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Infrared Absorption Spectra of Urea-formaldehyde Initial Condensation Products. II. Dimethylurea

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The infrared absorption spectra of symmetric and asymmetric dimethylurea have been observed in the 4000—400 cm^{-1} region. In order to investigate the amide characteristic bands, the spectra of $CH_3NHCONHCH_3$ and $CH_3NDCONDCH_3$ have also been measured in the solid and liquid states, and in solutions. The in-plane normal vibrations of these molecules have been calculated. As a result of our measurements and calculations, it has been found that: (1) The contribution of the polar resonance structure of asymmetric dimethylurea is small compared with that of symmetric dimethylurea, and molecular geometry contributes to the formation of hydrogen bonding. (2) From the position of the amide bands, the molecular configuration of symmetric dimethylurea is the "*trans*" form as well as that of methylurea. (3) The results of normal coordinate analysis show a good agreement with that observed within an average deviation of 2.6%

In a previous paper,[1] we reported the vibrational spectra of methylurea (MMU) as one of urea-formaldehyde initial condensation products; we also undertook a normal coordinate analysis of this molecule in order to determine the vibrational assignmments. The polar resonance structure of the H-N-C=O system has also been discussed on the basis of the assignments specified for the amide characteristic bands.[2]

As a continuation of that research, we have now extended our study to the vibrational spectra of symmetric and asymmetric dimethylurea (referred to as *s*-DMU and *a*-DMU). The observed bands of DMU have been assigned by comparing the spectra of MMU and by observing the changes in spectra according to the state of the aggregation in which the substance has been measured. The normal coordinate treatments of *s*-DMU have been made in order to give a basis for the assignments.

Becher and Griffel have observed the infrared spectra of *s*-DMU[3] and methylenediurea[4] in the NaCl region, and some of the spectral bands have been assigned empirically.

Experimental

Materials. The *s*-DMU was obtained from Wako Pure Chemical Industries, Ltd., and was purified by recrystallization from a chloroform or an acetone solution. It had a mp of 106°C (lit,[5] 107°C). The *a*-DMU was synthesized by adding dimethylamine to nitrourea,[6] and it was purified from a chloroform solution. It had a mp of 181.5—182.2°C (lit,[5] 182°C).

The *N*-deuterated compounds of these samples were obtained from simple exchange with D_2O at room temperature; the excess of D_2O was evaporated in vacuum after the exchange reaction had been completed.

Infrared Spectra. The infrared spectra were measured in the 4000—400 cm^{-1} region with a Hitachi EPI-2G Infrared Grating Spectrophotometer. The spectrometer was calibrated with standard polystyrene film H_2O vapor. The spectra of *s*-DMU and *s*-DMU-d*2 were measured in the solid and liquid states and in so-

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1) Y. Mido and H. Murata, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **90**, 254 (1969).

2) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956); T. Miyazawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **76**, 341, 821, 1018 (1955), *ibid.*, **77**, 171, 321, 526, 619 (1956).

3) H. J. Becher and F. Griffel, *Naturwissenschaften*, **43**, 467 (1956).

4), H. J. Becher, *Chem. Ber.*, **89**, 1593 (1956).

5) "Handbook of Chemistry and Physics," ed. by R. C. Weast, The Chemical Rubber Co., Ohio (1966), p. C-591.

6) F. Kurzer, "Organic Syntheses," **32**, 61 (1952).

*2 The d means *N*-deuterated compound.

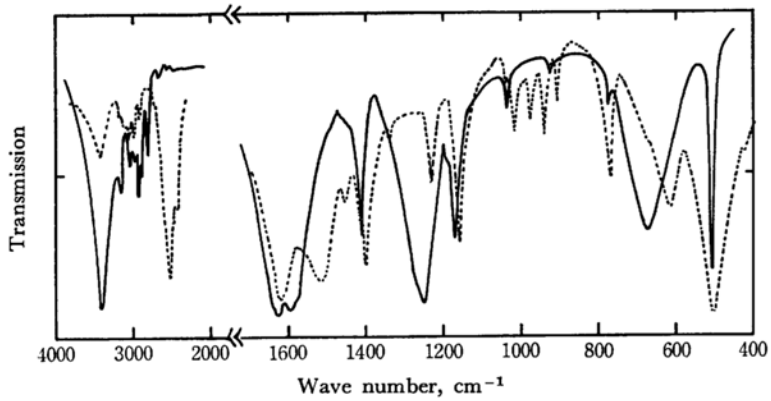

Fig. 1. Infrared spectra of *s*-DMU (solid line) and *s*-DMU-d (broken line) in the solid state.

