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Infrared study of five- and six-membered type cyclic imides

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Abstract

Compounds such as caffeine, isocaffeine, 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione, 1,3,5-trimethyluracil, 1,3,6-trimethyluracil, and hydantoins exhibit $\nu_{in-phase}(C=O)_2$, $\nu_{ip}(C=O)_2$, and $\nu_{out-of-phase}(C=O)_2$, $\nu_{op}(C=O)_2$, modes. The $\nu_{ip}(C=O)_2$ mode always occurs at higher frequency than the $\nu_{op}(C=O)_2$ mode in these five- and six-membered type cyclic imides. The frequency separation between $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ changes with change in physical state, and this frequency separation is larger in the solid state than it is in the vapor state. Moreover, the frequency separation between $\nu_{ip}(C=O)_2$ increases as the mole% CHCl₃/CCl₄ increases. The study also shows that in some cases $\nu_{op}(C=O)_2$ is in Fermi resonance with a combination tone. In all cases, the $\nu_{op}(C=O)_2$ mode decreases more in frequency than the $\nu_{ip}(C=O)_2$ modes for the five-membered type cyclic imides occur at higher frequency than the corresponding $\nu(C=O)_2$ modes for the six-membered type cyclic imides. These studies have also shown that different solute-solvent complexes are formed as the mole% CHCl₃/CCl₄ increases.

Keywords: Carbonyl groups; Imides, cyclic; Infrared spectrometry

1. Introduction

Group frequency data for compounds in a variety of physical phases can be found in reference books [1-3]. We have used vibrational spectroscopy to investigate solute-solvent interactions for a variety of chemical compounds [4-28], and these studies have also aided us in the elucidation of the structures of the solutes.

Six-membered cyclic imides type compounds such as caffeine, occur in nature. In addition, six-membered cyclic imides are useful for control of certain diseases; 5-fluorouracil is an example. Since these compounds have unique biological activity, we have undertaken a vibrational spectroscopic study of several compounds containing the basic six-membered cyclic imide structure.

The empirical structures of caffeine (I) and 5-fluorouracil (II) are given in Scheme 1. Another name for caffeine is 1,3,7-trimethyl-2,6-dioxopurine, and another name for 5-fluorouracil is 2,4-dioxo-5-fluoropyrimidine.

Hydantoins are five-membered rings which also contain an imide type structure. The structure of hydantoin (III) is given in Scheme 2. Hydantoin (III) is formed from a naturally occurring amino acid. It is of interest to compare infrared (IR) spectral data for hydantoins with those for caffeine, isocaffeine, 1,3-

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dimethyl-2,4-(1H,3H)-quinazolinedione, and uracils, since both five- and six-membered rings contain the amino imide type structure (IV) (see Scheme 3).

The present study of caffeine, isocaffeine, 1,3,5trimethyluracil, 1,3,6-trimethyluracil, and 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione in CCl₄ and/or CHCl₃ solutions is an extension of our interest in solute-solvent studies. In addition, correlations are presented for uracils and hydantoins whose IR data have been recorded in the solid phase.

2. Experimental

Infrared data were recorded using a Nicolet 710 FT-IR system. Stock solutions (0.125%) of 1,3,7-trimethyl-2,6-dioxopurine, commonly called caffeine, in CCl₄ solution and in CHCl₃ solution were prepared. One-millilitre aliquots of the 0.25% CCl₄ stock solution was put into glass bottles, and 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, or 1 ml of the 0.125% CHCl₃ stock solution was added to one of the bottles containing 1 ml of the 0.125% CCl₄ stock solution. One-millilitre aliquots of the 0.125% CHCl₃ stock solution were placed in glass bottles, and 0.1, 0.2, 0.3,





0.4, 0.5, 0.6, 0.7, 0.8, or 0.9 ml of the 0.125% CCl_{4} stock solution was added to one of the bottles containing 1 ml of the 0.125% CHCl₃ stock solution. The bottles were capped and shaken to insure uniform CHCl₃/CCl₄ solutions of caffeine. Spectral resolution for the recorded IR data is 2 cm^{-1} . The band width of ν (C=O) and other bands for compounds in the liquid, solution, or solid states are always a few cm^{-1} . This is because each molecule of the compound is in a slightly different environment relative to its neighboring molecules. Thus, each of these molecules absorb at a slightly different frequency, and this causes the relatively wide band. Therefore, in the condensed phases the bands are resolved using an instrument resolution significantly less than the IR bands being recorded, say 2 cm^{-1} .

