Infrared Study of Hydrogen-Bonded Complexes Involving Phenol Derivatives and Polyfunctional Bases. 2. 3-Methyl-4-pyrimidone, 1-Methyl-2-pyrimidone, 1,4,4-Trimethylcytosine, and 1,3-Dimethyluracil

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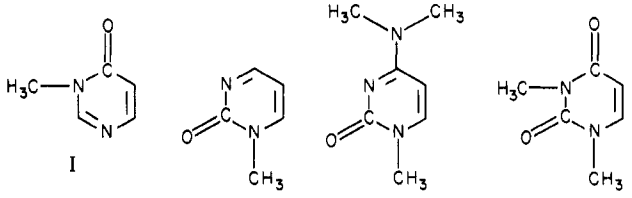
In this work, the electron-donating properties of 3-methyl-4-pyrimidone (I), 1-methyl-2-pyrimidone (II), 1,4,4-trimethylcytosine (III), 1,3-dimethyluracil (IV), and pyrimidine (V) have been studied by infrared spectrometry, using the phenol derivatives as reference acids. The thermodynamic parameters (K, $-\Delta H$, $-\Delta S$) determined in 1,2-dichloroethane (1,2-DCE) are ordered according to III > II > IV > V, the same order as that predicted from the pK_a value, with the exception of IV. For the same enthalpy of complex formation, the $\Delta\nu_{OH}$ values were markedly higher for V than for the complexes involving the other bases; this fact and the frequency lowering of the $\nu_{C=O}$ vibration clearly show that for compounds I–IV the carbonyl group is the preferred H-bond site. For IV, the infrared data suggest that complex formation takes place on the O_4 atom in agreement with the lower ionization potential of the n(O_4) electrons. As shown by the X-ray diffraction method and the infrared spectra available in the literature, protonation takes place on the nitrogen atom for I–III and on the O_4 atom for IV. This shows that, with the exception of IV, the preferred H-bonding site is not the preferred site of protonation. The intermolecular stretching vibrations ν_σ are observed between 130 and 110 cm^{-1} and the corresponding force constants k_σ are calculated by the Lippincott–Schroeder potential function. The k_σ values are compared with those of hydrogen bonds involving nitrogen and sulfur atoms. It is shown that, for the same enthalpy of complexation, the k_σ values are related to the extension of the lone-pair electrons of the base.

Introduction

In the second part of this work,[1] the electron-donating power of four heterocyclic polyfunctional bases of biological interest are studied by infrared spectroscopy, taking several phenol derivatives as reference acids. These bases are 3-methyl-4-pyrimidone (I),



I II III IV

1-methyl-2-pyrimidone (II), 1,4,4-trimethylcytosine (III), and 1,3-dimethyluracil (IV). In these bases, several sites, mainly the oxygen atom(s) and nitrogen atom, are available for hydrogen bonding. Owing to the very low solubility of the pyrimidones, cytosine, and uracil in the usual organic solvents, their electron-donating power towards a common proton donor has not been studied in solution; it must be pointed out however that the interaction between 1-cyclohexyluracil and water has been studied in chloroform solution,[2] and the displacements of the $\nu_{C=O}$ bands to lower frequencies suggest that both $C_2{=}O_2$ and $C_4{=}O_4$ carbonyl groups enter into hydrogen bonds. Further, the frequencies of some absorption bands in the nonsubstituted molecules are, in the solid state, influenced by strong NH···O=C hydrogen bonds.[3-10] To overcome these difficulties, we have studied the complexes between a set of common proton donors (phenol derivatives) and the N-methylated bases which are sufficiently soluble in 1,2-dichloroethane; some of them (3-methyl-4-pyrimidone and 1,3-dimethyluracil) are soluble in carbon tetrachloride. Further, these bases are not associated and the perturbations of the infrared absorptions on adding a proton donor can be considered as the net effect of the hydrogen bond. Moreover, it must be pointed out that the blocking of a proton-donor or -acceptor center of a molecule, for example by a methyl group, does not significantly change the acid–base properties of the other acceptor centers.[11] The pK_a values of cytosine, 1-methylcytosine and 1,4,4-trimethylcytosine are 4.45, 4.55,[12] and 4.20,[13] respectively.

In this work the thermodynamic data (formation constants; enthalpies and entropies of complex formation) of the complexes involving the 4 mentioned bases and 12 phenol derivatives are reported and compared with the complexes of the diazines,[1] more specifically pyrimidine. These data are correlated with the displacement of some internal modes of the molecules, mainly the ν_{OH} and $\nu_{C=O}$ vibrations. At last, the intermolecular stretching vibration lying in the far-infrared region and the corresponding force constant are reported and compared with other hydrogen-bonded systems.

Experimental Section

The spectrophotometers and the method to compute the formation constants and the corresponding enthalpies have been described in part 1.[1] Owing to the lower value of the molar extinction coefficient of the ν_{OH} band in 1,2-dichloroethane (1,2-DCE), higher concentrations of phenol derivatives were used; these ranged from 0.01 to 0.04 M. The concentrations of base varied from 0.02 to 0.22 M. In this limited range, no variations of the formation constants with the concentration could be observed and this indicates that only 1:1 complexes are present in solution. The far-infrared spectra were obtained by using benzene as a solvent.

