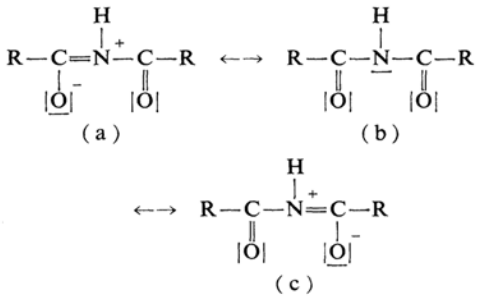

Fig. 2. Resonance structures of imides.

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[8] T. Shimanouchi, ibid., **17**, 245, 734, 848 (1949).

[9] The only exception was $F_{C\cdots C}$, which has been chosen to be 0.30 md./Å for *N*-methylacetamide[7].

[10] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaka Zassi*), **76**, 1132 (1955).

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

imides should exceed amides with respect to $K_{C=O}$ and vice versa with respect to K_{C-N} and H_{H-N-C}. In order to compensate for the decrease in the value of K_{C-N}, a marked increase in the value of $F_{C\cdots C}$ was necessary for the frequency fit in the A_1 C–N–C symmetric stretching frequency. As may be seen from Fig. 2, imides have non-localized electrons around the C–N–C linkage. Therefore, a resonance cross term[12] may be implicitly included in the effective value of $F_{C\cdots C}$. In this respect, it is reasonable that the $F_{C\cdots C}$ of diacetamide is comparable to the $F_{O\cdots N}$ rather than to the $F_{C\cdots C}$ of *N*-methylacetamide[7]. The repulsion between the oxygen atoms may also be expected to contribute to the effective value of the $F_{C\cdots C}$ of trans-trans diacetamide. The quantitative treatment of these contributions could not be undertaken without the determination of the lowest three skeletal deformation frequencies. The final set of the force constants obtained in the present calculation is shown in the second column of Table II. They reproduce the observed frequencies with deviations of less than 6%.

Numerical Calculation.—Most of the present calculations were carried out on the KDC-1 digital computer at Kyoto University. A program for the normal vibration calculation was constructed with reference to those of the previous investigators[13,14]. The library subroutines were used for the matrix multiplications and for the solution of the secular equations. These library subroutines were connected to the additional subroutines designed to calculate the $\boldsymbol{F}$ matrix[4], the Jacobian matrix[10], the potential energy distribution[15,16], and the $\boldsymbol{LL'}$ matrix[13]. The $\boldsymbol{F}$ matrix was calculated from the $\boldsymbol{A}_h$ matrices and the force constants, K_h, according to the formula[10]:

$$\boldsymbol{F}=\sum_h \boldsymbol{A}_h K_h$$

The program was designed to be appropriate to such a matrix, including many zero elements as $\boldsymbol{A}_h$. The construction of the $\boldsymbol{F}$ matrix requires the following input for a given matrix $\boldsymbol{A}_h$: (1) the values of the non-zero elements, (2) the indices denoting the locations of the non-zero elements, and (3) the number of the non-zero elements. The same input, together with the $\boldsymbol{L}$ matrix, was used to construct the Jacobian matrix. This method was quite effective in utilizing the memory of the computer and in reducing the computing time. The present calculations, which included four secular equations of the sixth order, the input, and output procedures, could be performed within fifty minutes.

Results and Discussion

In Table III, the final set of the calculated frequencies are listed, together with the potential energy distributions, and are compared with the observed frequencies. The previous assignments[1,11] of the characteristic frequencies are in good agreement with the results of the present calculations.