Samples of 1,3,5-trimethyluracil and 1,3,6-trimethyluracil were prepared and their IR spectra recorded in the same manner as discussed above. The IR frequencies reported for the in-phase $(C=O)_2$ stretching vibration, $\nu_{ip}(C=O)_2$, and the out of phase $(C=O)_2$ stretching vibration, $\nu_{op}(C=O)_2$, for the compounds studied in solution are determined and printed out by the data system's peak-picking algorithm.

IR data presented in Tables 4 and 5 are read visually from IR spectra in the Dow standard reference files or from Sadtler standard reference spectra (Bio-Rad Sadtler Research Division, Philadelphia, PA). The frequency data as visually determined from the recorded spectra are approximated (estimated ± 2 cm⁻¹).

3. Results and discussion

3.1. Solution phase data

IR data for caffeine in 0.125% CCl₄ and/or CHCl₃ solutions are given in Table 1.

3.2. Caffeine

Caffeine (I) has two carbonyl groups joined to the 1-N atom. In a case such as this one would expect that the two C=O groups would couple into an inphase $(C=O)_2$ stretching vibration, v_{ip} - $(C=O)_2$, and an out-of-phase $(C=O)_2$ stretching vibration, $\nu_{op}(C=O)_2$. In the vibrational cycle, the $v_{\rm cm}$ (C=O)₂ mode would be expected to have a larger dipole moment change during its cycle than the dipole moment change during a cycle of $\nu_{in}(C=O)_2$. Therefore, in the IR spectrum the $v_{op}(C=O)_2$ mode is expected to have a stronger absorption band than $v_{in}(C=O)_2$. In addition, the $v_{on}(C=O)_2$ mode would be expected to occur at a lower frequency than the $v_{in}(C=0)_2$ mode for the following reasons. During half of a cycle of $v_{00}(C=O)_2$ only one of the carbonyl carbon atoms is compressed into the ring while during half of a cycle of $\nu_{in}(C=O)_2$ both carbonyl carbon atoms are compressed into the ring. Thus, less energy is required to compress one carbonyl carbon atom into the ring during a cycle of $\nu_{on}(C=O)_2$ than



is required to compress both carbonyl carbon atoms into the ring during a cycle of $\nu_{ip}(C=O)_2$. In addition, the $\nu_{op}(C=O)_2$ mode is stabilized alternatively between the resonance forms shown in Scheme 4.

This type of alternate resonance does not occur for the $\nu_{ip}(C=O)_2$ mode [29]. Thus, while compressing favors higher energy for the coupled $\nu_{ip}(C=O)_2$ mode in imides, the valence bond electron delocalization through the central nitrogen atom favors lower energy for the coupled $\nu_{op}(C=O)_2$ mode. We suggest that both of these factors contribute to the actual normal vibrational frequencies for $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ in five- and six-membered type cyclic imides.

IR bands for caffeine are observed at 1710.63 and 1667.54 cm^{-1} in CCl₄ solution and at 1707.85 and

Table 1

Infrared data for caffeine in 0.125% carbon tetrachloride and/or chloroform solutions (0.203 mm KBr cell)