Products

3-Methyl-4-pyrimidone was obtained by methylation of 4-pyrimidone following the methods described in the literature.[14,15]

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TABLE I: Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between Substituted Phenols and 3-Methyl-4-pyrimidone[a]

phenol derivative	K^{298K}, dm³ mol⁻¹	K^{323K}, dm³ mol⁻¹	$-\Delta H$, kJ mol⁻¹	$-\Delta S^{298K}$, J K⁻¹ mol⁻¹	$\Delta\nu_{OH}$,[b] cm⁻¹
3,4-dimethyl	11.1	5.2	22.8	56.0	233
4-methoxy	12.2	6.3	23.1	56.1	240
phenol	15.6	7.8	23.6	56.3	251
4-fluoro	20.0	8.5	23.9	56.4	262
4-chloro	23.4	10.9	24.8	56.7	272
4-bromo	24.0	11.7	24.9	56.7	284
3-chloro	34.1	15.1	25.4	56.9	292
3-bromo	35.0	16.6	25.6	57.0	296
3,4-dichloro	42.3	19.1	26.5	57.3	302
3-nitro	57.8	22.3	27.1	57.6	316
3,5-dichloro	62.6	26.0	27.3	57.6	319
3,4,5-trichloro	75.5	32.9	28.2	58.0	325

[a] S = 1,2-DCE. [b] Broad band. Error on the maximum, ±10 cm⁻¹.

TABLE II: Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between Substituted Phenols and 1-Methyl-2-pyrimidone[a]

phenol derivative	K^{298K}, dm³ mol⁻¹	K^{323K}, dm³ mol⁻¹	$-\Delta H$, kJ mol⁻¹	$-\Delta S^{298K}$, J K⁻¹ mol⁻¹	$\Delta\nu_{OH}$,[b] cm⁻¹
3,4-dimethyl	12.4	6.5	23.7	58.1	282
4-methoxy	15.0	7.4	24.3	58.7	287
phenol	19.6	8.3	25.2	59.7	310
4-fluoro	24	11	25.7	60.3	324
4-chloro	35.6	16	27.3	62.0	330
4-bromo	38.2	15	27.5	62.2	337
3-fluoro	42.8	17	27.9	62.6	355
3-bromo	52.3	20	28.6	63.4	360
3,4-dichloro	86.2	29	30.2	65.2	380
3-nitro	111	43	31.3	66.3	391
3,5-dichloro	113	45	31.7	66.7	396
3,4,5-trichloro	163	63	33.3	68.4	415

[a] S = 1,2-DCE. [b] Broad band. Error on the maximum, ±10 cm⁻¹.

To 10 g of 4-pyrimidone dissolved in 100 mL of dimethylformamide was added 6 g of potassium hydroxide and, after 4 h, 15 g of iodomethane. After 20 h, dimethylformamide was evaporated with a rotary evaporator under reduced pressure; 100 mL of water was then added to the residue, which was further extracted 5 times with chloroform. The organic phase was dried on magnesium sulfate. After evaporation, the precipitate was collected and recrystallized from a mixture of ether–chloroform, which gave 4.6 g of 3-methyl-4-pyrimidone.

1-Methyl-2-pyrimidone was obtained by methylation of 2-pyrimidone by the same method; 2-pyrimidone was obtained by neutralization of 2-pyrimidone chlorohydrate according to the method of Hunt et al.[16]

1,4,4-Trimethylcytosine was synthetized by aminolysis of 4-ethoxy-1-methyl-2-pyrimidol obtained by methylation of 2,4-diethoxypyrimidine;[17] 25 g of 2,4-diethoxypyrimidone was dissolved in 25 g of distilled iodomethane. The solution was allowed to stand for 20 h darkness. The precipitate was then filtered and recrystallized from a mixture of ethanol–ether; this yields 23 g of 4-ethoxy-1-methyl-2-pyrimidol. This product was further dissolved in a solution of 20 mL of anhydrous methanol saturated with dimethylamine (30%). The reaction mixture was kept at 100 °C for 18 h; the precipitate was then filtered and recrystallized from a methanol–ether mixture. This yields 0.62 g of 1,4,4-trimethylcytosine.

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TABLE III: Thermodynamic Data for the Complexes between Substituted Phenols and 1,4,4-Trimethylcytosine[a]

phenol derivative	K^{298K}, dm³ mol⁻¹	K^{323K}, dm³ mol⁻¹	$-\Delta H$, kJ mol⁻¹	$-\Delta S^{298K}$, J K⁻¹ mol⁻¹
3,4-dimethyl	58	26	28.1	60.8
4-methoxy	72	32	29.3	62.7
phenol	104	46	31.4	66.1
4-fluoro	139	48	32.5	67.9
4-chloro	240	81	35.8	73.5
4-bromo	287	80	36.1	74.0
3-fluoro	384	102	37.2	75.7
3-chloro	484	135	37.9	77.0
3-bromo	514	150	38.6	78.2
3,4-dichloro	1038	254	42.3	84.7
3,4,5-trichloro	3487	952	48.6	94.7

[a] S = 1,2-DCE.

