INFRARED SPECTROSCOPIC STUDIES OF HYDROGEN BONDING IN N-METHYLACETAMIDE–N, N-DIMETHYL AMIDE AND N-METHYLACETAMIDE–N, N-DIPHENYL AMIDE COMPLEXES

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SPECTROSCOPIC studies of changes in vibration frequencies and integrated intensities of absorption bands arising out of stretching and bending modes of vibration give information in regard to the strength of the hydrogen bonding. Kartha *et al.*[1] and Venkata Ramiah *et al.*[2] studied hydrogen bonding of the type $O-H\ldots S$, $O-H\ldots O=C$ and $S-H\ldots O=C$ and calculated equilibrium constants. Recently the authors[3] have reported the frequency changes in N–H stretching band of N-methylacetamide in the presence of N, N-dimethylformamide and N, N-dimethylacetamide and computed the equilibrium constants of these complexes. The authors extend these results by studying spectral changes of the free N–H stretching absorption band of N-methylacetamide in the presence of N, N-dimethylpropionamide, N, N-diphenylformamide, N, N-diphenylacetamide and N, N-diphenylpropionamide. The equilibrium constants for each of these complexes are also reported.

Perkin Elmer model 221 Infrared Spectrophotometer with NaCl optics and matched quartz cells of 3 cm thickness were used for recording the free and bonded N-H stretching band of N-methylacetamide in solution of carbontetrachloride and in the presence of N, N-dimethyl amides and N, N-diphenyl amides. The experimental procedure and the method of evaluation of equilibrium constants adopted in these investigations are same as those reported in our earlier communication[3].

The free and bonded N–H stretching frequencies and the equilibrium constants for various complexes and different concentratoin are given in Tables I, II and III.

The results obtained earlier for N-methylacetamide–N, N-dimethylformamide and N–methylacetamide–N, N-dimethylacetamide complpexes are also given in these tables for comparison. The free and bonded N–H stretching absorption bands

TABLE I

The N–H stretching frequencies and equilibrium constants in N-methylacetamide–N, N-dimethylformamide and N-methylacetamide–N, N-diphenylformamide complexes

Tertiary amide		Molar concentration of NMA	Frequency of N–H stretching band		Frequency difference between bonded and free band (in cm^1)	Absorbance of free N–H stretching in the presence of tertiary amides	Equilibrium constant	Average K
Name of the amide	Molar concentration		Free band in CCl_4 (in cm^{-1})	Bonded band in the presence of amide (in cm^{-1})				
DMF	0·0250	0·0010	3,464	3,364	100	0·34	9·9	11·0
	0·0250	0·0015	3,464	3,364	100	0·49	12·0	
DMF	0·0125	0·0010	3,464	3,364	100	0·39	6·9	6·9
	0·0125	0·0015	3,464	3,364	100	0·57	6·9	
DPF	0·0254	0·00146	3,464	3,374	90	0·54	5·8	7·2
	0·0254	0·00187	3,464	3,374	90	0·65	8·6	
DPF	0·0127	0·00125	3,464	3,380	84	0·51	4·6	4·4
	0·0127	0·00170	3,464	3,380	84	0·69	4·2	

TABLE II

The N–H stretching frequencies and equilibrium constants in N-methylacetamide–N, N-dimethylacetamide and N-methylacetamide–N, N-diphenylacetamide complexes

Tertiary amide		Molar concentration of NMA	Frequency of N–H stretching band		Frequency difference between bonded and free band (in cm^{-1})	Absorbance of free N–H stretching in the presence of tertiary amides	Equilibrium constant	Average K
Name of the amide	Molar concentration		Free band in CCl_4 (in cm^{-1})	Bonded band in the presence of amide (in cm^{-1})				
DMA	0·0254	0·00125	3,464	3,340	124	0·208	64	66·0
	0·0254	0·00185	3,464	3,340	124	0·276	68	
DMA	0·0127	0·00125	3,464	3,380	124	0·390	30	32·5
	0·0127	0·00185	3,464	3,340	124	0·549	35	
DPA	0·0249	0·00146	3,464	3,360	104	0·432	17·7	17·0
	0·0249	0·00187	3,464	3,360	104	0·565	16·4	
DPA	0·01184	0·00125	3,464	3,372	92	0·455	13·9	14·8
	0·01184	0·00185	3,464	3,372	92	0·662	15·7	