Mole% CHCl ₃ /CCl ₄	$\frac{\nu_{ip}(C=O)_2}{(cm^{-1})}$	$\nu_{op}(C=0)_2$ (cm ⁻¹)	$\nu_{ip}(C=O)_2$ minus $\nu_{op}(C=O)_2$ (cm ⁻¹)	$A[\nu_{\rm ip}(\rm C=O)_2]$	$A[\nu_{ip}(C=O)_2]$	$\frac{A[\nu_{ip}(C=O)_2]}{A[\nu_{op}(C=O)_2]}$
0.00	1710 (2	1667.64	(cm)	0.102	0.000	0.(5
0.00	1/10.03	1007.54	43.09	0.193	0.298	0.65
10.74	1/10.17	1005.49	44.68	0.185	0.268	0.69
19.40	1709.65	1664.01	45.64	0.177	0.256	0.69
26.53	1709.22	1663.11	46.11	0.171	0.249	0.69
32.50	1708.95	1662.68	46.27	0.172	0.251	0.69
37.57	1708.68	1662.24	46.44	0.171	0.244	0.70
41.93	1708.58	1662.04	46.54	0.170	0.240	0.71
45.73	1708.46	1661.81	46.65	0.172	0.237	0.73
49.06	1708.38	1661.66	46.72	0.172	0.237	0.73
52.00	1708.29	1661.50	46.79	0.174	0.234	0.74
54.62	1708.25	1661.35	46.90	0.173	0.231	0.75
57.22	1708.17	1661.10	47.07	0.176	0.230	0.77
60.07	1708.13	1660.95	47.18	0.177	0.229	0.77
63.28	1708.07	1660.67	47.40	0.180	0.225	0.80
66.73	1708.03	1660.48	47.55	0.182	0.225	0.81
70.65	1708.00	1660.30	47.70	0.184	0.224	0.82
75.06	1707.96	1660.02	47.94	0.185	0.223	0.83
80.06	1707.92	1659.73	48.19	0.191	0.220	0.87
85.05	1707.90	1659.38	48.52	0.195	0.216	0.90
92.33	1707.87	1658.79	49.08	0.202	0.215	0.94
100.00	1707.85	1658.36	49.49	0.204	0.210	0.97
Δ (cm ⁻¹)	- 2.78	- 9.18	6.40			



1658.36 cm⁻¹ in CHCl₃ solution. Based on the above discussion the IR band in the region 1707.85-1710.63 cm⁻¹ is assigned as $\nu_{ip}(C=O)_2$ and the IR band in the region 1658.36-1667.54 cm⁻¹ is assigned as $v_{op}(C=O)_2$. We note that $v_{ip}(C=O)_2$ decreases by 2.78 cm⁻¹ while $\nu_{op}(C=O)_2^{\nu}$ decreases by 9.18 cm⁻¹ in going from CCl₄ solution to CHCl₃. These data also support our assignments of ν_{ip} - $(C=O)_2$ and $\nu_{op}(C=O)_2$, since $\nu_{op}(C=O)_2$ for phthalic anhydrides and for phthalimides always decreases more in frequency than $v_{in}(C=O)_2$ in going from CCl₄ solution to CHCl₃ solution [1]. Similarly, the $v_{asym}(NO_2)$ and $v_{asym}(SO_2)$ modes are also more affected in going from CCl₄ solution to CHCl₃ solution than are the corresponding $\nu_{sym}(NO_2)$ and $v_{sym}(SO_2)$ modes [1].

The Raman spectrum for caffeine in the solid state shows bands at 1699 and 1656 cm⁻¹ [2]. The 1699 cm⁻¹ Raman band is approximately twice as strong as the 1656 cm⁻¹ Raman band, and these intensity data support assignment of the 1699 cm⁻¹ Raman band to the $\nu_{ip}(C=O)_2$ mode and the 1656 cm⁻¹ Raman band to the $\nu_{op}(C=O)_2$ mode for caffeine.

The compound 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione (V) has the empirical structure as shown in Scheme 5.

In the solid phase the medium intensity IR band at 1701 cm⁻¹ is assigned to $\nu_{in}(C=O)_2$ and the strong band at 1659 cm⁻¹ is assigned to $v_{op}(C=O)_2$ for 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione. In the vapor phase this same compound exhibits $\nu_{in}(C=O)_2$ at 1727 cm⁻¹ and ν_{op} (C=O)₂ at 1694 cm⁻¹. Thus $v_{ip}(C=O)_2$ occurs at a ca. 26 cm⁻¹ higher frequency and $v_{op}(C=O)_2$ occurs at a ca. 35 cm⁻¹ higher frequency in going from the solid phase to the vapor phase. As discussed above comparable shifts in $v_{in}(C=O)_2$ and $v_{on}(C=O)_2$ were observed for caffeine in going from the solid phase to the vapor phase. The $\nu_{in}(C=0)_2$ mode for 1,3-dimethyl-2,4-(1H,3H) quinazolinedione occurs at a ca. 6 cm^{-1} lower frequency and the $v_{op}(C=O)_2$ mode occurs at ca. 5 cm^{-1} lower frequency than the comparable modes for caffeine when both samples are in the vapor phase



Fig. 1. Plot of $\nu_{ip}(C=0)_2$ for caffeine vs. mole% CHCl₃/CCl₄.



