

INFRARED STUDIES OF THE LESS STABLE *CIS* FORM OF N-METHYLFORMAMIDE AND N-METHYLACETAMIDE IN LOW-TEMPERATURE NITROGEN MATRICES AND VIBRATIONAL ANALYSES OF THE *TRANS* AND *CIS* FORMS OF THESE MOLECULES

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ABSTRACT

Recently studies of less stable rotational isomers became possible using a combination of low-temperature matrix-isolation infrared spectroscopy and either the high-temperature nozzle technique or irradiation with ultraviolet or near-infrared light. In this paper the infrared spectra of the less stable *cis* form of N-methylformamide and N-methylacetamide and their variously deuterated species were obtained in low-temperature nitrogen matrices using the high-temperature nozzle technique. The assignments of the bands due to the *cis* form as well as the *trans* form were made on the basis of normal-coordinate calculations.

INTRODUCTION

In recent years we studied the vibrational spectra of less stable isomers of 1,3-butadiene (ref.1), 1,3,5-hexatriene (ref.2), and N-methylthioacetamide (ref.3) using a combination of the high-temperature nozzle technique and matrix-isolation spectroscopy. Other authors have also reported similar studies on 1,3-butadiene (refs.4-6). These studies have established the existence of the *s-cis* form of 1,3-butadiene, a few *s-cis* forms of 1,3,5-hexatriene, and the *cis* form of N-methylthioacetamide. Photoisomerization of these molecules during deposition or in low-temperature matrices has also been observed (refs.1-3,5)

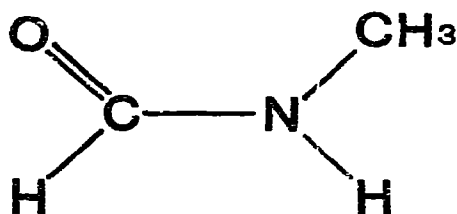
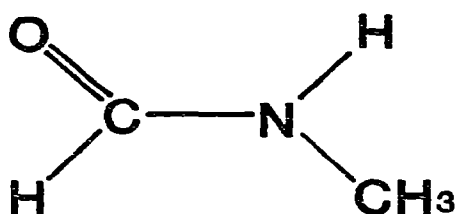
On the other hand, interest in near-infrared-induced conformational isomerization has also been increasing. We have studied the near-infrared-induced conformational isomerization of 2-chloroethanol (ref.7), ethylene glycol (ref.8), allylamine (ref.9), and allyl alcohol (ref.9).

In short, matrix-isolation spectroscopy combined with the high-temperature nozzle technique or irradiation of light in the ultraviolet to near-infrared region provides a useful means to investigate less stable conformers as well as the mechanism of conformational isomerization

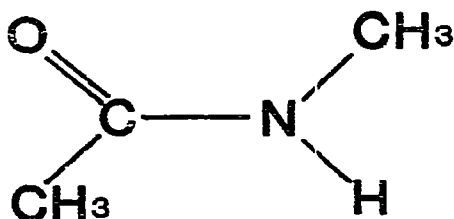
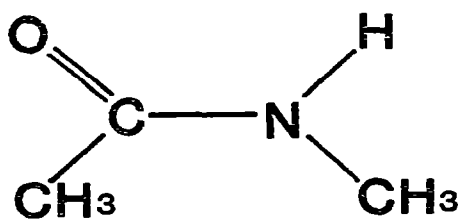
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In this paper we wish to report the observation of the infrared spectra of the *cis* form of N-methylformamide and N-methylacetamide, together with the assignments of the infrared bands of the *trans* and *cis* forms of these molecules and variously deuterated species in low-temperature matrices. The force fields which can reproduce the vibrational frequencies of the matrix-isolated *trans* and *cis* forms are also obtained.

*trans**cis*

N-Methylformamide

*trans**cis*

N-Methylacetamide

## METHODS

### Matrix-isolation measurements

N-Methylformamide (NMFA) and N-methylacetamide (NMAA) purchased from Tokyo Chemical Industry Co. were purified by distillation under reduced pressure. Various deuterated species ( $\text{HCONDCD}_3$ ,  $\text{DCONHCH}_3$  and  $\text{HCONHCD}_3$  for NMFA,  $\text{CH}_3\text{CONDCD}_3$ ,  $\text{CD}_3\text{CONHCH}_3$ ,  $\text{CD}_3\text{CONDCD}_3$ ,  $\text{CH}_3\text{CONHCD}_3$  and  $\text{CH}_3\text{CONDCD}_3$  for NMAA) were prepared by the reaction of corresponding methylformate or methylacetate and methylamine, followed by the substitution of NH hydrogen with deuterium when necessary. Vapour of each compound was mixed with an inert gas ( $\text{N}_2$  and Ar) at room temperature and was left overnight. The total pressure of such a mixed gas was 500 Torr for NMFA and 200 Torr for NMAA, and the sample/matrix ratio was 1/2000 for both compounds. The premixed gas was then deposited through a Pyrex