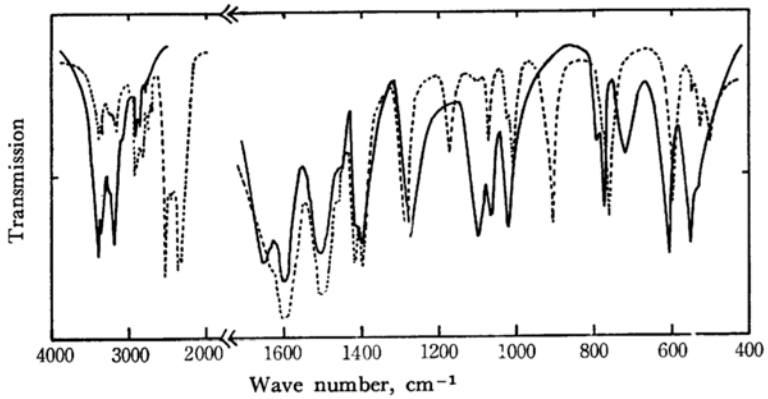

Fig. 2. Infrared spectra of *a*-DMU (solid line) and *a*-DMU-d (broken line) in the solid state.

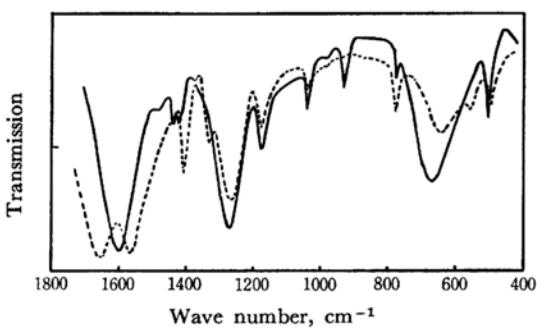

Fig. 3. Infrared spectra of *s*-DMU in liquid state (broken line) and its *quenched* sample (solid line).

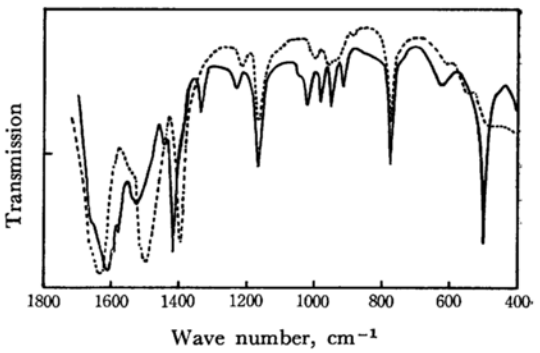

Fig. 4. Infrared spectra of *s*-DMU-d in liquid state (broken line) and its *quenched* sample (solid line).

lutions. The solid-state spectra were taken in a KBr disk and in Nujol mull;[*3] they are shown in Fig. 1. The liquid-state spectra in a capillary heated at 107—110° C and the spectra of the sample cooled from the molten liquid in a capillary (the *quenched* sample) are shown in Figs. 3 and 4, in which the *quenched* sample spectra differ from the solid-state ones. The spectra of *a*-DMU and *a*-DMU-d were also measured in the solid state and in solutions; they are shown in Fig. 2. The spectra of *s*- and *a*-DMU dissolved in H_2O and D_2O are shown in Figs. 6 and 7 respectively. The observed frequencies are summarized in Tables 5 and 6.

[*3] The preparations of KBr disk exchanged the deuterium of d-compounds for normal hydrogen and weakened the strength of ν(ND), but in Nujol mull such a phenomenon was observed little.