TABLE IV: Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between Substituted Phenols and 1,3-Dimethyluracil[a]

phenol derivative	K^{298K}, dm³ mol⁻¹	K^{323K}, dm³ mol⁻¹	$-\Delta H$, kJ mol⁻¹	$-\Delta S^{298K}$, J K⁻¹ mol⁻¹	$\Delta\nu_{OH}$,[b] cm⁻¹
3,4-dimethyl	8.3	4.5	21.1	53.1	191
4-methyl	8.9	4.7	21.4	53.5	194
phenol	10.4	5.4	22.0	54.0	210
4-fluoro	13.2	6.3	22.4	54.3	221
4-chloro	16.0	7.6	23.4	55.2	231
4-bromo	17.1	8.3	23.5	55.3	238
3-chloro	21.6	9.5	24.0	55.7	248
3-bromo	22.0	9.6	24.2	55.9	252
3,4-dichloro	27.5	12.5	25.3	56.8	268
3-nitro	35.5	15.0	25.9	57.4	273
3,5-dichloro	39.0	18.1	26.2	57.6	279
3,4,5-trichloro	49.8	22.7	27.2	58.5	295

[a] S = 1,2-DCE. [b] Broad band. Error on the maximum, ±10 cm⁻¹.

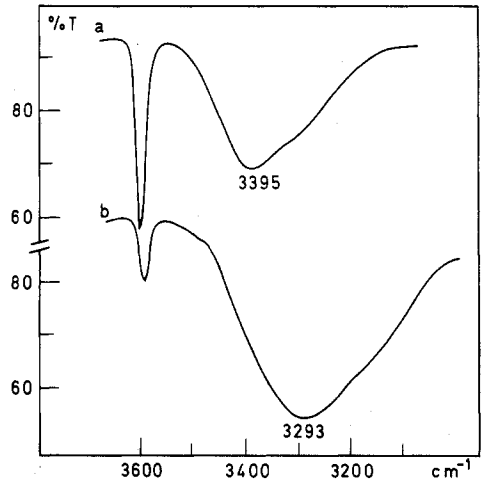

Figure 1. Infrared spectrum (3800–3000 cm⁻¹) of solutions of (a) 1,3-dimethyluracil (C = 0.01 M) and phenol (C = 0.005 M) and (b) 1,3-dimethyluracil (C = 0.01 M) and 3,4,5-trichlorophenol (C = 0.005 M). S = CCl_4.

2,4-Diethoxypyrimidone and 1,3-dimethyluracil are from Vega Biochemicals; 4-pyrimidone and 2-pyrimidone chlorohydrate are from Aldrich.

Results and Discussion

Thermodynamic Data and Interaction Site. Tables I–IV list the formation constants and the enthalpies and entropies of complex formation, along with the frequency shifts of the ν_{OH} stretching vibration for the complexes between several phenol derivatives and 3-methyl-4-pyrimidone, 1-methyl-2-pyrimidone, 1,4,4-trimethylcytosine, and 1,3-dimethyluracil. All the data are obtained in 1,2-DCE. One example of spectra in the ν_{OH} range

TABLE V: Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between Substituted Phenols and Pyrimidine[a]

phenol derivative	K^{298K}, dm³ mol⁻¹	K^{323K}, dm³ mol⁻¹	$-\Delta H$, kJ mol⁻¹	$-\Delta S^{298K}$, J K⁻¹ mol⁻¹	$\Delta\nu_{OH}$,[b] cm⁻¹
3,4-dimethyl	4.8	2.6	19.9	53.4	371
4-methoxy	5.1	2.8	20.2	53.8	373
phenol	6.3	3.4	20.9	54.5	379
4-fluoro	7.6	3.9	21.2	54.9	385
4-chloro	9.8	4.7	22.3	56.1	391
4-bromo	9.1	4.8	22.4	56.3	398
3-fluoro	11.4	5.3	22.7	56.6	405
3-bromo	12.7	5.9	23.1	56.8	406
3,4-dichloro	17.6	7.2	24.2	58.4	420
3-nitro	17.7	8.9	25.0	59.2	426
3,5-dichloro	21.4	9.6	25.2	59.5	428
3,4,5-trichloro	24.8	11.6	26.3	60.8	435

[a] S = 1,2-DCE. [b] Broad band. Error on the maximum, ±10 cm⁻¹.