tube (inner diameter 1.8 mm) onto a CsI plate maintained at 20 K. The temperature of the Pyrex tube (nozzle) was varied by a tungsten heater tightly wound around it and was monitored with a thermocouple placed inside the tube. The deposition time was about 80 minutes. For cooling the CsI plate a CTI Cryodyne Model 21 was used.

Infrared spectra were recorded on a HITACHI 260-50 infrared spectrophotometer. The quality of the observed spectra was better when nitrogen was used as the matrix gas. Therefore, the infrared spectra obtained in the nitrogen matrices will be used in the following discussion.

#### Normal-coordinate calculations

The normal-coordinate calculations were performed using the programme NCTS (ref. 10) on a HITAC M200H computer system at the Computer Centre of the University of Tokyo.

The structural parameters of the *trans* form of NMFA and NMAA were taken from refs. 11 and 12, respectively. The internal coordinates including the torsional

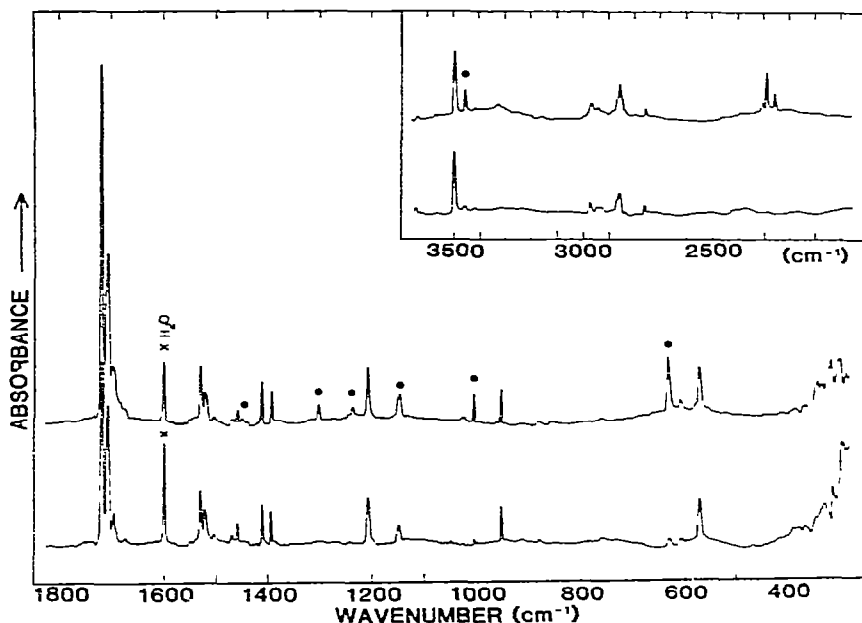


Fig. 1. Infrared spectra of N-methylformamide in  $N_2$  matrices at 20 K. The lower spectrum, obtained for the matrix sample deposited from the nozzle at room temperature, the upper spectrum, obtained for the matrix sample deposited from the nozzle at 770 K. The bands marked with a dot are due to the *cis* form.

and the out-of-plane bending coordinates were defined according to the IUPAC recommendations (ref.13) and were consistent with those used by Sugawara et al. (refs.14,15). The conformations of the methyl groups were assumed as follows; the eclipsed form with respect to the central C-N bond for the N-methyl group in both NMFA (ref.14) and NMAA (ref.15), and the staggered form with respect to the central C-N bond for the C-methyl group in NMAA (ref.15). The *cis* form was assumed to have a planar structure obtained by 180° rotation about the central C-N bond of the corresponding *trans* form.