Fig. 2. Plot of ν_{on} (C=O)₂ for caffeine vs. mole% CHCl₃/CCl₄.

where intermolecular hydrogen bonding between N-H:O=C does not play a role. We attribute the shift to lower frequency to the larger resonance contribution of the benzo group to the C=O group as compared to the five-membered ring present in caffeine.

Fig. 1 is a plot of $\nu_{ip}(C=O)_2$ for caffeine vs. mole% CHCl₃/CCl₄, and this plot shows that $\nu_{ip}(C=O)_2$ decreases in frequency as the mole% CHCl₃/CCl₄ decreases.

Fig. 2 is a plot of $\nu_{op}(C=O)_2$ for caffeine vs. mole% CHCl₃/CCl₄, and this plot shows a break at ca. 23 mole% CHCl₃/CCl₄. This break indicates that the type of intermolecularly hydrogen bonded com-

 $(CCl_4)_n + (Cl_3CH)_m$

plexes formed between caffeine and the solvent system changes at ca. 23 mole% $CHCl_3/CCl_4$. The complexes presented below help to explain the frequency behavior of $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ with change in the mole% $CHCl_3/CCl_4$.

The 2-carbonyl group for caffeine is expected to be more basic than the 6-carbonyl group, since the 2-carbonyl group is joined to two N-CH₃ groups while the 6-carbonyl group is joined to one N-CH₃ group and to an sp^2 carbon atom. A hydrogen bonded complex between the Cl₃CH proton and the free pair of electrons on the oxygen atom of the 2-carbonyl group of caffeine would then be expected to be



Scheme 6.



Fig. 3. Plot of $\nu_{op}(C=O)_2$ vs. $\nu_{ip}(C=O)_2$ for caffeine at 0.125% concentration in CCl₄ and/or CHCl₃ solution in the solvent mole% range 0-100.

formed before forming a complex with the free pair of electrons on the oxygen atom of the 6-carbonyl group. Therefore, at concentrations below ca. 23 mole% CHCl₃/CCl₄ a complex such as VI is possible while at higher mole% $CHCl_3/CCl_4$ a complex such as VII is possible (see Scheme 6). However, additional intermolecular hydrogen bond complexing between a CCl₃H proton and sites on the basic nitrogen atoms of the five-membered ring are also most likely being formed as the mole% $CHCl_3/CCl_4$ is increased. The continual decrease in frequency of $v_{op}(C=O)_2$ as the mole% CHCl₃/CCl₄ increases depends most likely upon the number of Cl₃CH molecules in the hydrogen bonded complex [viz. (Cl₃CH:ClCl₂CH)_n:ClCl₂CH:O=C]. The larger the number n in the hydrogen bonded complex the lower the $\nu_{op}(C=O)_2$ frequency. This same statement also applies to the $\nu_{in}(C=O)_2$ mode. In the case of acetone [7], the shift in the ν (C=O) mode frequency with change in the mole% $CHCl_3/CCl_4$ is attributed to intermolecular hydrogen bonding of the CHCl₃ proton and the carbonyl group (CCl₃H · · · O=C), and also to the reaction field of the solvent. The reaction field of the solvent is defined by the following equation [30]:

$$|R| = (\epsilon - 1)/(2\epsilon + n^2)$$

where ϵ is the dielectric constant and *n* is the refractive index of the solvent system.

The mole% CHCl₃/CCl₄ values plotted vs. the calculated |R| values for the corresponding CHCl₃/CCl₄ solutions correlate in a linear manner [7], and we suggest the reaction field also contributes to the $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ shifts for the compounds included in this study.

Fig. 3 shows a plot of $\nu_{op}(C=O)_2$ vs. $\nu_{ip}(C=O)_2$ for caffeine. The plot shows that as $\nu_{op}(C=O)_2$ decreases in frequency, $\nu_{ip}(C=O)_2$ decreases also in frequency, but not in a linear manner.