TABLE 1. SYMMERTRY COORDINATES

Symmetry species		Symmetry coordinates*	Vibrational mode	Abbr.
A_1	S_1	$(R_3+R_4-2R_1+R_{13}+R_{12}-2R_{11})/\sqrt{12}$	CH_3 antisym. stretching	$\nu_a(CH)$
	S_2	$(R_3+R_4+R_1+R_{12}+R_{13}+R_{11})/\sqrt{6}$	CH_3 sym. stretching	$\nu_s(CH)$
	S_3	$(2\alpha_6-\alpha_3-\alpha_5+2\varepsilon_6-\varepsilon_2-\varepsilon_4)/\sqrt{12}$	CH_3 antisym. deformation	$\delta_a(CH_3)$
	S_4	$(\alpha_I-\alpha_{II}+\varepsilon_I-\varepsilon_{II})/\sqrt{12}$*	CH_3 sym. deformation	$\delta_s(CH_3)$
	S_5	$(2\alpha_1-\alpha_2-\alpha_4+2\varepsilon_1-\varepsilon_3-\varepsilon_5)/\sqrt{12}$	CH_3 rocking	$\delta_r(CH_3)$
	S_6	(R_8)	CO stretching	ν(CO)
	S_7	$(R_6+R_{10})/\sqrt{2}$	NH sym. stretching	ν_s(NH)
	S_8	$(R_5+R_7)/\sqrt{2}$	CN_2 sym. stretching	$\nu_s(CN_2)$
	S_9	$(R_2+R_9)/\sqrt{2}$	CH_3-N sym. stretching	ν_s(C'N)
	S_{10}	$(\beta_2-\beta_3+\delta_3-\delta_2)/2$	NH sym. deformation	δ_s(NH)
	S_{11}	$(2\beta_1-\beta_2-\beta_3+2\delta_1-\delta_2-\delta_3)/\sqrt{12}$	CH_3-NC deformation	δ_s(C'NC)
	S_{12}	$(2\gamma_1-\gamma_2-\gamma_3)/\sqrt{6}$	NCN sym. deformation	δ_s(NCN)
B_2	S_1	$(R_3+R_4-2R_1+2R_{11}-R_{12}-R_{13})/\sqrt{12}$	CH_3 antisym. stretching	ν_a(CH)
	S_2	$(R_3+R_4+R_1-R_{11}-R_{12}-R_{13})/\sqrt{6}$	CH_3 sym. stretching	ν_s(CH)
	S_3	$(2\alpha_6-\alpha_3-\alpha_5-2\varepsilon_6+\varepsilon_2+\varepsilon_4)/\sqrt{12}$	CH_3 antisym. deformation	$\delta_a(CH_3)$
	S_4	$(\alpha_I-\alpha_{II}-\varepsilon_I+\varepsilon_{II})/\sqrt{12}$*	CH_3 sym. deformation	$\delta_s(CH_3)$
	S_5	$(2\alpha_1-\alpha_2-\alpha_4-2\varepsilon_1+\varepsilon_3+\varepsilon_5)/\sqrt{12}$	CH_3 rocking	$\delta_r(CH_3)$
	S_6	$(R_6-R_{10})/\sqrt{2}$	NH antisym. stretching	ν_a(NH)
	S_7	$(R_5-R_7)/\sqrt{2}$	CH_2 antisym. stretching	$\nu_a(CN_2)$
	S_8	$(R_2-R_9)/\sqrt{2}$	CH_2-N antisym. stretching	ν_a(C'N)
	S_9	$(\beta_2-\beta_3-\delta_3+\delta_2)/2$	NH antisym. deformation	δ_a(NH)
	S_{10}	$(\gamma_2-\gamma_3)/\sqrt{2}$	NCO deformation	δ(NCO)
	S_{11}	$(2\beta_1-\beta_2-\beta_3-2\delta_1+\delta_2+\delta_3)/\sqrt{12}$	CH_3-NC antisym. deformation	δ_a(C'NC)

* $\alpha_I=\alpha_3+\alpha_5+\alpha_6$, $\alpha_{II}=\alpha_1+\alpha_2+\alpha_4$, $\varepsilon_I=\varepsilon_2+\varepsilon_4+\varepsilon_6$, $\varepsilon_{II}=\varepsilon_1+\varepsilon_3+\varepsilon_5$

Normal Coordinate Treatment

The frequency calculations for *s*-DMU were made by means of Wilson's *GF* matrix method.[7] The *trans* symmetric plane model (C_{2v}) was adopted except for two hydrogen atoms attached to each of the two methyl carbon atoms (C')*4 (see Fig. 5). The normal vibrations are classified into the 23 in-plane modes (A_1 : 12, B_2 : 11) and the 13 out-of-plane modes (A_2 : 6, B_1 : 7), the A_2 species of which is infrared-inactive. The normal coordinate treatment was made for the in-plane vibrations using the internal coordinates shown in Fig. 5 and the symmetry coordinates given in Table 1. The potential function used is that of the Urey-Bradley type,[8] and the structural parameters (Table 2)*5 and the force constants (Table 3) are the same as those of the MMU transferred directly from urea,[9] *N*-methylacetamide,[10] and *N*-methylformamide.[11] The observed and calculated frequencies are listed in Table 4, together with the main potential energy distributions (P.E.D.).[12] The frequencies show a good agreement with the observed values (an average deviation of 2.6%),*6 indicating that the transferabilities of the force constants and the potential function are sufficient for this molecule. However, some of the calculated values deviate considerably from the observed values. The deviations of $\delta_s(CH_3)$, $\delta_a(CH_3)$, $\delta_r(CH_3)$, and ν(C'N) for *s*-DMU are similar to those for MMU;[1] this probably

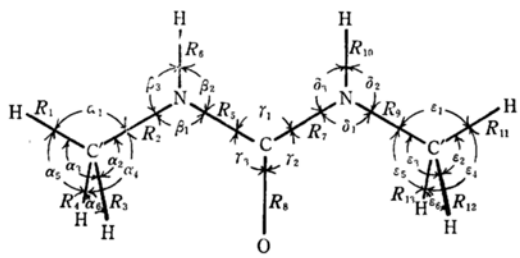

Fig. 5. The internal coordinate of *s*-DMU.