TABLE VI: Thermodynamic Data and $\Delta\nu_{OH}$ Values for the Complexes between Substituted Phenols and 1,3-Dimethyluracil[a]

phenol derivative	K^{298K}, dm³ mol⁻¹	K^{323K}, dm³ mol⁻¹	$-\Delta H$, kJ mol⁻¹	$-\Delta S^{298K}$, J K⁻¹ mol⁻¹	$\Delta\nu_{OH}$,[b] cm⁻¹
3,4-dimethyl	33	15	22.7	47.2	208
4-methoxy	37	19	23.2	47.4	206
phenol	40	23	23.9	47.8	216
4-fluoro	58	29	24.3	48.0	231
4-chloro	94	36	25.5	48.5	243
4-bromo	92	37	25.6	48.6	250
3-fluoro	88	45	26.0	48.8	253
3-chloro	112	53	26.2	48.9	260
3-bromo	134	57	26.5	49.0	262
3,4-dichloro	196	70	27.7	49.7	276
3-nitro	241	93	28.5	50.1	284
3,5-dichloro	250	115	28.8	50.2	287
3,4,5-trichloro	363	156	30.0	50.9	300

[a] S = CCl_4. [b] Broad band. Error on the maximum, ±10 cm⁻¹.

is shown in Figure 1 relative to dimethyluracil complexes where it can be seen that the frequency shift and the broadness of the band increase with the acidity of the proton-donor molecule. For the complexes of 1,4,4-trimethylcytosine the $\Delta\nu_{OH}$ values could not be measured with accuracy owing to overlapping of the $\nu_{OH\cdots N}$ band with the ν_{CH} absorptions. For its complex with phenol, the band is observed at about 3145 cm⁻¹ ($\Delta\nu_{OH}$ = 405 cm⁻¹).

In order to compare the data of the present work with data for the diazine systems obtained in carbon tetrachloride solutions, the thermodynamic constants and the $\Delta\nu_{OH}$ values have also been measured for the pyrimidine complexes in 1,2-DCE and for the dimethyluracil complexes in carbon tetrachloride. The results are reported in Tables V and VI. The comparison between the results shows that increasing the solvent polarity has a marked influence on the formation constants; for the pyrimidine–phenol complex, the K^{298K} values are 17 and 6.3 M⁻¹ in CCl_4 and 1,2-DCE, respectively; the $-\Delta H$ values are less sensitive to environmental effects and are 22.7 and 20.9 kJ mol⁻¹ in these two solvents. The same remark also holds for the $\Delta\nu_{OH}$ values, which are respectively 385[1] and 379 cm⁻¹ in CCl_4 and in 1,2-DCE. These conclusions are also valuable for the dimethyluracil complexes; Tables IV and VI allow one to compare the experimental data in the two mentioned solvents. It should be mentioned however that the study of the solvent effect is not the main scope of this work but is necessary because most of the thermodynamic data obtained by infrared spectrometry are relative to CCl_4.[18]

All the results reported in Tables I–V show that the complexes are stronger when the acidity of the proton derivative increases. A least-mean-squares treatment of log K–pK_a (phenol) gives the

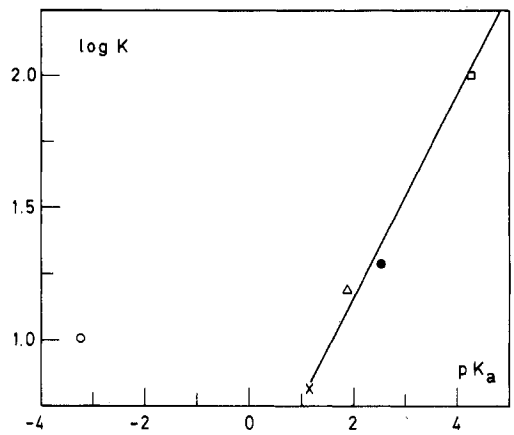

Figure 2. log K (for unsubstituted phenol) as a function of the pK_a of the base: (□) 1,4,4-trimethylcytosine; (●) 1-methyl-2-pyrimidone; (△) 3-methyl-4-pyrimidone; (×) pyrimidine; (○) 1,3-dimethyluracil.

following relations with correlation coefficients between 0.98 and 0.99:

3-methyl-4-pyrimidone

$$\log K^{298K} = 4.45 - 0.33pK_a$$

$$\log K^{323K} = 3.85 - 0.30pK_a \quad (1)$$

1-methyl-2-pyrimidone

$$\log K^{298K} = 5.63 - 0.44pK_a$$

$$\log K^{323K} = 4.79 - 0.39pK_a \quad (2)$$

1,4,4-trimethylcytosine

$$\log K^{298K} = 8.96 - 0.69pK_a$$

$$\log K^{323K} = 6.93 - 0.53pK_a \quad (3)$$

1,3-dimethyluracil

$$\log K^{298K} = 4.06 - 0.30pK_a$$

$$\log K^{323K} = 3.44 - 0.27pK_a \quad (4)$$

pyrimidine

$$\log K^{298K} = 3.63 - 0.28pK_a$$

$$\log K^{323K} = 3.01 - 0.25pK_a \quad (5)$$

As indicated by the results of Tables I–V (S = 1,2-DCE), the thermodynamic parameters (K, $-\Delta H$, $-\Delta S$) for a given phenol derivative are ordered according to

1,4,4-trimethylcytosine > 1-methyl-2-pyrimidone > 3-methyl-4-pyrimidone > 1,3-dimethyluracil > pyrimidine

pK_a = 4.20[13] pK_a = 2.50[19] pK_a = 1.84[20] pK_a = −3.25[21] pK_a = 1.23[22]