TABLE III

The N–H stretching frequencies and equilibrium constants in N-methylacetamide–N, N-dimethylpropionamide and N-methylacetamide—N, N-diphenylpropionamide complexes

Tertiary amide		Molar concentration of NMA	Frequency of N–H stretching band		Frequency difference between bonded and free band (in cm^{-1})	Absorbance of free N–H stretching in the presence of tertiary amides	Equilibrium constant	Average K
Name of the amide	Molar concentration		Free band in CCl_4 (in cm^{-1})	Bonded band in the presence of amide (in cm^{-1})				
DMP	0·0243	0·00146	3,464	3,348	116	0·275	51·7	51·3
	0·0243	0·00187	3,464	3,348	116	0·362	50·8	
DMP	0·0122	0·00125	3,464	3,350	114	0·407	25·2	25·5
	0·0122	0·00166	3,464	3,350	114	0·540	25·9	
DPP	0·0247	0·00146	3,464	3,364	100	0·450	15·6	15·2
	0·0247	0·00189	3,464	3,364	100	0·585	14·9	
DPP	0·0166	0·00146	3,464	3,375	89	0·510	13·2	13·3
	0·0166	0·00184	3,464	3,375	89	0·635	13·5	

of N-methylacetamide in the presence of N, N-dimethylacetamide, N, N-diphenylacetamide, N, N-dimethylpropionamide and N, N-diphenylpropionamide are given in Figs. 1 and 2,