Figs. 4 and 5 show plots of $\nu_{ip}(C=O)_2$ vs. the IR absorbance ratio $A[\nu_{ip}(C=O)_2]/A[\nu_{op}(C=O)_2]$ and $\nu_{op}(C=O)_2$ vs. the IR absorbance ratio $A[\nu_{ip}(C=O)_2]/A[\nu_{op}(C=O)_2]$ for caffeine, respectively. These plots show that as the $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ modes decrease in frequency the band intensity ratio $A[\nu_{ip}(C=O)_2]/A[\nu_{op}(C=O)_2]$ increases. Thus, the dipole moment change for ν_{ip} - $(C=O)_2$ hydrogen bonded complexes increases while the dipole moment change for $\nu_{op}(C=O)_2$ hydrogen bonded complexes decrease as the mole% CHCl₃/ CCl₄ increases. Fig. 5 also suggests the formation of two different types of complexes as was suggested from the study of Fig. 2.

Fig. 6 shows a plot of the frequency difference

between $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ for caffeine vs. mole% CHCl₃/CCl₄. This plot clearly shows that the frequency separation between these two $\nu(C=O)_2$ modes increases as the mole% CHCl₃/CCl₄ increases. This plot suggests that a third complex is formed at mole% CHCl₃/CCl₄ concentrations above ca. 52%.

3.3. Isocaffeine

Table 2 lists IR data for isocaffeine in CHCl₃/ CCl_4 solutions (isocaffeine is insoluble in CCl_4). The $v_{in}(C=O)_2$ mode for isocaffeine is assigned at 1711.33 cm^{-1} and $\nu_{op}(C=O)_2$ is assigned at 1663.95 cm⁻¹ in CHCl₃ solution. In going from 10.74 mole% $CHCl_3/CCl_4$ to 100 mole% $CHCl_3/CCl_4$, the $v_{on}(C=O)_2$ mode decreases by 9.23 cm⁻¹ while the v_{in} (C=O)₂ mode decreases by 5.32 cm⁻¹. Figs. 7 and 8 show plots of $\nu_{in}(C=O)_2$ vs. mole% CHCl₃/ CCl_4 and $\nu_{on}(C=O)_2$ vs. mole% $CHCl_3/CCl_4$, respectively. The plots in Figs. 7 and 8 show a break near 52 mole% CHCl₃/CCl₄ which suggests that there is a distinct change in the solute-solvent complex at this break point in each of the plots. Fig. 8 also shows a break point near 20 mole% CHCl₃/CCl₄ which suggests a distinct change in the solute-solvent complex not readily apparent in Fig. 7.

Fig. 9 shows a plot of $\nu_{op}(C=O)_2$ vs. $\nu_{ip}(C=O)_2$ for isocaffeine in CHCl₃/CCl₄ solutions, and the plot is linear between 19.40 and 100 mole% CHCl₃/CCl₄.

3.4. 1,3,5-Trimethyluracil

Table 3 lists IR data for 1,3,5-trimethyluracil (1,3,5-TMU) in 0.125% CHCl₃ and/or CCl₄ solutions. Three strong IR bands are observed in the region expected for the two carbonyl stretching bands for 1,3,5-TMU. These bands occur at 1706.62, 1670.92, and 1653.53 cm⁻¹ in CCl₄ solution and at 1699.99, 1668.64, and 1640.44 cm⁻¹ in CHCl₃ solution. In CCl_4 solution the band intensities are 0.128, 0.230, and 0.176 and in CHCl₃ solution these intensities are 0.124, 0.166, and 0.255 for the three bands listed in decreasing frequency, respectively. The highest frequency band in this set of data we assign to the $\nu_{in}(C=O)_2$ mode for 1,3,5-TMU. This assignment is based upon both its frequency and IR band intensity. Assignment of $\nu_{on}(C=O)_2$ is not straight forward, and will be discussed later.

Fig. 10 shows plots of the IR bands for 1,3,5-TMU occurring in the regions $1640.44-1653.53 \text{ cm}^{-1}$ and $1668.64-1670.92 \text{ cm}^{-1}$ vs. mole% CHCl₃/CCl₄. Both bands decrease in frequency as the mole% CHCl₃/CCl₄ increases. An interesting feature of the







Fig. 5. Plot of $\nu_{op}(C=O)_2$ vs. $A[\nu_{ip}(C=O)_2]/A[\nu_{op}(C=O)_2]$ for caffeine at 0.125% concentration in CCl₄ and/or CHCl₃ solution in the solvent mole% range 0-100.

