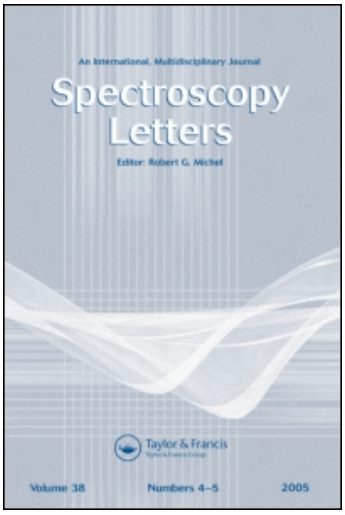

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FT-IR Study of the Interaction Between 1,3-Dimethyluracil and the Lithium Ion

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FT-IR STUDY OF THE INTERACTION BETWEEN 1,3-DIMETHYLURACIL AND THE LITHIUM ION

Key words. FT-IR spectra, dimethyluracil, Li^+ complex.

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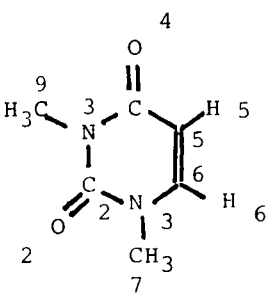
INTRODUCTION

Protonation and complexation of nucleic acid bases with metal ions have a profound influence on their structure and reactivity[1-3]. Although the interaction between carbonyl bases and the Li^+ ion has been studied by vibrational spectroscopy[4-8] and ab initio calculations[8-15], no experimental results are available for the complexation between this ion and carbonyl bases derived from nucleic acids. In this work, the interaction between 1,3-dimethyluracil (DMU)



and LiI is studied in acetonitrile as a solvent. The FT-IR spectrum of the complex in the solid state is also investigated; as shown by theoretical calculations[15], complex formation of thymine with Li^+ leads to structural changes in the base moeity and as a consequence, marked changes in the vibrational spectrum are to be expected.

EXPERIMENTAL

The spectra have been recorded on the FT-IR Bruker IFS-88 spectrophotometer with a rseolution of 2 cm^{-1} (32 scans).

The complex between DMU and LiI was studied in acetonitrile as a solvent; the solutions were prepared under dry nitrogen atmosphere. The complex in the solid state has been prepared from an equimolecular solution of the base and the salt and the spectrum of the solid adduct has been recorded in KBr disc.

LiI is from Janssen Chimica. Acetonitrile from Merck has been distilled over P_2O_5. DMU from Sigma was used without further purification.

RESULTS AND DISCUSSION

a. Interaction between DMU and LiI in Acetonitrile

LiI dissolved in acetonitrile is completely dissociated into ions; in this solvent, Li^+ has a coordination number of four in the first solvation shell[17]. The "ion-cage" vibrations are observed at about 405 cm^{-1} [17-18]. Owing to overlapping with solvent absorptions, only a few bands of DMU could be studied in solution. In the $\nu_{C=O}$ region, two bands are observed at 1709 and 1668 cm^{-1}; in a previous work[19], these two bands have been assigned to vibrational modes having predominantly $\nu_{C=O_2}$ and $\nu_{C=O_4}$ character, contrarily to