This order is the same as the one predicted from the pK_a in aqueous solutions, with the exception of dimethyluracil, which is characterized by much higher K and $-\Delta H$ values than those predicted from its pK_a; this appears clearly in Figure 2, where log K (for the complex of unsubstituted phenol) has been plotted against the pK_a of the base. This point will be discussed later. It must also be pointed out that, for pyrimidine, the $\Delta\nu_{OH}$ values are higher than those expected from the values of the enthalpies of complex formation. As a general matter of fact, as the strength

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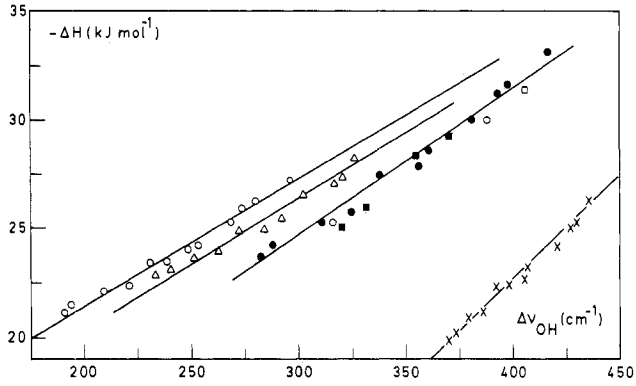

Figure 3. $-\Delta H$ (kJ mol^{-1}) as a function of $\Delta\nu_{OH}$ (cm^{-1}): (□) 1,4,4-trimethylcytosine; (●) 1-methyl-2-pyrimidone; (△) 3-methyl-4-pyrimidone; (○) 1,3-dimethyluracil; (■) dimethylacetamide; (×) pyrimidine.

of the hydrogen bond increases, the $\Delta\nu_{OH}$ values increase; as discussed in numerous works,[18] the slope and the intercept of a $-\Delta H$ vs. $\Delta\nu$ correlation for reference acids depend on the donor site among other factors. As can be seen from Figure 3, where $-\Delta H$ has been plotted against $\Delta\nu_{OH}$, the complexes of pyrimidine seem to belong to another family; for the same $-\Delta H$ value, for example 25 kJ mol^{-1}, $\Delta\nu_{OH}$ is markedly higher (by more than 100 cm^{-1}) for the pyrimidine than for the pyrimidone, uracil, and cytosine complexes. This suggests that the donor site, which is necessarily the N atom in pyrimidine, is the C=O function for the other bases. As shown by this figure also, the points relative to dimethylacetamide,[18] which undoubtedly forms C=O···HO bonds with phenol derivatives, are situated on the same straight line as 3-methyl-4-pyrimidone.

The following equations were obtained by a least-mean-squares treatment:

1-methyl-2-pyrimidone

$$-\Delta H \text{ (kJ mol}^{-1}) = 3.66 + 0.070\Delta\nu_{OH} \text{ (cm}^{-1}) \quad (r = 0.985)$$

3-methyl-4-pyrimidone

$$-\Delta H \text{ (kJ mol}^{-1}) = 9.61 + 055\Delta\nu_{OH} \text{ (cm}^{-1}) \ (r = 0.984)$$

1,3-dimethyluracil

$$-\Delta H \text{ (kJ mol}^{-1}) = 9.83 + 0.058\Delta\nu_{OH} \text{ (cm}^{-1}) \quad (r = 0.994)$$

pyrimidine

$$-\Delta H \text{ (kJ mol}^{-1}) = -13.78 + 0.091\Delta\nu_{OH} \text{ (cm}^{-1})$$
$$(r = 0.989)$$

As discussed in an earlier work,[23] for the same $-\Delta H$ value, the $\Delta\nu_{OH}$ value is higher for OH···N than for OH···O=C hydrogen bonds and this fact can be explained by a greater charge transfer in the OH···N bonds; this is in agreement with the theory of Allen,[24] who has shown that the charge transfer is ordered according to the extension of the free electron pair of the base, equal to 1.77 Å for a nitrogen atom and 1.58 Å for an oxygen atom.

The formation of hydrogen bonds at the carbonyl is also shown by the frequency shift of the $\nu_{C=O}$ band to lower frequencies; these are summarized in Table VII for the two pyrimidones and for 1,3-dimethyluracil. In free cytosine, two bands are observed between 1700 and 1600 cm^{-1}; the first one at 1672 cm^{-1} involves mainly a $\nu_{C=O}$ vibration and the second one at 1638 cm^{-1} a ring stretching vibration; owing to the overlapping between this last band and the shifted $\Delta\nu_{C=O}$ band of the complex, the $\Delta\nu_{C=O}$ values higher than 25 cm^{-1} were not measurable; for the complex between unsubstituted phenol, the $\Delta\nu_{C=O}$ value was 22 cm^{-1}.