absorbance data is that the IR band in the region $1669.82-1670.92 \text{ cm}^{-1}$ has a higher intensity than the band in the region $1646.08-1653.53 \text{ cm}^{-1}$. These bands are observed in $\text{CHCl}_3/\text{CCl}_4$ solutions in the 0-32.5 mole% range. In the $\text{CHCl}_3/\text{CCl}_4$ mole% range 37.57-100, the IR band in the region

1640.44–1645.63 cm⁻¹ has a higher intensity than the IR band in the region 1668.64–1669.74 cm⁻¹. These data indicate that these two bands are in Fermi resonance (FR). We have calculated the unperturbed $\nu_{op}(C=O)_2$ and the unperturbed combination tone (CT) by the method of Langseth and Lord [31,32].



Fig. 6. Plot of the frequency difference between $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ for caffeine at 0.125% solution in CCl₄ and/or CHCl₃ solutions vs. mole% CHCl₃/CCl₄.

Table 2 Infrared data for isocaffeine in $CHCl_3/CCl_4$ solutions (saturated at less than 0.06% in a 1.00 mm KBr cell)

Mole% CHCl ₃ /CCl ₄	$\nu_{ip}(C=O)_2$	$\nu_{op}(C=0)_2$ (cm ⁻¹)	$A[\nu_{ip}(C=O)_2]$ (cm ⁻¹)	$A[\nu_{\rm op}({\rm C=O})_2]$	$A[\nu_{ip}(C=0)_2]/A[\nu_{op}(C=0)_2]$	$ \nu_{ip}(C=O)_2 \text{ minus} $ $ \nu_{op}(C=O)_2 $ (cm^{-1})
0.00	_		_		-	_
10.74	1716.65	1673.18	-	-	-	43.74
19.40	1716.30	1668.96	0.016	0.019	0.84	47.34
26.53	1715.52	1668.21	0.025	0.034	0.74	47.31
32.50	1714.85	1667.46	0.036	0.053	0.68	47.39
37.57	1714.57	1667.14	0.041	0.075	0.55	47.43
41.93	1714.35	1666.80	0.061	0.093	0.66	47.55
45.73	1713.87	1666.38	0.071	0.109	0.65	47.46
49.06	1713.95	1666.41	0.070	0.096	0.73	47.54
52.00	1713.69	1666.28	0.086	0.134	0.64	47.41
54.62	1713.20	1665.88	0.140	0.220	0.64	47.32
57.22	1712.84	1665.54	0.225	0.355	0.63	47.30
60.07	1712.76	1665.43	0.316	0.505	0.63	47.33
63.28	1712.65	1665.31	0.281	0.435	0.65	47.34
66.73	1712.41	1665.00	0.255	0.383	0.67	47.41
70.65	1712.45	1664.94	0.317	0.495	0.64	47.51
75.06	1712.18	1664.77	0.355	0.543	0.65	47.41
80.06	1712.13	1664.71	0.336	0.521	0.64	47.42
85.05	1711.84	1664.42	0.324	0.500	0.65	47.39
92.33	1711.55	1664.16	0.339	0.522	0.65	47.38
100.00	1711.33	1663.95	0.317	0.487	0.65	47.38
Δ (cm ⁻¹)	-5.32	-9.23				

Fig. 10 also shows the plots of unperturbed ν_{op} -(C=O)₂ and unperturbed CT vs. mole% CHCl₃/CCl₄. These plots show that unperturbed ν_{op} (C=O)₂

occurs at higher frequency than unperturbed CT in the range 0-32.5 mole% CHCl₃/CCl₄, and in the 37.57-100 mole% CHCl₃/CCl₄ range unperturbed



Fig. 7. Plot of $\nu_{ip}(C=0)_2$ for isocaffeine vs. mole% CHCl₃/CCl₄.



Fig. 8. Plot of $\nu_{op}(C=O)_2$ for isocaffeine vs. mole% CHCl₃/CCl₄.

 $\nu_{op}(C=O)_2$ occurs at lower frequency than unperturbed CT.