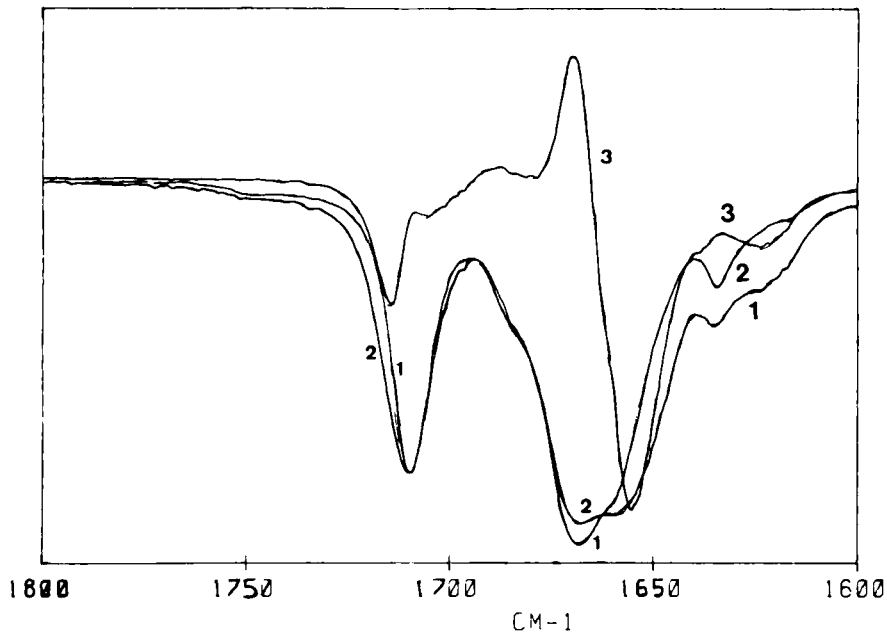


FIGURE 1 FT-IR spectrum in the $\nu_{C=O}$ region of
1. DMU (c = 0.144 M)
2. DMU (c = 0.144 M) + LiI (c = 0.138 M)
solvent = CH_3CN
3. Difference spectrum between 2 and 1.

results from ab initio calculations which give an inverse assignment[20].

As shown in Fig. 1, in the presence of LiI, a broadening to the high frequency side of the $\nu_{C=O_2}$ band, a decrease of the intensity of the $\nu_{C=O_4}$ band and a new absorption to the low frequency side of this band are observed. The difference spectrum shows new bands at 1714 cm^{-1} ($\Delta\nu$ = +5 cm^{-1}) and 1655 cm^{-1} ($\Delta\nu$ = -13 cm^{-1}). This spectral behaviour strongly suggests that the Li^+ ion is bonded to the O_4 atom, the shift of the $\nu_{C=O_2}$

TABLE 1

F_B, F_A, c_{AB} and K Values for the Interaction between DMU and LiI in Acetonitrile (T° = 298 K)

F_B (M)	F_A (M)	c_{AB} (M)	K (M^{-1})
0.144	0.036	0.014	4.9
0.144	0.138	0.044	4.7
0.161	0.041	0.018	5.5
0.161	0.055	0.025	6.1
			$\overline{K} = 5.3 \pm 0.6$ M^{-1}

band to higher wavenumbers indicating a decreasing delocalization within this bond. This agrees with the theoretical predictions of Del Bene[16] who has shown that the complex of uracil formed with Li^+ associated at O_4 has a stabilization energy of -55.4 kcal.mol^{-1} and is slightly preferred to the complex formed at O_2 which has a stabilization energy of -53.9 kcal.mol^{-1}. It must be pointed out however that when LiI is in great excess with respect to DMU, a second band to the low frequency side of the $\nu_{C=O_2}$ band (1700 cm^{-1}) is observed and this can be assigned to complex formation on the O_2 atom. Small frequency shifts of the bands at 1150, 809 and 685 cm^{-1} are also observed.

An attempt was made to calculate the equilibrium constant. For a given formal concentration of base (F_B), the concentration of free base (c_B) can be computed from the absorbance of the $\nu_{C=O_4}$ band.