The group-coordinate force field (GCFF, ref.16) was used for the normal-coordinate analysis. The force constants were refined in the following way. For the *trans* and *cis* forms of NMFA and the *trans* form of NMAA, the values obtained by multiplying a factor (0.83 for NMFA and 0.82 for NMAA) to the *ab initio* force constants calculated by Sugawara et al. (refs.14,15) were used as the initial set of force constants. Then, the least-squares adjustments of only the diagonal force constants were carried out to obtain a good fit between the observed and calculated frequencies of normal and variously deuterated species. In the course of this least-squares fitting, many off-diagonal force constants which had little effects on the calculated frequencies were put equal

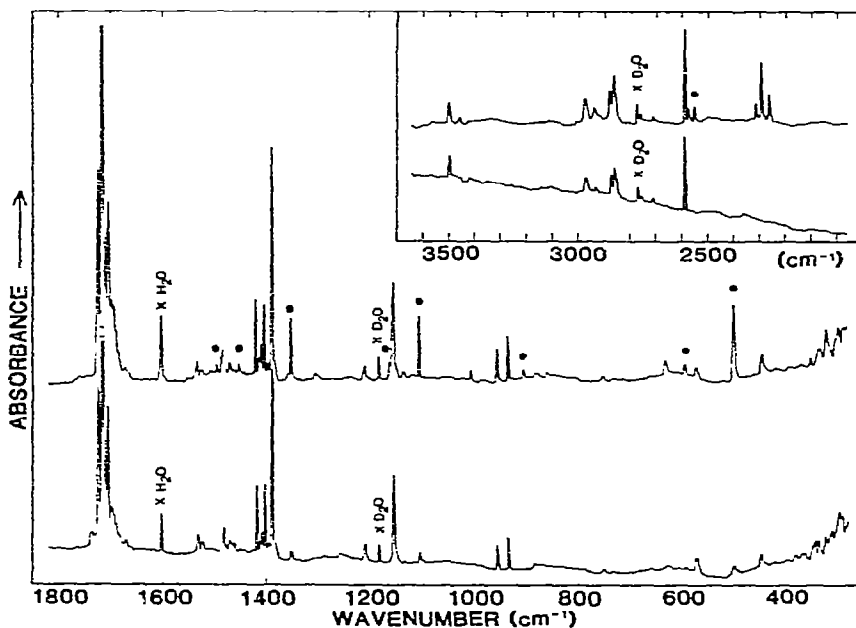


Fig. 2. Infrared spectra of N-methylformamide-N- $d_1$  in  $N_2$  matrices at 20 K. See the caption of Fig. 1 also.

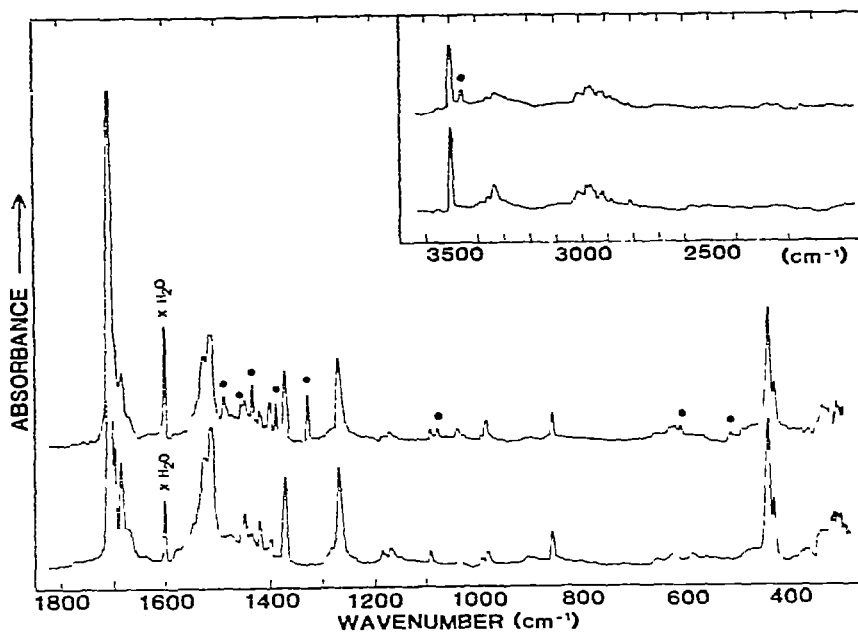


Fig. 3 Infrared spectra of N-methylacetamide in  $N_2$  matrices at 20 K. See the caption of Fig. 1 also.