Figure 4 clearly indicates that there is a linear relation between $-\Delta H$ and $\Delta\nu_{C=O}$; however, two straight lines are obtained, one

TABLE VII: $\Delta\nu_{C=O}$ Values for the Complexes between Phenol Derivatives and 3-Methyl-4-pyrimidone, 1-Methyl-2-pyrimidone, and 1,3-Dimethyluracil

	$\Delta\nu_{C=O}$,[a] cm^{-1}		
phenol derivative	3-methyl-4-pyrimidone[b]	1-methyl-2-pyrimidone[c]	1,3-dimethyluracil[d]
3,4-dimethyl	15	18	13
4-methyl	15	18	13
phenol	16	18	14
4-fluoro	16	19	15
4-chloro	16	20	15
4-bromo	16	21	15
3-fluoro	17	21	15
3-chloro	18	22	15
3-bromo	18	22	15
3,4-chloro	19	22	16
3-nitro	19	23	16
3,5-dichloro	19	23	16
3,4,5-trichloro	20	24	17

[a] Registered in extended scale. Error on the maxima, ±1 cm^{-1}. [b] S = 1,2-DCE; $\nu_{C=O}$ in the free molecule = 1687 cm^{-1}. [c] S = 1,2-DCE; $\nu_{C=O}$ in the free molecule = 1676 cm^{-1}. [d] S = CCl_4; $\nu_{C=O}$ in the free molecule = 1674 cm^{-1}.

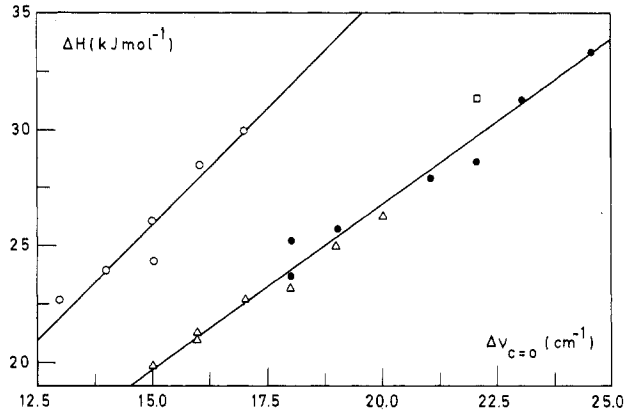

Figure 4. $-\Delta H$ (kJ mol^{-1}) as a function of $\Delta\nu_{C=O}$ (cm^{-1}): (○) 1,3-dimethyluracil; (●) 1-methyl-2-pyrimidone; (△) 3-methyl-4-pyrimidone; (□) 1,4,4-trimethylcytosine.

for the adducts of 1,3-dimethyluracil, the second one for the other complexes; as a matter of fact, we were able to show in a recent work on the complexes of different carbonyl bases $R_1R_2C=O$ that the $\Delta\nu_{C=O}$ values depend not only on the enthalpies of complex formation but also on the delocalization effects exerted by the substituents R_1 and R_2.[25] For the complexes studied in this work, the net effect of the delocalization of the free electron pair of the nitrogen atom over the carbonyl group(s) must be lower in 1,3-dimethyluracil, which contains two carbonyl functions; this is in agreement with calculated electronic density on the oxygen atom; although the total net charges strongly depend on the method used, the mean values reported in ref 11 are −0.47 and −0.40 e for the carbonyl oxygen of cytosine and uracil.

In uracil, two carbonyl bonds are available for hydrogen-bond formation; as shown by Figure 5, two bands are observed at 1717 and 1674 cm^{-1}; although the data on potential energy distribution are not always reliable, most of the recent works attribute these two absorptions to vibrations involving mainly a stretching motion of the $C=O_2$ and $C=O_4$ groups.[5,26-28] Figure 5 shows that for equimolecular concentrations only the second band is shifted by complex formation; the first band does not decrease in intensity. This strongly suggests that the H bonding takes place on the

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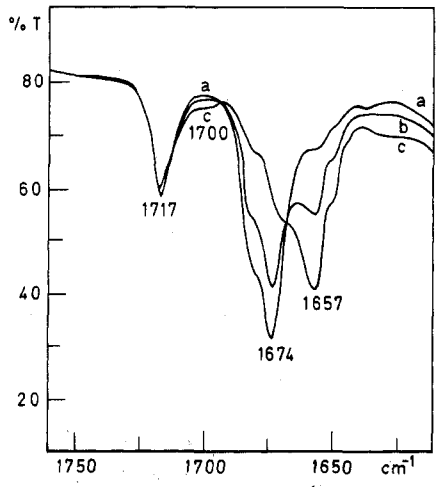

Figure 5. Infrared spectrum (1750–1650 cm^{-1}) of solutions of (a) 1,3-dimethyluracil (C = 0.010 M); (b) 1,3-dimethyluracil (C = 0.010 M) and phenol (C = 0.005 M); (c) 1,3-dimethyluracil (C = 0.010 M) and phenol (C = 0.02 M).

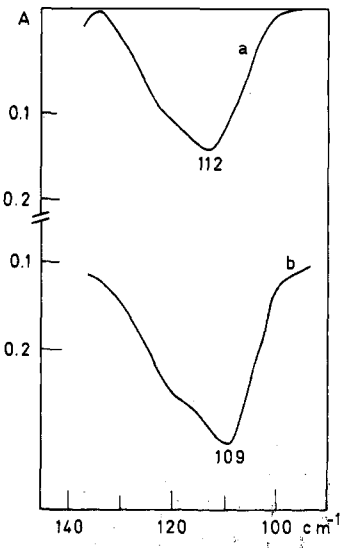

Figure 6. Far-infrared spectrum (140–100 cm^{-1}) of (a) the complex between 1,3-dimethyluracil and 3-nitrophenol and (b) the complex between 1,3-dimethyluracil and 3,4-dichlorophenol. Concentrations = 0.25 M. S = C_6H_6. The spectra have been obtained by substracting from the spectrum of the ternary solution the spectra of the individual components and of the solvent.