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

*4 C' denotes the methyl carbon atoms.

8) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

*5 The structural analysis has not been reported for *s*-DMU.

9) A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **10**, 170 (1957).

10) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

11) I. Suzuki, This Bulletin, **35**, 540 (1962).

12) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1952); I. Nakagawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **74**, 243 (1953).

*6 In the case of MMU; 2.3%.

Table 2. Structural parameters*4,*5

C'-N	1.47Å[a]	C-N	1.335Å[b]	C-O	1.262Å[b]
C'-H	1.09Å[c]	N-H	1.000Å[e]		
α_1, ε_1*	109°28'[e]	β_1, γ_1, δ_1**	120°00'[e]		

Table 3. Force constants (md/Å)

K(CH)	4.42[a]	H(NCN)	0.72[b]	F(N···N)	0.613[b]
K(C'N)	3.15[c]	H(NC'H)	0.28[c]	F(N···H)	0.52[c]
K(CN)	5.50[c]	H(HC'H)	0.45[c]	F(H···H)	0.03[c]
K(NH)	6.1[d]	H(CNC')	0.2[a]	F(C···C')	0.3[a]
K(CO)	6.5[b]	H(CNH)	0.35[a]	F(C···H)	0.5[a]
		H(C'NH)	0.15[a]	F(C'···H)	0.5[a]
		H(OCN)	0.12[b]	F(O···N)	1.566[b]
		H(HNH)	0.38[b]	F(H···H)	0.0[b]
κ	0.0 mdÅ[e]				

* The bond angles around the C' atom.
** The bond angles around the C and N atoms.
a) *N*-Methylacetamide, Ref. 10. b) Urea, Ref. 9. c) *N*-Methylformamide, Ref. 11.
d) Methylamine, A. Yamaguchi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **80**, 1105 (1959).
e) Assumption.

means that the corresponding force constants are not sufficiently good. On the other hand, the difference between the deviation for *s*-DMU and that for MMU (−0.4%) of the amide III bands may be attributed to the steric or electronic effect of methyl groups.[1] The deviation of δ(NCN) for *s*-DMU is more than that for MMU (0.2%), but the deviation of δ(NCO) for *s*-DMU is less than that for MMU (8.1%). The same tendency was found in methylenediurea.[13] Accordingly, the geometry of the molecule may strongly affect these vibrations.

The numerical calculations in the present treatment of normal vibrations were carried out with a HITAC 103 computer (Hitachi Ltd.) at Hiroshima University.

Results and Discussion

There are many points of similarity between the spectra of *s*-DMU and MMU,[1] but those of *a*-DMU differ from those of *s*-DMU and MMU in the numbers of the spectral bands (see Figs. 1 and 2). If the bonding of *s*-DMU as a whole is analogous to that of urea,[9,14-16] the *s*-DMU molecule can be expected to possess the considerable double-bond character of the C-N bonds and to have an approximately plane structure. Then, *s*-DMU will have three possible configurations with respect to the relative positions of two imides and a carbonyl group, the *cis-cis*, *cis-trans*, and *trans-trans* configurations of which the *cis-trans* one (C_s symmetry) is less expected than the other ones (C_{2v} symmetry).

Miyazawa and his co-workers investigated the infrared spectra of various monosubstituted amides[2,10] and of diketopiperazine,[17] and concluded that the characteristic amide bands of the *trans*-CONH group are different from those of the *cis*-CONH group. Lane and his colleagues[18] showed in their study of the methylthiourea metal complexes that the molecular form of this ligand exists in the *trans* form in comparison with the *trans*- and *cis*-thioamide. Generally the amide frequencies are markedly affected by hydrogen-bonding effects, so considerable shifts can occur on passing from the solid to a solution; moreover, the shifts are often very useful for assigning the observed bands.[2,19] A similar consideration of the amide bands of *s*-DMU will provide information regarding the configuration of *s*-DMU.