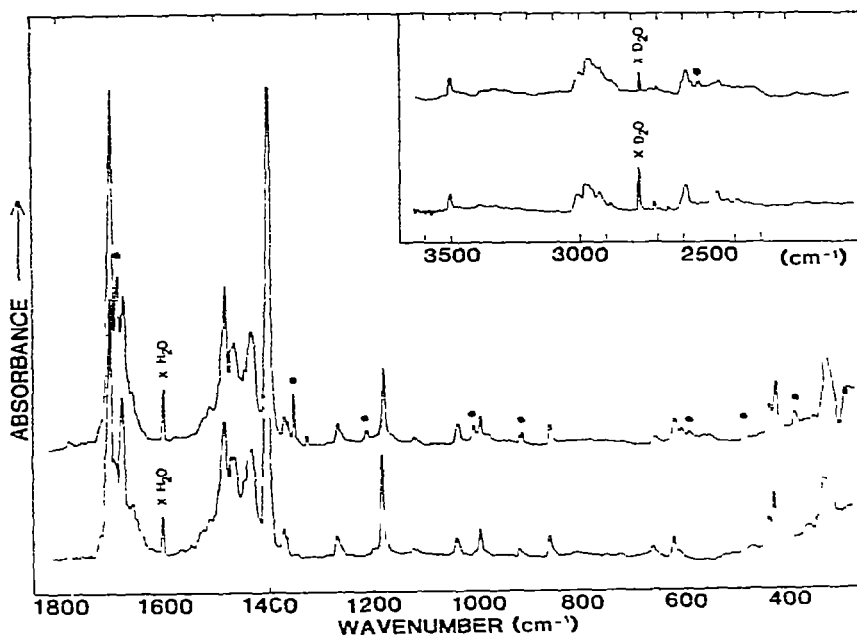


Fig. 4. Infrared spectra of N-methylacetamide- $N-d_1$  in  $N_2$  matrices at 20 K. See the caption of Fig. 1 also.

to zero, since the purpose of this fitting was to derive a practical force field which could be used for establishing reliable assignments of the observed bands. (An off-diagonal force constant whose omission affected any calculated frequency by less than  $10\text{ cm}^{-1}$  was put equal to zero.) For the *cis* form of NMAA the force constants of the *trans* form were transferred without modification, and no least-squares fitting was attempted, because the number of the observed data was not enough.

## RESULTS

In Figs. 1-4 are shown the infrared spectra of NMFA, NMAA and their  $N$ -deuterated species in  $N_2$  matrices at 20 K as the typical examples. The lower spectra in Figs. 1-4 were obtained for the matrix samples deposited from the room-temperature nozzle, and the upper spectra for the matrix samples deposited from the nozzle at 770 K. The lower spectra are undoubtedly due to the *trans* form except for the bands of remaining  $H_2O$  and  $D_2O$ . In the upper spectra, however, a number of new bands are observed in addition to the *trans* bands. By analogy with the case of *N*-methylthioacetamide (ref.3), it is reasonable to regard these newly observed bands, particularly those marked with a dot in Figs. 1-4, as arising from the *cis* form. Some newly observed bands (for example, the three bands at about  $2300\text{ cm}^{-1}$  in Figs. 1 and 2) must be assigned to thermally decomposed products. These bands were not observed for the matrix samples deposited from the nozzle at 470 K, whereas the bands marked with a dot were clearly observed. The intensities of the bands with a dot increased, as expected for the *cis* bands, relatively to the intensities of the *trans* bands, when the nozzle temperature was raised. A rough estimate of the enthalpy difference between the *trans* and *cis* forms gave a value of about  $1.3\text{ kcal mol}^{-1}$  for NMFA and  $2.3\text{ kcal mol}^{-1}$  for NMAA.

In dilute chloroform solutions the NH stretching bands of free NMFA in the *trans* and *cis* forms were found at  $3466$  and  $3429\text{ cm}^{-1}$ , respectively (ref.17). These frequencies correspond, respectively, with  $3490$  and  $3452\text{ cm}^{-1}$  observed in Fig. 1. For NMAA in dilute chloroform solutions at room temperature the NH stretching band of only the *trans* form was observed at  $3468\text{ cm}^{-1}$  (ref.17), whereas in  $N_2$  matrices the *trans* bands were observed at  $3498$  and  $3493\text{ cm}^{-1}$  and the *cis* bands at  $3458$  and  $3453\text{ cm}^{-1}$  (Fig. 3). The small splittings of these NH stretching bands in  $N_2$  matrices are due to matrix site effects. It is noted that the NH stretching frequencies are considerably higher in  $N_2$  matrices than in chloroform solutions and that the NH stretching frequency of the *cis* form is lower than that of the *trans* form by about  $40\text{ cm}^{-1}$  in both NMFA and NMAA.

Similar infrared measurements in  $N_2$  matrices were performed for  $D\text{CONHCH}_3$ ,  $H\text{CONHCD}_3$ ,  $\text{CD}_3\text{CONHCH}_3$ ,  $\text{CD}_3\text{CONDCD}_3$ ,  $\text{CH}_3\text{CONHCD}_3$  and  $\text{CH}_3\text{CONDCD}_3$ , and the *cis* bands were identified for each deuterated species.

## DISCUSSION

The band assignments for the *trans* and *cis* forms of NMFA and NMAA based on the normal-coordinate calculations are given in Tables 1-4. Similar tables for the deuterated species are available on request to the authors.