$$K = \frac{F_B - c_B}{c_B - c_A} = \frac{c_{AB}}{c_B(F_A - c_{AB})}$$

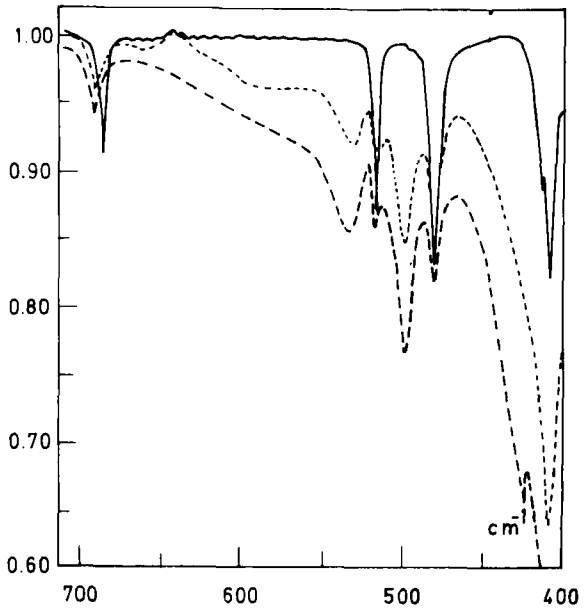


FIGURE 2 FT-IR spectrum (700-400 cm^{-1}) of
—— DMU (c = 0.144 M)
··· DMU (c = 0.144 M) and LiI (c = 0.138 M)
--- DMU (c = 0.144 M) and LiI (c = 0.295 M)

c_{AB} and F_A being the complex and the formal concentration of LiI.

These concentrations and the equilibrium constant (K) are listed in Table 1.

As a matter of fact, the experimental Li^+ affinities of oxygen bases in the gas phase are between 40 and 60 $kcal.mol^{-1}$ [21] and as a consequence, a much higher K value in the gas phase can be predicted. In solution, the K value is associated with the equilibrium

$$Li^+(C\equiv N)_4 + DMU \qquad Li^+(C\equiv N)_3DMU + -C\equiv N$$

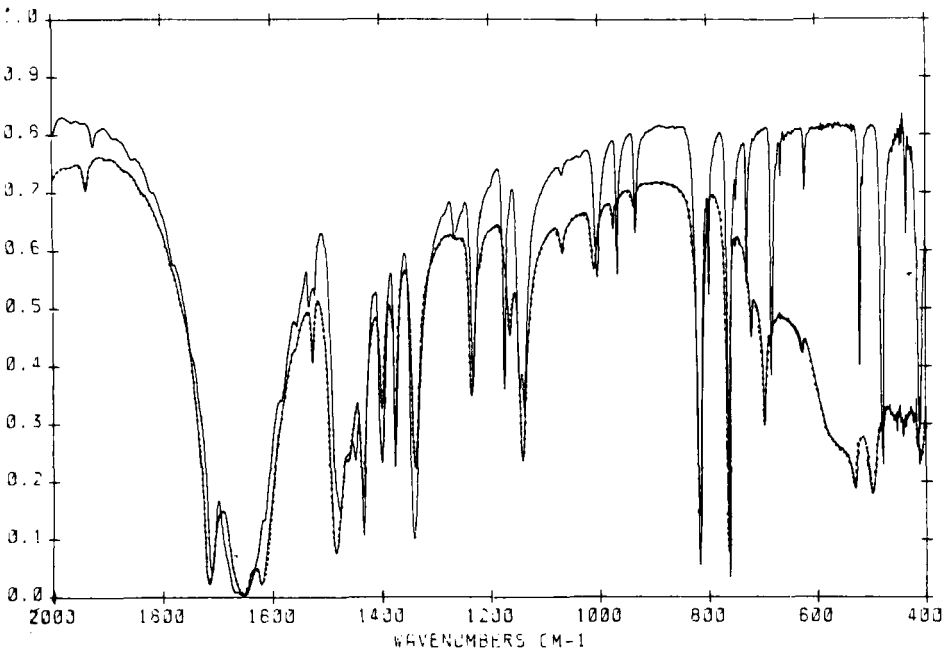


FIGURE 3 FT-IR spectrum of DMU (—) and the DMU.LiI adduct (--) in the solid state

As shown in Fig. 2, a broad band is observed between 650 and 400 cm^{-1} ($\nu_{max} \sim 500\ cm^{-1}$); this absorption is assigned to the ν_{Li^+-O} vibration. The $\nu_{Li^+-C\equiv N}$ vibration is observed at 405 cm^{-1} in agreement with literature data[17-18].

b. Complex between DMU and LiI in the Solid State

The spectrum of the complex in the solid state is reproduced in Fig. 3 and the infrared data for free DMU and the complex are listed in Table 2.