Amide I, II, and III Bands. In *s*-DMU, the amide I, II, and III bands usually observed in 1700—1250 cm^{-1} region can be related to ν(CO), ν(CN), and δ(NH), as is shown in the P.E.D. of Table 4, but they are not pure vibrations. The amide I band observed at 1625 cm^{-1} has the greatest contribution of ν(CO) and a smaller one of δ(NH), since the band shows a small frequency shift on deuteration. On the other hand, the amide II

13) Y. Mido and H. Murata, to be published.
14) R. D. Waldron and R. M. Badger, *J. Chem. Phys.*, **18**, 566 (1950).
15) P. Vaughan and J. Donohue, *Acta Cryst.*, **5**, 530 (1967).
16) E. R. Andrew and D. Hyndman, *Proc. Phys. Soc. (London)*, **66A**, 1187 (1953).
17) K. Fukushima, Y. Ideguchi and T. Miyazawa, This Bulletin, **37**, 349 (1964).
18) T. J. Lane, A. Yamaguchi, J. V. Quagliano, J. A. Ryan and S. Mizushima, *J. Am. Chem. Soc.*, **81**, 3824 (1959).
19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York (1958), p. 203.

Table 4. Observed (ν_o) and calculated (ν_c) freqvencies (in cm^{-1}) and potential energy distributions (P.E.D. in %)

		$CH_3NHCONHCH_3$				$CH_3NDCONDCH_3$				I[b]	II[c]
		ν_o	ν_c	Δ[a]	P.E.D. (%)	ν_o	ν_c	Δ[a]	P.E.D. (%)		
A_1	ν_1	3485[d]	3482	0.0	ν(NH)100	2503	2544	+1.6	ν(ND)100	1.39	1.37
	ν_2	2980	2966	−0.7	ν(CH)100	3000	2966	−1.1	ν(CH)99	0.99	1.00
	ν_3	2930	2879	−1.7	ν(CH)99	2950	2880	−2.5	ν(CH)99	0.99	0.99
	ν_4	1625	1628	+0.2	ν(C=O)46, ν(CN)23 δ(NCN)16, δ(NH)15	1620	1593	−1.7	ν(C=O)52, ν(CN)23 δ(NCN)16	1.00	1.02
	ν_5	1455	1484	+2.0	$\delta(CH_3)$85, $\delta_r(CH_3)$11	1455	1483	+1.9	$\delta(CH_3)$89, $\delta_r(CH_3)$10	1.00	1.00
	ν_6	1410	1472	+4.4	$\delta_s(CH_3)$96	1397	1470	+5.2	$\delta_s(CH_3)$94	1.00	1.00
	ν_7	1328	1423	+7.1	δ(NH)52, ν(CN)24 ν(C'N)13, ν(C=O)8	941	927	−1.5	δ(ND)55, ν(C'N)25 $\delta_r(CH_3)$9	1.42	1.54
	ν_8	1170	1142	−2.4	$\delta_r(CH_3)$46, ν(C=O)25 $\delta(CH_3)$7	1160	1127	−2.8	$\delta_r(CH_3)$50, ν(C'N)22 ν(C=O)11	1.01	1.01
	ν_9	1132[d]	1125	−0.6	ν(C'N)62, ν(CN)9 δ(NH)9	1231	1294	+5.1	ν(C'N)30, ν(CN)30 δ(ND)30, $\delta_r(CH_3)$7	0.94	0.87
	ν_{10}	980	963	−1.7	ν(CN)20, $\delta_r(CH_3)$35 ν(C=O)15	977	961	−1.6	ν(CN)24, ν(C=O)25 $\delta_r(CH_3)$24, δ(ND)7	1.00	1.00
	ν_{11}	504	461	−8.5	δ(NCN)46, ν(C'N)20 ν(CN)20, δ(C'NC)9	490	447	−8.8	δ(NCN)46, ν(CN)20 ν(C'N)19, δ(C'NC)10	1.03	1.03
	ν_{12}		202		δ(C'NC)78, δ(NCN)22		200		δ(C'NC)77, δ(NCN)23		1.01
B_2	ν_{13}	3485[d]	3480	−0.0	ν(NH)100	2448	2451	+0.0	ν(ND)100	1.42	1.37
	ν_{14}	2980	2966	−0.7	ν(CH)100	3000	2966	−1.1	ν(CH)99	0.99	1.00
	ν_{15}	2930	2879	−1.7	ν(CH)99	2950	2880	−2.5	ν(CH)99	0.99	0.99
	ν_{16}	1596	1570	−1.6	ν(CN)61, δ(NH)30 δ(NCO)6	1510	1534	+1.6	ν(CN)76, δ(ND)10 δ(NCO)9	1.06	1.02
	ν_{17}	1455	1483	+1.9	$\delta(CH_3)$86, $\delta_r(CH_3)$8	1455	1478	+1.6	$\delta(CH_3)$81, δ(CN)7	1.00	1.00
	ν_{18}	1410	1469	+4.2	$\delta_s(CH_3)$100	1397	1469	+5.2	$\delta_s(CH_3)$90, ν(C'N)7	1.01	1.00
	ν_{19}	1266	1311	+3.6	δ(NH)63, ν(CN)31	941	925	−1.7	δ(ND)56, ν(C'N)36	1.35	1.42
	ν_{20}	1170	1117	−4.5	$\delta_r(CH_3)$72, ν(C'N)12	1160	1112	−4.1	$\delta_r(CH_3)$76, ν(C'N)8 $\delta(CH_3)$8	1.01	1.00
	ν_{21}	1037	1000	−3.6	ν(C'N)78, $\delta_r(CH_3)$12	1018	1047	+2.9	ν(C'N)47, δ(ND)36 ν(CN)13	1.02	0.96
	ν_{22}	672	650	−3.3	δ(NCO)65, δ(C'NC)23	620	641	+3.4	δ(NCO)67, δ(C'NC)25	1.08	1.01
	ν_{23}		282		δ(C'NC)72, δ(NCO)29		281		δ(C'NC)70, δ(NCO)27		1.00