In this study the spectra in the region below  $400\text{ cm}^{-1}$  could not be well determined because of instrumental problems. Therefore, the observed frequencies in this region are not as reliable as those in the other region. In the least-squares fitting a smaller weight (zero in some cases) was put to these low-frequency data. As a result, the agreement between the observed and calculated frequencies in the low-frequency region is not always satisfactory.

Some characteristics in the infrared spectra of the matrix-isolated *trans* and *cis* forms of NMFA and NMAA will be described below.

### Trans-NMFA

Most of the clearly observed bands in the lower spectrum of Fig. 1 can be assigned to the fundamentals of *trans*-NMFA as given in Table 1. In the Amide I region around  $1700\text{ cm}^{-1}$ , at least three bands are observed. Measurements of the concentration dependence indicate that these bands, particularly the strong ones at  $1721$  and  $1708\text{ cm}^{-1}$ , are due to monomeric *trans*-NMFA. Therefore, this multiplicity of bands should be attributed to either matrix site effects or the Fermi resonance or to a combination of these effects. Similarly, three bands are observed in the Amide II region around  $1500\text{ cm}^{-1}$ , and this multiplicity of bands also should be interpreted as described above. The strongest bands in the Amide I and II regions, namely the  $1721\text{ cm}^{-1}$  band and the  $1528\text{ cm}^{-1}$  band, were tentatively taken as the fundamentals.

In the spectrum of NMFA-N- $d_1$  (Fig. 2) a multiplet whose pattern is different from that of the normal species is found in the Amide I region. A characteristic feature in Fig. 2 is the presence of a strong band at about  $1336\text{ cm}^{-1}$ . This band is assigned to a mode in which the N-CH<sub>3</sub> symmetric deformation, the N-CH<sub>3</sub> stretch and the CO-ND stretch are mixed.

### Cis-NMFA

A marked spectral difference between the *cis* and *trans* forms of NMFA is that the *cis* form has no strong (or medium-intensity) band at around  $1500\text{ cm}^{-1}$ . In fact, the normal-coordinate calculations show that such a mode as could correspond to the Amide II of the *trans* form is not found for the *cis* form (Table 2). However a mode which is similar to the Amide III of the *trans* form exists with the calculated frequency of  $1301\text{ cm}^{-1}$  (Table 2). The observed  $1302\text{ cm}^{-1}$  band is most reasonably assigned to this mode. It is noted that the Amide III band of the *trans* form is located at a much lower frequency,  $1207\text{ cm}^{-1}$  (Table 1).

Trans-NMAA

Like the case of *trans*-NMFA, the Amide I and II bands of *trans*-NMAA are split (Fig. 3), though the multiplet patterns are different between NMAA and NMFA. On N-deuteration a strong band appears at  $1398\text{ cm}^{-1}$  (Fig. 4), which corresponds to the  $1386\text{ cm}^{-1}$  band of *trans*-NMFA-N- $d_1$  (Fig. 2). Most of the observed bands except for a few bands in the region below  $700\text{ cm}^{-1}$  can be reasonably assigned (Table 3). The assignments of the out-of-plane vibrations in the region below  $700\text{ cm}^{-1}$  should be studied further.

Cis-NMAA

As given in Table 4, all the observed bands of *cis*-NMAA (and deuterated species) can be accounted for using the results of normal-coordinate calculations which utilize the force constants of the *trans* form without modification. An interesting feature which is different from *cis*-NMFA is the existence of the Amide II type mode in *cis*-NMAA. This mode has a calculated frequency of  $1487\text{ cm}^{-1}$  and is assignable to the observed band at  $1485\text{ cm}^{-1}$  (Table 4). In *cis*-NMAA a band which is assignable to the Amide III type mode is found at  $1325\text{ cm}^{-1}$ , whereas in *trans*-NMAA the Amide III band is found at  $1266\text{ cm}^{-1}$ .

## APPENDIX

The force constant matrices for the *trans* and *cis* forms of NMFA are given in Tables 5 and 6. As mentioned earlier, the group coordinates used are defined in the same way as given in ref. 14, and therefore the same units are used for the force constants.

The force constants for the *trans* and *cis* forms of NMAA, the out-of-plane force constants in particular, are still to be refined. However, they are available on request to the authors.