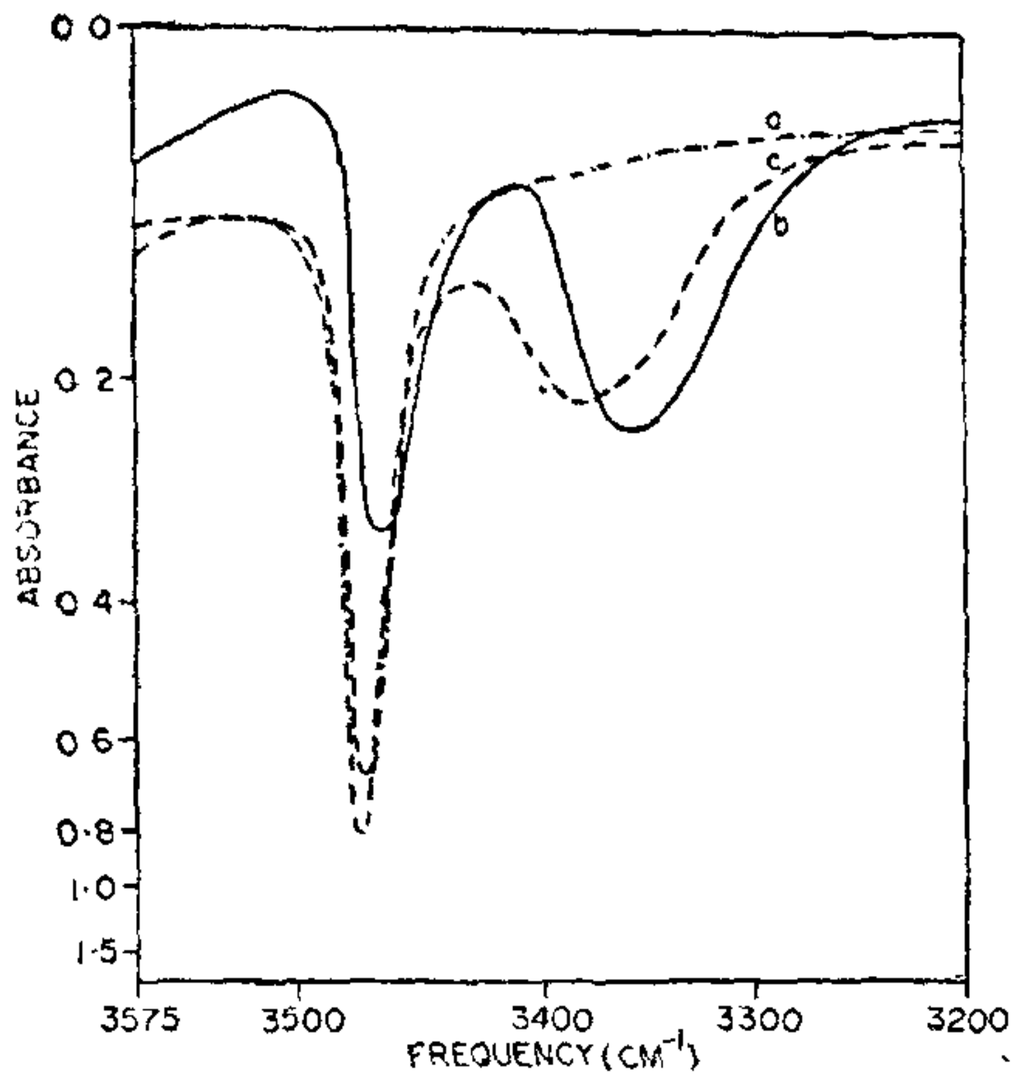

FIG. 1. Infrared spectra of N–H stretching band of N-methylacetamide (*a*) in carbon tetrachloride, (*b*) in CCl_4 in the presence of dimethylacetamide, (*c*) in CCl_4 in the presence of diphenylacetamide.