C=O_4 carbonyl function. The difference in H-bonding capability is also manifested in uracil crystals, where only the O_4 atom participates in the bonding.[29] This result is also in agreement with the lower ionization potential of the n(O_4) electrons (10.11 eV) as compared with that of the n(O_2) electrons (11.16 eV).[30] Ab initio SCF calculations of the ground-state water–uracil complexes[31] are not very conclusive because they lead to the existence of cyclic structures in which a water molecule bridges N_1–H and O_2, N_3–H and O_2, N_3–H and O_4. However, when complex formation on the carbonyls is considered, a slightly more stable struture is found when O_4 acts as an electron donor.

As shown by Figure 5, when the phenol derivative is in excess, the band at 1717 cm^{-1} decreases in intensity and a weak band at about 1700 cm^{-1} is observed; this absorption is probably ascribable to the formation of an H bond on the O_2=C function.

We are now able to discuss the results presented in Figure 2, where log K (for unsubstituted phenol) was plotted against the pK_a of the base. A linear relation is observed except for 1,3-dimethyluracil, whose formation constant is much higher than predicted from its pK_a in aqueous solution. As discussed before, for all the carbonyl bases studied in this work, the preferred H-bonding site is the carbonyl group. As shown by X-ray diffraction methods, 2-pyrimidone,[32] 4-pyrimidone,[33] and cytosine[34] are protonated at the nitrogen atom; the study of the infrared and Raman spectra leads to the same conclusions[35,36] and ab initio calculations have shown that, in cytosine, N_3 is the preferred site of protonation.[37] Thus, for the two pyrimidones and for 1,4,4-trimethylcytosine, the preferred site of H bonding is not the preferred site of protonation. The situation seems to be different for uracil: 1-methyluracil and other uracil residues protonate at the O_4 oxygen atom as shown by X-ray diffraction methods, the mean C=O_4 distance being 1.227 Å in the neutral uracil residues and 1.280 Å in the protonated residues. It can be concluded that in the uracil derivatives, the preferred site of H bonding is the preferred site of protonation, both sites being the O_4 oxygen atom. This must be at the origin of the strong deviation observed for 1,3-dimethyluracil in Figure 2; the bases which are protonated at the N atom are situated on the same straight line.

TABLE VIII: Experimental ν_σ Values and k_{OH} and k_σ Values Computed from the Lippincott-Schroeder Function for Complexes between Phenol Derivatives and 3-Methyl-4-pyrimidone and 1,3-Dimethyluracil[a]

	3-methyl-4-pyrimidone			1,3-dimethyluracil		
phenol derivative	ν_σ,[a] cm^{-1}	k_{OH}, N m^{-1}	k_σ, N m^{-1}	ν_σ,[a] cm^{-1}	k_{OH}, N m^{-1}	k_σ, N m^{-1}
3,4-dimethyl	126	641	9.97	110	652	7.94
4-methyl	129	639	10.09	111	651	8.12
phenol	134	628	11.94	111	645	9.06
4-fluoro	132	619	13.66	112	640	9.77
4-chloro	131	618	13.80	112	636	10.05
4-bromo	132	613	14.66	111	635	10.08
3-fluoro	133	611	15.11	112	631	11.34
3-chloro	130	610	15.42	111	629	11.70
3-bromo	132	608	15.73	112	628	11.94
3,4-dichloro	122	606	16.05	109	620	13.38
3-nitro	133	602	17.05	112	618	13.80
3,5-dichloro	119	601	17.21	112	615	14.37
3,4,5-trichloro	120	598	17.74	113	610	15.27

[a] S = C_6H_6. T^0 = 298 K. [b] Error on the absorption maximum = ±2 cm^{-1}.

Internal Vibrational Modes. As discussed in part 1, upon complexation the internal modes of pyrimidine, which are usually shifted to higher frequencies by a few wavenumbers, are mainly the vibrations of the ring. For the complexes studied in this work, the ring vibrations remain practically unchanged, showing that complex formation on an exocyclic atom has no influence on the ring vibrations of the base. The in-plane bending mode of the C=O group is shifted by 5–10 cm^{-1} to higher wavenumbers. For example, this mode is observed at 567 cm^{-1} in free 3-methyl-4-pyrimidone and at 575 cm^{-1} in its complex with phenol.