As shown by these results, the frequency shift of the $\nu_{C=O_4}$ vibration (-45 cm^{-1}) is much higher in

TABLE 2

Infrared Data for DMU free and complexed with LiI (cm^{-1}) (KBR disc).

Free DMU	DMU.LiI	Assignment[b]
1710	1715	$\nu C{=}O_2$
1665	1620	$\nu C{=}O_4$
1652	1653	$\nu C{=}C$
1534	1526	$2\gamma C{=}O$
1523		
1478	1485	$\delta^{as}CH_3$
1447	~1465[a]	νC_2N_3 νN_1C_2
1434	1434	$\delta^{as}CH_3$
1400	1398	$\delta^{s}CH_3$
1375	1375	δC_5H
1341	1337	νN_3C_4
1263	- [a]	νC_2N_3
1231	1233	νC_1C_7 δC_6H
1174	1164	r_{CH_3}
1145	1140	r_{CH_3}
1137		
1003	1010	νC_4C_5
965	972[a]	?
932	932[a]	νN_3C_9 γCH
816	816	see descrip-
798	764	tion in the text
761		
728	719	ν_{ring} δ_{ring}
684	696	νC_3C_4 ν_{ring} (?)
623	626	$\delta C_4{=}O$
522	531	ring def.
479	500	ring def.

(a) strong intensity decrease; (b) ν = stretching, δ = i.p. deformation, γ = o.o.p. deformation, r = rocking Assignment from ref. 19.

the solid complex than in acetonitrile solution and this result agrees with the previous discussion. Similar results have been obtained by Popov et al.[4] for 2-pyrrolidones complexed with $LiClO_4$. In dioxane solution the $\Delta\nu_{C=O}$ value is -21 cm^{-1} while in the solid state, the $\nu_{C=O}$ band shifts to lower values by 40-45 cm^{-1}.

The in-plane deformation and the rocking vibrations of the CH_3 group are somewhat perturbed in frequency and intensity. The same remark also holds for vibrations involving an in-plane and out-of-plane deformation of the CH bond. The vibrations associated with ν_{C-C} or ν_{C-N} stretching modes undergo frequency shifts and intensity variations, this is the case for the bands observed at 1447 cm^{-1} ($\Delta\tilde{\nu}$ = -18 cm^{-1}), at 1341 cm^{-1} ($\Delta\tilde{\nu}$ = -4 cm^{-1}), at 1003 cm^{-1} ($\Delta\tilde{\nu}$ = +7 cm^{-1}) and at 684 cm^{-1} ($\Delta\tilde{\nu}$ = +12 cm^{-1}). These vibrations have been assigned to $\nu_{C_2N_3}$, $\nu_{N_1C_2}$, $\nu_{N_3C_4}$, $\nu_{C_2N_3}$ and $\nu_{C_3C_4}$ vibrations but they involve probably a ring stretching mode of the "whole" ring. These perturbations can be explained by small variations of the C_2N_3, N_1C_2, N_3C_4, C_2N_3 and C_3C_4 distances by complex formation with Li^+. The calculations of Del Bene[16] have shown that the C_2N_3 distance increases by 0.025 Å, the C_4N_3 distance decreases by 0.010 Å, the C_4C_5 distance decreases by 0.043 Å and that the C_5C_6 distance increases by 0.025 Å by complex formation of uracil with Li^+.

Further the bands at 522 and 479 cm^{-1} probably originating from out-of-plane deformations, are shifted by about +20 cm^{-1}.