The calculated values for the imide I frequencies elucidate well the facts that the A_1 frequency (ν_1) is about 40 cm^{-1} higher than the B_2 frequency (ν_7) and that it does not shift on deuteration, while the B_2 frequency undergoes a low-frequency shift by about 15 cm^{-1}. The vibrations responsible for these frequencies are almost all localized at the C=O stretching coordinates (S_3 and S_9). The imide II and III frequencies (ν_8 and ν_9) belonging to the B_2 species are contributed mainly from the C–N stretching and the N–H in-plane deformation vibrations, as was suggested in a previous paper[11]. It may be seen from the present calculations, however, that the energetic contribution of the C–C stretching vibration is also important for the imide III frequency. In contrast with the imide I and II frequencies, the imide III frequency seems to vary with the change of one or both of the frameworks attached to the –CONHCO– group from the methyl to the higher alkyl groups[11]. This fact may reasonably be expected from the present calculations, which show that interaction between the –CONHCO– group and the alkyl framework vibrations is involved in the imide III frequency.

With respect to the imide II′ frequency (ν_8'), the contribution of the C–N stretching vibration is three times as energetically important as that of the N–D in-plane deformation vibration. The smallness of the contribution of the C–C stretching vibration seems to be related to the slight dependence of this frequency upon the change of the alkyl group[11]. The imide II, III and II′ frequencies of trans-trans diacetamide are quite analogous to, respectively, the amide II, III and II′ frequencies of *N*-methylacetamide in the trans configuration[7] in their potential energy distributions. It is of interest that the appreciable difference in the corresponding force constants

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[12] T. Shimanouchi, International Symposium on Molecular Structure and Spectroscopy, Tokyo (1962); see also S. Califano and B. L. Crawford, Jr., *Spectrochim. Acta*, **16**, 889 (1960).

[13] T. Shimanouchi and I. Suzuki, *J. Mol. Spectroscopy*, **6**, 227 (1961); **8**, 222 (1962).

[14] J. Overend and J. R. Scherer, *J. Chem. Phys.*, **32**, 1289 (1960).

[15] Y. Morino and K. Kuchitsu, ibid., **20**, 1809 (1953).

[16] I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 243 (1953).

TABLE III. FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTIONS

$CH_3CONHCOCH_3$

Symmetry species	No.	ν_{calcd}	ν_{obs}	Deviation*1	Assignment*2	P. E. D.*3
A_1	ν_1	1732	1734	0.1	Imide I (sym.)	$S_1(11)$, $S_3(84)$
	ν_2	1289	1295	0.5	ν_{C-N-C} (sym.)	$S_1(61)$, $S_2(39)$
	ν_3	1036	1035	0.1	Skeletal	$S_1(24)$, $S_4(35)$, $S_6(23)$
	ν_4	639	625	2.2	Imide IV	$S_2(51)$, $S_5(18)$, $S_6(8)$
	ν_5	375	—	—		$S_5(69)$
	ν_6	193	—	—		$S_4(52)$, $S_6(55)$
B_2	ν_7	1697	1690	0.4	Imide I (antisym.)	$S_9(85)$, $S_{10}(11)$
	ν_8	1507	1505	0.1	Imide II	$S_7(37)$, $S_{10}(69)$
	ν_9	1203	1236	2.4	Imide III	$S_7(55)$, $S_8(23)$, $S_{10}(20)$
	ν_{10}	896	920	2.3	ν_{C-C}	$S_7(11)$, $S_8(69)$
	ν_{11}	511	523	2.3	Imide IV	$S_{11}(86)$
	ν_{12}	436	—	—		$S_{12}(82)$

$CH_3CONDCOCH_3$

Symmetry species	No.	ν_{calcd}	ν_{obs}	Deviation*1	Assignment*2	P. E. D.*3
A_1	ν_1'	1730	1734	0.2	Imide I (sym.)	$S_1(10)$, $S_3(85)$
	ν_2'	1288	1295	0.6	ν_{C-N-C} (sym.)	$S_1(60)$, $S_2(39)$
	ν_3'	1015	1035	1.8	Skeletal	$S_1(26)$, $S_4(34)$, $S_6(23)$
	ν_4'	637	625	1.9	Imide IV	$S_2(51)$, $S_5(17)$, $S_6(8)$
	ν_5'	375	—	—		$S_5(69)$
	ν_6'	193	—	—		$S_4(52)$, $S_6(55)$
B_2	ν_7'	1681	1675	0.4	Imide I (antisym.)	$S_9(94)$
	ν_8'	1375	1348	2.0	Imide II′	$S_7(78)$, $S_8(10)$, $S_{10}(29)$
	ν_9'	1007	951	5.9	Imide III′	$S_8(42)$, $S_{10}(49)$
	ν_{10}'	861	901	4.4	ν_{C-C}	$S_7(18)$, $S_8(42)$, $S_{10}(19)$
	ν_{11}'	504	523	3.6	Imide IV	$S_{11}(86)$
	ν_{12}'	434	—	—		$S_{12}(84)$