a) Percent deviation: $\Delta=[(\nu_c-\nu_o)/\nu_o]\times100$. b) Ratio ν_o of *s*-DMU to ν_o of *s*-DMU-d: $I=[\nu_o(s\text{-DMU})/\nu_o(s\text{-DMU-d}]$.
c) Ratio ν_c of *s*-DMU to ν_c of *s*-DMU-d: $II=[\nu_c(s\text{-DMU})/\nu_c(s\text{-DMU-d})]$. d) ν_o in chloroform solution; in ν_1, ν_o for free molecule.

Table 5. Observed frequencies (in cm^{-1}) of *sym*-dimethylurea

(I) $CH_3NHCONHCH_3$						(II) $CH_3NDCONDCH_3$				
Solid	Quenched sample	Liquid	$CHCl_3$ soln. concd.	soln.[a] dil.	Assign.	Solid	Quenched sample	Liquid	$CHCl_3$ soln.	Assign.
			3485	3485						
3360	3375	3360	3385	3402	ν(NH)	3000	3000		3005	
3165	3190					2950	2955	2955	2955	ν(CH)
3040	3060						2908		2885	
2980	2958	2960	3015	3015	ν(CH)		2805		2800	
2930	2908			2915		2695	2680	2660	2654	
	2815	2815	2820	2820		2503	2485		2500	ν(ND)
1625	1597	1653	1628	1673	amide I	2448	2450	2450	2448	
1569		1563	1582	1553	amide II	1620	1609	1633	1622	amide I′
1455	1441		1450	1450	$\delta_a(CH_3)$	1510	1523	1498	1500	amide II′
1410	1421	1410	1414	1413	$\delta_s(CH_3)$	1455	1442			$\delta_a(CH_3)$
		1331	1328	1326	amide III	1397	1420	1401	1401	$\delta_s(CH_3)$
1266	1269	1266	1273	1253	amide III	1231	1235	1219		ν(C′N)
1170	1176	1173	1173	1170	$\delta_r(CH_3)$	1160	1166	1167	1164	$\delta_r(CH_3)$
		1154	1132		ν(C′N)	1018	1026	1000		ν(C′N)
1037	1040	1040	1043	1042	ν(C′N)	977	983	958		ν(CN)
980					ν(CN)	941	949	934		amide III′
925	929	880	915[b]		$\delta_r(CH_3)_o$	906	916	898		$\delta_r(CH_3)_o$
772	773	773	772[b]		amide VI	769	772	773		amide VI′
672	672	632	654[b]		amide V, IV	620	624	625		amide IV′
		562	564	557	amide V					
504	501	504	508	501	δ(NCN)	490	500	497	495	δ(NCN)

a) Concd. and dil. mean concentrations of 0.5 and 0.06 mol/l respectively.
b) CH_3CN solution.

Table 6. Observed frequencies (in cm^{-1}) of *asym*-dimethylurea

$(CH_3)_2NCONH_2$		$(CH_3)_2NCOND_2$	Assignment	$(CH_3)_2NCONH_2$		$(CH_3)_2NCOND_2$	Assignment
Solid	$CHCl_3$ soln.	Solid		Solid	$CHCl_3$ soln.	Solid	
3400	3545			1273		1287	ν(C′N)
3355	3443		ν(NH)			1172	$\delta(ND_2)$
3197	3200			1097	1076		$\delta_r(NH_2)$
2925	2980	2920		1067	1059	1072	$\delta_r(CH_3)$
2857	2943	2960	ν(CH)	1022	1014	1008	ν(CN)
2800	2873	2800				908	$\delta_r(ND_2)$
		2546		793		793	
		2375	ν(ND)	773	768[b]	760	amide VI and VI′
		2343					
1655	1657	1600	amide I and I′	720			$\pi(NH_2)$
				604	594	597	amide IV and IV′
1600	1591		$\delta(NH_2)$				
1510	1485	1510	amide II and II′	552	517	528	δ(NCN)
						500	$\pi(ND_2)$
1450	1452	1450	$\delta_a(CH_3)$				
1412	1398	1415	$\delta_s(CH_3)$				
1400		1399					

a) 0.09 mol/l solution.
b) Acetone solution.

band at 1596 cm^{-1} has the contribution of ν(CN) mainly, but that of δ(NH) is not negligible, since on deuteration the band shifts to 1510 cm^{-1} (amide II′ band*7).