There is some doubt on the assignment of the vibrational modes between 816 and 761 cm^{-1}. In a low temperature Ar matrix, the two bands observed at 803 and 763 cm^{-1} in DMU have been assigned to $\gamma_{C=O}$ vibrations[20]. Further, the bands observed at 832 and 755 cm^{-1} in uracil isolated in Ar have been assigned to the $\gamma_{C=O_4}$ and $\gamma_{C=O_2}$

TABLE 3

Experimental $\nu_{C=O}$ Values and Calculated $r_{C=O}$ Values

	$\nu_{C=O_2}$ cm^{-1}	$\nu_{C=O_4}$	$r_{C=O_2}$ Å	$r_{C=O_4}$
Uracil	1 710	1 670	1.219[a]	1.221[a]
Uracil.Li^+	1 716[b]	1 620[b]	1.210[c]	1.278[c]
Uracil.H^+	1 704[d]	1 523[d]	1.207[e]	1.367[e]

(a) ref. 16 ; (b) this work; (c) ref. 16 ; (d) ref. 25 ; (e) ref. 24 .

vibrations coupled with γ_{CH} modes[22]. In the DMU.LiI complex, the bands observed at 816 and 761 cm^{-1} remain practically unchanged, the first band shifting slightly to lower frequencies and the second one shifting slightly to higher frequencies. This behaviour strongly suggests that the bands at 816 and 716 cm^{-1} originate from ring vibrations probably coupled with γ_{CH} vibrations. This attribution is strengthened by the high intensity of the two absorptions. The band at 798 cm^{-1} disappears in the complex and probably overlaps with the 816 cm^{-1} absorption while the 684 cm^{-1} band shifts to 696 cm^{-1}. It seems therefore likely that these two absorptions contain some contribution of the $\gamma_{C=O_4}$ mode. This agrees with the recent interpretation of the vibrational spectra of uracil from scaled ab initio quantum mechanical force fields[23] which predict the $\gamma_{C=O}$ mode at 804 cm^{-1} and the coupled $\gamma_{C_5H} + \gamma_{C_4=O}$ mode at 718 cm^{-1}.

Fig. 3 also shows the broad absorption ($\tilde{\nu}_{max} \simeq 500$ cm^{-1}) assigned to the ν_{Li^+-O} vibration; this absorption is characterized by a transmission window which originates from the 522 cm^{-1} level.

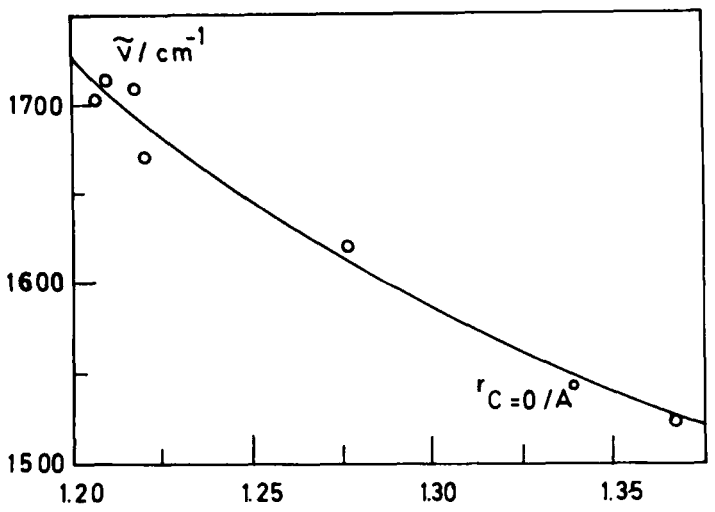


FIGURE 4 $\nu_{C=O}$ (cm^{-1}) as a function of $r_{C=O}$ (Å)

At last, Table 3 compares the values of the frequencies of the $\nu_{C=O_2}$ and $\nu_{C=O_2}$ vibrations and the $r_{C=O_2}$ and $r_{C=O_4}$ distances for free uracil and its complex with Li^+ and H^+.

The distances have been computed by ab initio calculations[16,24] for uracil and the frequencies have been approximately determined for DMU and its complex with Li^+ or H^+ in the solid state[25]. There is a small difference between the experimental $r_{C=O_2}$ and $r_{C=O_4}$ values in DMU which are respectively equal to 1.225 Å and 1.227 Å [26] and the calculated distances in uracil, which are 1.219 Å ($r_{C=O_2}$) and 1.221 Å ($r_{C=O_4}$). These small differences do not affect the correlation illustrated in Fig. 4 where the $r_{C=O}$ values range from 1.22 to 1.37 Å.

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