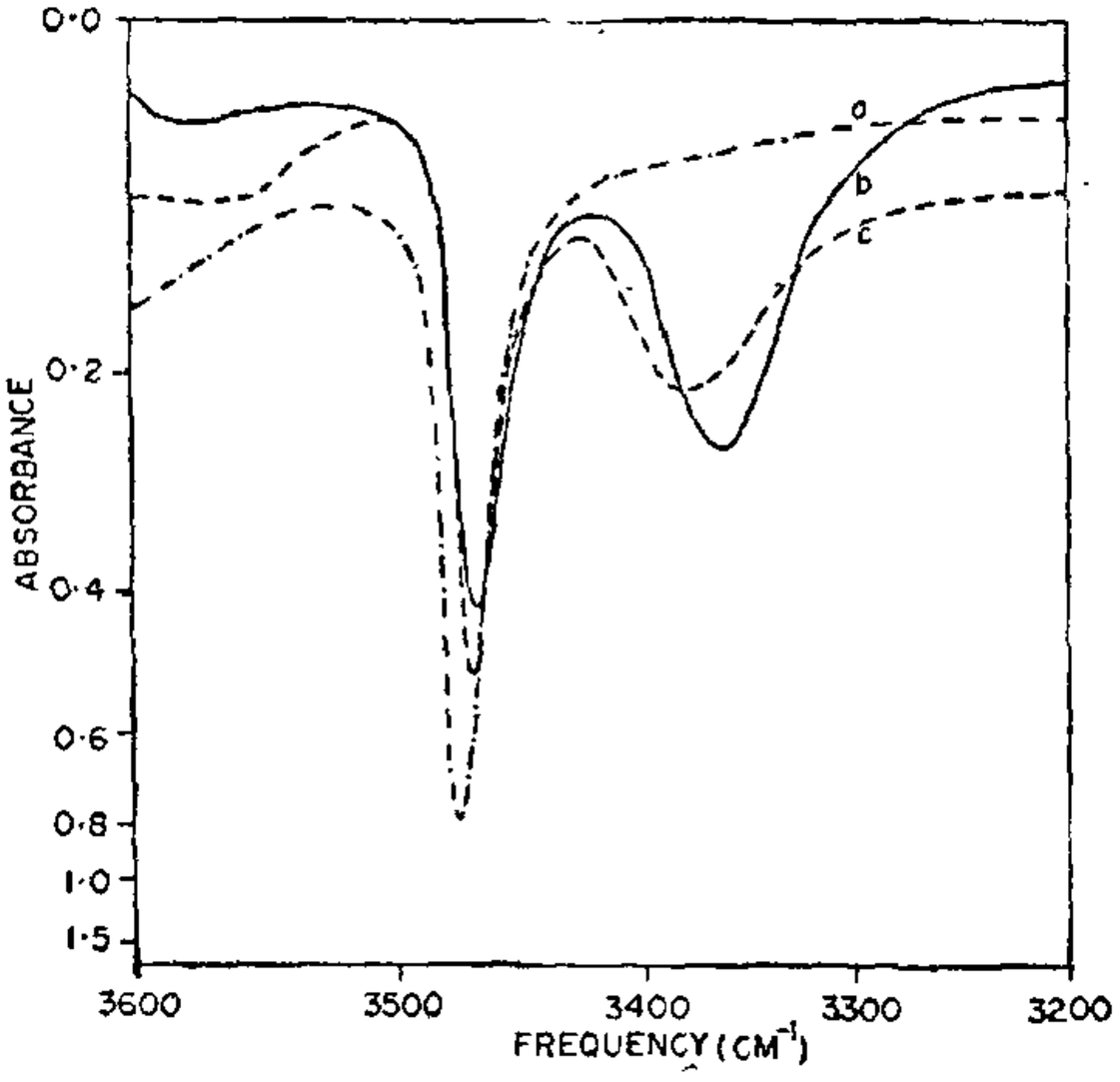

FIG. 2. Infrared spectra of N–H stretching band of N-methylacetamide (*a*) in carbon tetrachloride, (*b*) in CCl_4 in the presence of dimethylpropionamide, (*c*) in CCl_4 in the presence of diphenylpropionamide.

The main results that emerge out of these studies are :

(*i*) the frequency difference between the free and bonded N–H stretching frequencies of N-methylacetamide is highest in the presence of N, N-dimethylacetamide and lowest in the presence of N, N-dimethylformamide ;

(*ii*) similarly the frequency difference between the free and bonded N–H stretching frequencies of N-methylacetamide is highest in the presence of N, N-diphenylacetamide and lowest in the case of N, N-diphenylformamide ;

(*iii*) the frequency difference between the free and bonded N–H stretching frequencies of N-methylacetamide is higher in the presence of N, N-dimethyl amide than in the presence of the corresponding diphenyl amide ;

(*iv*) the values of equilibrium constants are highest in N-methylacetamide–N, N-dimethylacetamide complex and lowest in N-methylacetamide–N, N-dimethylformamide complex ;

(*v*) similarly the value of equilibrium constants are highest in N-methylacetamide–N, N-diphenylacetamide complex and lowest in N-methylacetamide–N, N-diphenylformamide complex ;

(*vi*) the equilibrium constants have higher values in N-methylacetamide–N, N-dimethyl amide complexes than in the case of N-methylacetamide-N, N-diphenyl amide complexes.

These results indicate that the hydrogen bonding in N-methylacetamide–N, N-dimethyl amide complexes is stronger than in N-methylacetamide–N, N-diphenyl amide complexes.

In amide molecules there are two resonant structures which contribute to the ground state of the molecule ; the dipolar resonant structure arises out of the interaction of π orbitals of CO group and $2p_z$ orbital of nitrogen atom. But in diphenyl amides there is a competitive effect of the phenyl ring for the lone pair of electrons on the nitrogen atom, with the result that the contribution of the dipolar resonant structure to the ground state of the molecule is considerably reduced. This explains the manifestation of weaker hydrogen bonding in N-methylacetamide–N, N-diphenyl amide complexes, compared to that in the corresponding N-methylacetamide–N, N-dimethylamide complexes.

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