TABLE 1  
Observed infrared and calculated frequencies of *trans*-HCONHCH<sub>3</sub>,  
and their assignments

Obs.	Calc.	Assignment (P.E.D.)				
In-plane modes						
3490	3491	N-H	S	(100+)		
2960	2965	NCH <sub>3</sub>	AS	(101+)		
	2942	NCH <sub>3</sub>	SS	(100+)		
2854	2854	C-H	S	(100+)		
1721	1719	C=O	S	(88+)	C-H B (13-)	
1528	1527	N-H	B	(57-)	CO-NH S (26+)	NCH <sub>3</sub> R (10+)
1458	1458	NCH <sub>3</sub>	AD	(92+)		
1410	1407	NCH <sub>3</sub>	SD	(102+)		
1392	1395	C-H	B	(88+)		
1207	1218	N-CH <sub>3</sub>	S	(35-)	CO-NH S (32+)	N-H B (15+)
1148	1149	NCH <sub>3</sub>	R	(88+)	N-H B (15+)	
951	942	N-CH <sub>3</sub>	S	(61+)	CO-NH S (30+)	
761	758	O=CH-N	B	(63+)	C-NH-C B(14-)	NCH <sub>3</sub> R (9-)
237	261	C-NH-C	B	(82+)	O=CH-N B(17+)	
Out-of-plane modes						
2944	2938	NCH <sub>3</sub>	AS	(100+)		
1467	1471	NCH <sub>3</sub>	AD	(91+)	NCH <sub>3</sub> R (12+)	
1148	1150	NCH <sub>3</sub>	R	(87+)	NCH <sub>3</sub> AD (10-)	
880	881	C-H	B	(106+)		
570	576	CO-NH	T	(77-)	N-H B (44-)	
368	361	N-H	B	(58+)	CO-NH T (24-)	
	103	N-CH <sub>3</sub>	T	(97+)		

Abbreviations: S, stretch; AS, asymmetric stretch; SS, symmetric stretch; B, bend; P, rock; AD, asymmetric deformation; SD, symmetric deformation; T, torsion.

TABLE 2  
Observed infrared and calculated frequencies of *cis*-HCONHCH<sub>3</sub>,  
and their assignments

Obs.	Calc.	Assignment (P.E.D.)			
In-plane modes					
3452	3452	N-H	S	(100+)	
	2965	NCH <sub>3</sub>	AS	(101+)	
	2942	NCH <sub>3</sub>	SS	(100+)	
2853	2853	C-H	S	(100+)	
	1720	C=O	S	(75-)	CO-NH S ( 22+) C-H B ( 15+)
	1492	NCH <sub>3</sub>	AD	(78+)	NCH <sub>3</sub> R ( 9+)
	1477	NCH <sub>3</sub>	SD	(31+)	N-H B ( 24-) NCH <sub>3</sub> AD ( 19-)
1448	1439	NCH <sub>3</sub>	SD	(69+)	N-CH <sub>3</sub> S ( 15+) N-H B ( 14+)
	1376	C-H	B	(77+)	N-H B ( 15+)
1302	1301	CO-NH	S	(48-)	N-H B ( 22-) O=CH-N B( 8+)
1144	1153	N-CH <sub>3</sub>	S	(53+)	NCH <sub>3</sub> R ( 35+) O=CH-N B( 6-)
1003	1003	NCH <sub>3</sub>	R	(45+)	N-CH <sub>3</sub> S ( 24-) CO-NH S ( 14-)
	591	O=CH-N	B	(56+)	N-CH <sub>3</sub> S ( 14+) CO-NH S ( 7-)
	285	C-NH-C	B	(91+)	O=CH-N B( 22-)

(continued)

(continued)

## Out-of-plane modes

	2938	NCH <sub>3</sub> AS (100-)			
	1465	NCH <sub>3</sub> AD ( 92+)	NCH <sub>3</sub> R ( 12+)		
1236	1160	NCH <sub>3</sub> R ( 85+)	NCH <sub>3</sub> AD ( 9-)		
	949	C-H B ( 84+)			
629	641	CO-NH T ( 97-)	N-H B ( 24+)	C-H B ( 19+)	
	198	N-H B ( 77-)	C-H B ( 17-)	CO-NH T ( 13+)	
	113	N-CH <sub>3</sub> T ( 92+)			

See the footnote in Table 1.