*1 $|\nu_{obs}-\nu_{calcd}|/\nu_{obs}\times 100$
*2 ν: stretching, see also Ref. 11.
*3 $F_{ii}L_{is}^2/\lambda_s\times 100$

between these compounds does not produce any difference in the energetic natures of the corresponding characteristic vibrations. Besides the N–D in-plane deformation vibration, the contribution of the C–C stretching vibration is important for the imide III′ frequency (ν_9'), on which it has been revealed that the influence of the alkyl group is also appreciable[11]. The difference between the observed and the calculated values (56 cm^{-1}) for the imide III′ frequency may be attributed to the disregard of the interaction with the B_2 CH_3 rocking vibration in the present calculations. This is suggested by the facts that the intensity of the 1035 cm^{-1} band of diacetamide in form B is appreciably reduced on deuteration and that a weak band appears at 1100 cm^{-1} for diacetamide-d in form B[1]. For the undeuterated species, it seems that the absorption due to the B_2 CH_3 rocking vibration is overlapped by the 1035 cm^{-1} band due to the A_1 skeletal vibration. For the deuterated species, however, the B_2 CH_3 rocking vibration seems to couple with the N–D in-plane deformation vibration, thus giving rise to the 1100 cm^{-1} band and pushing the imide III′ frequency down from the uncoupled value near the calculated frequency (1007 cm^{-1}) to the observed frequency (951 cm^{-1}). This interpretation may be confirmed by the application of the product rule[4] to the B_2 frequencies. As is shown in Table IV, we have obtained a good agreement between the observed and the theoretical ratios by employing the frequencies ν_i and ν_i' (i=7, 8, 9 and 10) which are shown in Table III, together with two additional frequencies: 1035 cm^{-1} for the undeuterated species and 1100 cm^{-1} for the deuterated species.

The present calculations show that the two imide IV frequencies assigned previously to the two C=O in-plane deformation vibrations[1] are essentially different from each other in their vibrational modes. The B_2 frequency (ν_{11}) arises from the almost pure CH_3–C=O bending vibration, while the A_1 frequency (ν_4) has a complicated vibrational mode to which

TABLE IV. PRODUCT RULE RATIOS

Symmetry species	Observed* ratio $\Pi\nu_i/\Pi\nu_i'$	Theoretical ratio $[\lvert G(H)\rvert/\lvert G(D)\rvert]^{1/2}$
B_2	1.41	1.40

* ν_i: 1690, 1505, 1236, 1035 and 920
ν_i': 1675, 1348, 1100, 951 and 901

the C–C stretching, CH_3–C=O bending, and CH_3–C=O rocking vibrations contribute. Such a mixing of vibrational modes is also seen for the A_1 skeletal frequency (ν_3). Further discussion of the vibrational modes of ν_3 and ν_4, however, will not be undertaken here since these mixed vibrational modes are probably affected by those force constants related mainly to the unobserved frequencies below 450 cm^{-1}.

Summary

A normal coordinate analysis of the in-plane vibrations of diacetamide and of diacetamide-d taking the trans-trans configuration has been undertaken. The calculated frequencies agree well with the observed frequencies for the crystals in form B. The Urey-Bradley force field has been adopted, and the force constants obtained have been interpreted in terms of the difference in resonance structures between amides and imides. It has been shown that the vibrational modes of the characteristic imide frequencies are closely related to the behavior of the corresponding characteristic bands upon the change in the alkyl frameworks attached to the imide group.

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Faculty of Pharmacy
Kyoto University
Sakyo-ku, Kyoto