The amide III band at 1266 cm^{-1} has the main

*7 The prime means the amide band on the d-compounds.

Table 7. Characteristic amide frequencies for urea derivatives (in cm^{-1})

Amide band		I	II	III	
Methylurea	Solid	1651	1575	1353	
(MMU)	Liquid	1663	1550	1346	
	Solution				
	CH_3CN	1680	1516	1325	
	$CHCl_3$	1679	1509	1338	
sym-Dimethylurea	Solid	1625	1596	—	1266
(*s*-DMU)	Liquid	1653	1562	1331	1266
	Solution				
	CH_3CN	1678	1546	1320	1259
	$CHCl_3$	1673	1553	1326	1253
sym-Diethylurea*	Solid	1638	1598	—	1268
(*s*-DEU)	Liquid	1635	1547	1320	1252
	Solution				
	CH_3CN	1672	1535	1330	1242
	$CHCl_3$	1660	1531	1320	1235

* Unpublished data.

contribution of δ(NH), together with the additional ones of ν(CN) and ν(C'N). Contrary to the expectation of a strong peak from *trans* amides,[2,10] the amide III' band is observed at 941 cm^{-1} as a weak one. The reason for this may be that there is a considerable mixed-contribution of ν(C'N) to the band.

In the spectra in the liquid and solutions, two noticeable bands appear newly near 1330 and 560 cm^{-1}. The former is assigned to the amide III band because: (1) Figs. 6 and 7 illustrate the spectra of both DMU dissolved in water, but in *s*-DMU the marked band disappears in a D_2O solution, and in *a*-DMU, even in a H_2O solution. (2) In the solid-state spectra for *s*-DMU, the strong amide III band is likely to have a shoulder band towards a higher frequency. (3) The investigation of the N-H stretching region in *s*-DEU[20] can not show the possibility of the rotational isomer.[21] (4) The spectra in MMU do not show the corresponding bands (see Table 7).

From Table 5, it can be found that the amide I band decreases and the II band increases in frequency on passing along the series solution, liquid, solid, and *quenched* sample (in the *quenched* sample, the two bands overlap). This can be explained by the fact that the contribution of the polar resonance structure increases on passing along this series. The changes in the frequencies of the amide bands with the change in state are shown in Table 7 and compared with those of analogues, where similar tendencies are found in all. Accordingly, from the positions of the amide bands, the configuration of *s*-DMU as well as that of MMU is concluded to be the "*trans-trans*" form.

On the other hand, as the *a*-DMU molecule does not include the -CO-NH- group, the polar resonance structure may contribute less than that for *s*-DMU. In *a*-DMU, the isotopic shift from the amide II band to the II' band is very little, but in *s*-DMU, it is quite large (86 cm^{-1}) and the amide II' bands in *s*- and *a*-DMU are observed at the same positions. There is a similar relation between *s*- and *a*-DEU[20]; these questions were discussed in a previous paper.[1]

It can be concluded that the contribution of the polar resonance structure of the asymmetric form is smaller than that of the symmetric form, since the molecular geometry affects the formation of hydrogen-bondings and since the contribution of ν(CN) to the amide II band in the asymmetric form is larger than that in the symmetric form.

NH_2 Deformation Vibrations. In *a*-DMU, the ratios of the NH_2 band to the ND_2 band are 1.37 and 1.21 for $\delta(NH_2)$ and $\delta_r(NH_2)$ respectively. When we multiply a ratio of $\delta(ND_2)$ to $\delta(NH_2)$ by a ratio of $\delta_r(ND_2)$ to $\delta_r(NH_2)$ such as the product rule, the product values are regularly within 1.67 ± 0.02; urea: 1.69,[9],*8 MMU: 1.66,[1] *a*-DMU; 1.66 and *a*-DEU: 1.68.[20]

Amide IV, V, and VI Bands and δ(NCN). The amide IV, V, and VI bands are related to δ(NCO), out-of-plane; π(NH), and π(CO) respectively.[2,10,19] In *s*-DMU, three amide bands and δ(NCN) can be predicted in the region from 800 to 400 cm^{-1}, in which the band at 672 cm^{-1} can easily be assigned to the amide V band because of its breadth and susceptibility to a change of state, while the band at 772 cm^{-1} can be assigned to the

20) Y. Mido and H. Murata, to be published.
21) I. Suzuki, M. Tsuboi, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **16**, 471 (1960).