TABLE 3

Observed infrared and calculated frequencies of *trans*-CH<sub>3</sub>CONHCH<sub>3</sub>, and their assignments

Obs.	Calc.	Assignment (P.E.D.)					
In-plane modes							
3498	3499	N-H	S	(100+)			
3008	3004	CCH <sub>3</sub>	AS	(101+)			
2973	2974	NCH <sub>3</sub>	AS	(101+)			
2958	2951	CCH <sub>3</sub>	SS	(100+)			
2915	2916	NCH <sub>3</sub>	SS	(100+)			
1707	1706	C=O	S	( 86+)	C-CO-N	B ( 9+)	
1511	1516	N-H	S	( 48-)	CO-NH	S ( 31+)	NCH <sub>3</sub> R ( 11+)
1445	1454	NCH <sub>3</sub>	AD	( 72+)	NCH <sub>3</sub>	SD ( 18+)	N-H B ( 8+)
1432	1441	CCH <sub>3</sub>	AD	( 97-)			
1419	1409	NCH <sub>3</sub>	SD	( 81+)	NCH <sub>3</sub>	AD ( 21-)	
1370	1365	CCH <sub>3</sub>	SD	(103+)			
1266	1299	CO-NH	S	( 25-)	C=O	B ( 22+)	N-H B ( 19+)
1168	1154	NCH <sub>3</sub>	R	( 61+)	N-H	B ( 18+)	N-CH <sub>3</sub> S ( 9+)
1089	1105	N-CH <sub>3</sub>	S	( 56+)	CCH <sub>3</sub>	R ( 20-)	
980	978	CCH <sub>3</sub>	R	( 46-)	CH <sub>3</sub> -C	S ( 24+)	N-CH <sub>3</sub> S ( 17-)
857	863	CO-NH	S	( 35+)	CH <sub>3</sub> -C	S ( 14+)	NCH <sub>3</sub> R ( 13-)
658	637	C=O	B	( 43+)	CH <sub>3</sub> -C	S ( 32+)	C-NH-C B ( 6+)
429	427	C-CO-N	B ( 59+)		C=O	B ( 21-)	CCH <sub>3</sub> R ( 12-)
279	265	C-NH-C	B ( 68+)		C-CO-N	B ( 26-)	
Out-of-plane modes							
3008	3002	CCH <sub>3</sub>	AS	(101+)			
2973	2968	NCH <sub>3</sub>	AS	(100+)			
1472	1462	NCH <sub>3</sub>	AD	( 96+)			
1432	1437	CCH <sub>3</sub>	AD	( 95-)			
	1135	NCH <sub>3</sub>	R	( 91+)			
1037	1042	CCH <sub>3</sub>	R	( 74+)	C=O	B ( 10-)	
619	589	CO-NH	T	( 39+)	N-H	B ( 37+)	
439	535	C=O	B	( 88-)	CCH <sub>3</sub>	R ( 22-)	N-H B ( 10+)
	143	CO-NH	T ( 63+)		N-H	B ( 59-)	
	82	N-CH <sub>3</sub>	T (114+)		NCH <sub>3</sub>	R ( 28-)	CH <sub>3</sub> -C T ( 18-)
	74	CH <sub>3</sub> -C	T (133+)		CCH <sub>3</sub>	R ( 34+)	C=O B ( 28+)

See the footnote in Table 1.

TABLE 4

Observed infrared and calculated frequencies of  $\alpha$ -c-CH<sub>3</sub>CONHCH<sub>3</sub>, and their assignments

Obs.	Calc.	Assignment (P.E.D.)			
In-plane modes					
3458	3498	N-H	S (100+)		
	3004	CCH <sub>3</sub>	AS (101+)		
	2974	NCH <sub>3</sub>	AS (101+)		
	2951	CCH <sub>3</sub>	SS (100+)		
	2916	NCH <sub>3</sub>	SS (100+)		
	1708	C=O	S (86+)	C-CO-N B( 9+)	
1485	1487	N-H	B (46+)	NCH <sub>3</sub> R (16-)	CO-NH S (16-)
1454	1453	NCH <sub>3</sub>	AD (62+)	NCH <sub>3</sub> SD (20+)	N-H B (17+)
1432	1441	CCH <sub>3</sub>	AD (97+)		
	1408	NCH <sub>3</sub>	SD (78+)	NCH <sub>3</sub> AD (24-)	
1387	1365	CCH <sub>3</sub>	SD (103+)		
1325	1335	CO-NH	S (37+)	C=O B (23+)	N-H B (19+)
	1157	N-CH <sub>3</sub>	S (48+)	NCH <sub>3</sub> R (38+)	C-NH-C B( 6-)
1075	1103	NCH <sub>3</sub>	R (31-)	N-CH <sub>3</sub> S (30+)	N-H B (13-)
	1003	CCH <sub>3</sub>	R (59-)	CO-NH S (11-)	CH <sub>3</sub> -C S (10+)
	803	CH <sub>3</sub> -C	S (47+)	CO-NH S (26+)	N-CH <sub>3</sub> S (11+)
607	583	C=O	B (41-)	CH <sub>3</sub> -C S (12-)	N-CH <sub>3</sub> S (12+)
510	520	C-CO-N	B( 41-)	C-NH-C B( 28+)	C=O B (28+)
	243	C-NH-C	B( 58+)	C-CO-N B( 42+)	
Out-of-plane modes					
	3002	CCH <sub>3</sub>	AS (101+)		
	2968	NCH <sub>3</sub>	AS (100+)		
	1462	NCH <sub>3</sub>	AD (96+)		
	1437	CCH <sub>3</sub>	AD (95+)		
	1137	NCH <sub>3</sub>	R (89+)		
	1046	CCH <sub>3</sub>	R (71+)	C=O B (11-)	
	651	N-H	B (29+)	C=O B (24+)	CO-NH T (22+)
	488	C=O	B (63+)	CO-NH T (18-)	CCH <sub>3</sub> R (13+)
	148	CO-NH	T (61+)	N-H B (59-)	
	81	N-CH <sub>3</sub>	T (120-)	NCH <sub>3</sub> R (29+)	
	72	CH <sub>3</sub> -C	T (138+)	CCH <sub>3</sub> R (35+)	C=O B (34+)