Intermolecular Stretching Vibration. The far-infrared spectra have been studied for the 3-methyl-4-pyrimidone and 1,3-dimethyluracil systems. Very few far-infrared results are available for OH···O=C bonds. Some spectra are reproduced in Figure 6. It must be pointed out that, owing to the weak intensity of the intermolecular stretching vibration, higher acid and base concentrations (about 0.25 M) were used. As shown by the figure, the ν_σ band presents an asymmetry to the high-frequency side and this is probably ascribable to complexes of higher stoichiometry

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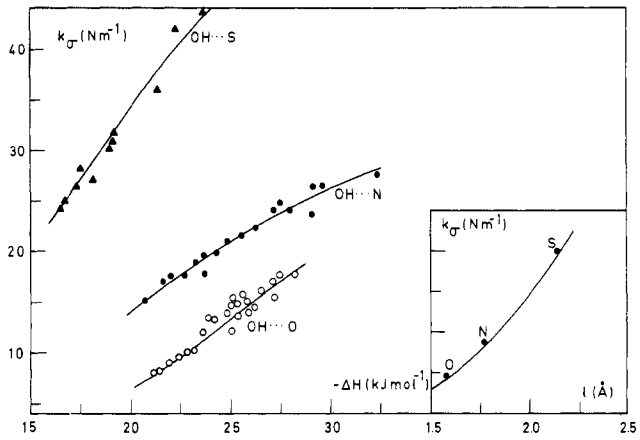

Figure 7. k_σ (N m^{-1}) as a function of $-\Delta H$ (kJ mol^{-1}) for OH···O, OH···N, and OH···S hydrogen bonds. Right quarter of the figure: k_σ (N m^{-1}) as a function of the lone-pair extent l (Å) of the base.

involving two or more phenol molecules. The ν_σ valles listed in Table VIII are very insensitive to the strength of the interaction and do not allow one to distinguish between the OH···O and OH··N bonds; indeed, for the complexes between pyrimidine and the same proton donors,[1] the experimental values varied only between 113 and 120 cm^{-1}.

The force constant k_σ of the intermolecular vibration and that of the ν_{OH} vibraiton, k_{OH}, have been computed by the Lippincott-Schroeder unidimensional function,[38,39] using for the dissociation energy of the OH bond a value of 447 kJ mol^{-1}; further, the OH···O distances have been estimated by the relation of Nakamoto et al.[40] The k_{OH} and k_σ values are listed in Table VIII. As can be seen from this table and from Figure 7, the k_σ values are related to the enthalpies of formation but more interesting is the comparison between other systems; in Figure 7, k_σ has been plotted against $-\Delta H$ for OH··N[1] and OH···S[41] H bonds. It clearly appears that the k_σ values are markedly higher for the OH···S bonds. The theory of Allen[24] predicts that the degree to which the lone pair of the base overlaps AH (in our case OH) is the principal factor governing k_σ. In order to compare this theory with the experimental data, the k_σ values—for a given $-\Delta H$ value—have been compared with the extension of the lone pair of the base. For a $-\Delta H$ value of 22 kJ mol^{-1}, the k_σ values are as follows: OH···O bonds, k_σ = 9 N m^{-1}; OH···N bonds, k_σ = 17 N m^{-1}; OH···S bonds, k_σ = 40 N m^{-1}. The lone-pair extensions of the O, N, and S atoms are respectively 1.58, 1.77, and 2.13 Å. The right quarter of Figure 7 indicates that k_σ (at constant $-\Delta H$) is very nicely related to the lone-pair extension.

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Registry No. I, 6104-45-6; II, 3739-81-9; III, 2228-27-5; IV, 874-14-6; V, 289-95-2; phenol, 108-95-2; 3,4,5-trichlorophenol, 609-19-8.

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Protonation of the Methyl Orange Derivative of Aspartate Adsorbed on Colloidal Silver: A Surface-Enhanced Resonance Raman Scattering and Fluorescence Emission Study

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Absorption, resonance Raman, and fluorescence emission spectra of the protonated form of the azo dye, dabsyl aspartate, DABS-ASP, were measured both in aqueous solution and on colloidal silver particles. Spectra taken as a function of pH were used to estimate pK_a values of the conjugate acid, HDABS-ASP, in solution and on colloidal silver. Surface enhancement of resonance Raman scattering and fluorescence emission intensity in HDABS-ASP ranged from 20 to 300 and 1 to 20, respectively, for total silver concentrations of 0.02-0.30 g/L. Surface-enhanced resonance Raman scattering (SERRS) excitation profiles peaked at 540 nm for HDABS-ASP-silver hydrosols at pH ~4.6 and matched the absorption peak position at the same pH. Both the red-shifted absorption maximum and the higher enhancements under more acidic conditions were correlated with more extensive aggregation in the silver hydrosols. Lower SERRS (10^2-10^3) and fluorescence emission (1-10) enhancements for chromophoric adsorbates on colloidal silver than SERS enhancements (10^5-10^6) for nonchromophoric adsorbates were attributed to shorter excited-state lifetimes for DABS-ASP and HDABS-ASP near a lossy silver surface and possibly longer surface-to-chromophore distances.

Introduction

The detection of Raman band enhancements up to 10^6-fold for molecules adsorbed on silver and other metal surfaces has precipitated a flurry of activity in the area of surface-enhanced Raman scattering[1-6] (SERS). Other surface-enhanced phenomena such as surface-enhanced resonance Raman scattering[7-15] (SERRS) and surface-enhanced luminescence emission[16-20] from chromo-

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