*8 In urea, there are two ratios for A_1 and B_2 species concerned with these vibrations and this value is the average of these ratios.

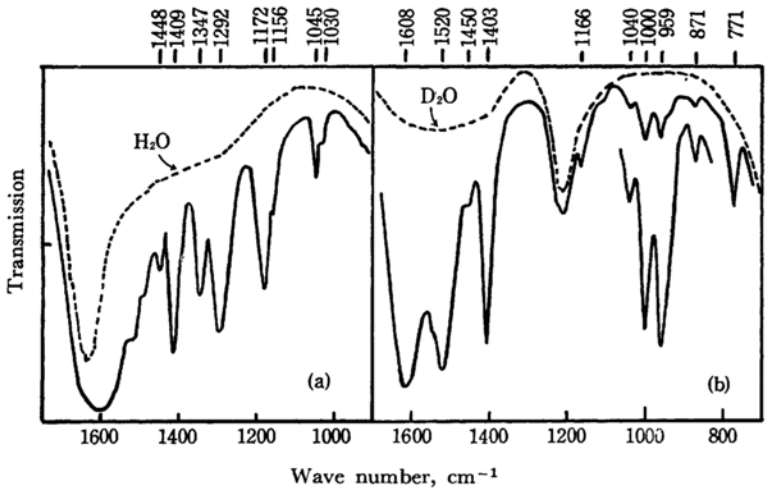

Fig. 6. Infrared spectra of *s*-DMU dissolved in (a) H_2O and (b) D_2O.

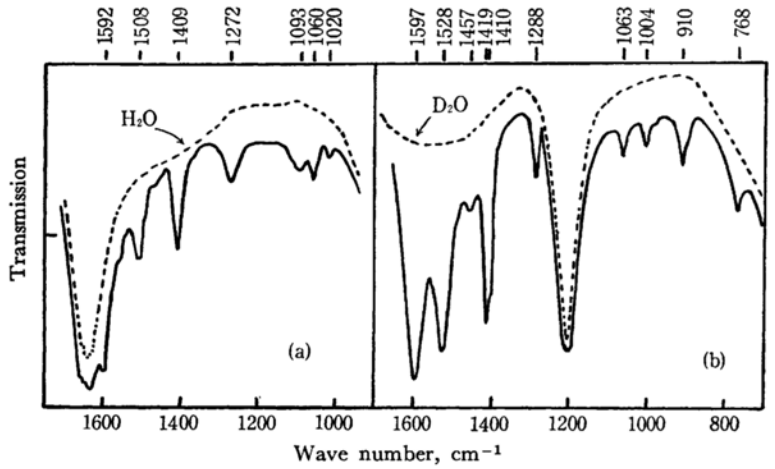

Fig. 7. Infrared spectra of *a*-DMU dissolved in (a) H_2O and (b) D_2O.

VI band because this band appears at a fixed position in the spectra of urea derivatives and because the band is hardly affected at all by deuteration. There are three bands observed in this region; the position of the V band is higher than that in MMU by 72 cm^{-1}, while the IV band in MMU has been assigned to 653 cm^{-1}; in *s*-DMU, however, the IV band is not observed in this position. Therefore, it may be considered that the IV band in *s*-DMU is covered with the V band and, on deuteration, appears at 622 cm^{-1} because the V band shifts toward a lower frequency side. The band at 504 cm^{-1} can be assigned to the undecided vibration, δ(NCN). In *a*-DMU, the bands at 773, 720, 604, and 552 cm^{-1} are associated with the amide VI band, $\pi(NH_2)$, the amide IV band and δ(NCN) respectively.

The Other Bands. In *s*-DMU, the bands at 1455, 1410, 1170, and 925 cm^{-1} (in *a*-DMU, the bands at 1450, 1412 and 1400, and 1067 cm^{-1}) are assigned to $\delta_a(CH_3)$, $\delta_s(CH_3)$, $\delta_r(CH_3)_i$, and $\delta_r(CH_3)_o$ respectively by comparing the vibrational frequencies of the related compounds of the CH_3 group attached to the nitrogen.[2] In *s*-DMU-d, the band at 1231 cm^{-1} corresponds to the band at 1212 cm^{-1} in *s*-DEU-d^{20}[10] and can be assigned to ν(C'N) of A_1, but in *s*-DMU and *s*-DEU there are no corresponding bands in this region. The weak bands at 1037 and 980 cm^{-1} in *s*-DMU and at 1018 and 977 cm^{-1} in *s*-DMU-d are assigned to the ν(C'N) of B_2 and the ν(CN) of A_1 respectively.