See the footnote in Table 1.

TABLE 5  
Force constant matrix for *trans*-HCONHCH<sub>3</sub>

In-plane modes											
C-H S	4.47										
C=O S	0.33	11.77									
C-H B	0.0	0.29	0.67								
O=CH-N B	-0.14	0.28	0.0	1.31							
CO-NH S	0.0	1.26	-0.26	0.33	6.55						
N-H S	0.0	0.0	0.0	0.0	0.0	6.72					
N-H B	0.0	0.0	0.0	0.07	0.20	0.0	0.57				
C-NH-C B	0.0	0.0	0.0	0.0	0.20	0.0	0.0	0.57			
N-CH <sub>3</sub> S	0.0	0.0	0.0	0.0	0.19	0.0	-0.17	0.26	5.38		
NCH <sub>3</sub> SS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.97	
NCH <sub>3</sub> SD	0.0	0.0	0.0	0.0	0.05	0.0	0.03	0.0	-0.53	0.0	0.63
NCH <sub>3</sub> AS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NCH <sub>3</sub> AD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NCH <sub>3</sub> R	0.0	0.0	0.0	0.0	0.0	0.0	-0.07	-0.05	0.0	0.0	0.0
Out-of-plane modes											
C-H D	0.50										
CO-NH T	0.09	0.37									
N-H B	0.02	-0.05	0.14								
N-CH <sub>3</sub> T	0.0	0.0	0.0	0.02							
NCH <sub>3</sub> AS	0.0	0.0	0.0	0.0	4.62						
NCH <sub>3</sub> AD	0.0	0.0	0.0	0.0	-0.14	0.58					
NCH <sub>3</sub> R	-0.03	0.0	0.0	0.0	0.0	-0.03	0.87				

Units are the same as adopted in ref. 14.

TABLE 6  
Force constant matrix for  $\text{cis-HCONHCH}_3$

In-plane modes												
C-H S	4.47											
C=O S	0.34	11.31										
C-H B	0.0	0.29	0.66									
O=CH-N B	-0.14	0.24	0.0	1.05								
CO-NH S	0.0	1.23	-0.28	0.21	7.53							
N-H S	0.0	0.0	0.0	0.0	0.0	6.58						
N-H B	0.0	0.0	-0.03	-0.09	0.14	0.0	0.52					
C-NH-C B	0.0	0.0	0.0	0.10	0.24	0.0	0.0	0.52				
N-CH <sub>3</sub> S	0.0	0.0	0.0	0.0	0.16	0.0	-0.17	0.22	5.56			
NCH <sub>3</sub> SS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.97		
NCH <sub>3</sub> SD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.52	0.0	0.67	
NCH <sub>3</sub> AS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.74
NCH <sub>3</sub> AD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.17
NCH <sub>3</sub> R	0.0	0.0	0.0	0.0	0.0	0.0	-0.06	-0.06	0.0	0.0	0.0	0.61
												0.79
Out-of-plane modes												
C-H B	0.53											
CO-NH T	-0.13	0.43										
N-H B	0.08	-0.01	0.10									
N-CH <sub>3</sub> T	0.0	0.0	0.0	0.02								
NCH <sub>3</sub> AS	0.0	0.0	0.0	0.0	4.62							
NCH <sub>3</sub> AD	0.0	0.0	0.0	0.0	-0.14	0.58						
NCH <sub>3</sub> R	0.0	0.0	0.0	0.0	0.0	-0.03	0.88					

Units are the same as adopted in ref. 14.

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