Fig. 11 shows a plot of $\nu_{ip}(C=O)_2$ for 1,3,5-TMU vs. mole% CHCl₃/CCl₄. This plot shows that the $\nu_{in}(C=O)_2$ mode shifts to lower frequency as the

mole% CHCl₃/CCl₄ is increased. The unperturbed $\nu_{op}(C=O)_2$ mode decreases by 10.97 cm⁻¹ in going from CCl₄ solution to CHCl₃ solution while the corresponding decrease in frequency for $\nu_{ip}(C=O)_2$ is 6.63 cm⁻¹. The fact that unperturbed $\nu_{op}(C=O)_2$ de-



Fig. 9. Plot of $\nu_{00}(C=O)_2$ vs. $\nu_{10}(C=O)_2$ for isocaffeine in CHCl₃ and/or CHCl₃ solution in the solvent mole% range 0-100.



Fig. 10. Plots for $\nu_{op}(C=O)_2$ and a combination tone (CT) in Fermi resonance and the calculated unperturbed $\nu_{op}(C=O)_2$ and CT frequencies for 1,3,5-trimethyluracil vs. mole% CHCl₃/CCl₄.

creases more in frequency than $\nu_{ip}(C=O)_2$ in going from 0 to 100 mole% CHCl₃/CCl₄ adds support to the assignment of unperturbed $\nu_{op}(C=O)_2$.

Comparison of the frequency separation between $\nu_{ip}(C=O)_2$ and unperturbed $\nu_{op}(C=O)_2$ of 43.24 cm⁻¹ at 0 mole% CHCl₃/CCl₄ and 47.58 cm⁻¹ at

100 mole% CHCl₃/CCl₄ for 1,3,5-TMU vs. the comparable frequency separation of 43.09 cm⁻¹ at 0 mole% CHCl₃/CCl₄ and 49.49 cm⁻¹ at 100 mole% CHCl₃/CCl₄ for caffeine also adds support to the assignment of unperturbed ν_{op} (C=O)₂ for 1,3,5-TMU.



Fig. 11. Plot of $\nu_{ip}(C=0)_2$ for 1,3,5-trimethyluracil vs. mole% CHCl₃/CCl₄.

Table 3												
Infrared data for	1,3,5-trimeth	yluracil in 0.1	125% carbon	tetrachloride	and/or ch	nloroform s	colutions (0.203	mm KBr cell)				
Mole%	(1)	(2)	(3)	(4)	(5)	(9)	(1)	(8)	(6)	(10)	(11)	(12)
CHCl ₃ /CCl ₄	vip-	In FR	In FR	A∫ ν _{ip} -	A(2)	A(3)	Unperturbed	Unperturbed	Ξ	Ξ	Ξ	Ê (E)
	$(C=0)_{2}$			$(C=0)_{2}$			$\nu_{op}(C=0)_2$	5	sminus	minus	minus	minus
		•							6	5	(3)	(8)
		(cm ⁻¹)	(cm ⁻¹)				(cm ⁻¹)	(cm ⁻¹)	(cm^{-1})	(cm ⁻¹)	(cm ⁻¹)	(cm^{-1})
00.00	1706.62	1653.53	1670.92	0.128	0.176	0.230	1663.38	1661.06	43.24	53.09	35.70	45.55
10.74	1705.65	1650.59	1670.31	0.116	0.164	0.206	1661.56	1659.33	44.08	55.06	35.34	46.32
19.40	1704.61	1648.30	1670.08	0.110	0.166	0.196	1660.09	1658.28	44.52	56.31	34.53	46.32
26.53	1703.35	1646.66	1669.91	0.115	0.183	0.195	1658.65	1657.91	44.70	56.69	33.44	45.43
32.50	1703.01	1646.08	1669.82	0.113	0.183	0.185	1658.01	1657.88	45.00	56.93	33.19	45.12
37.57	1702.71	1645.63	1669.74	0.116	0.188	0.186	1657.62	1657.74	45.09	57.08	32.97	44.96
41.93	1702.42	1645.26	1669.65	0.115	0.189	0.179	1657.12	1657.78	45.30	57.16	32.77	44.63
45.73	1701.98	1644.77	1669.54	0.123	0.201	0.183	1656.57	1657.73	45.41	57.21	32.44	44.24
49.06	1701.97	1644.77	1669.53	0.118	0.198	0.178	1656.49	1657.81	45.48	57.20	32.44	44.16
52.00	1701.82	1644.59	1669.48	0.131	0.217	0.194	1656.33	1657.73	45.49	57.23	32.34	44.09
54.62	1701.64	1644.35	1669.42	0.117	0.195	0.172	1656.09	1657.67	45.54	57.29	32.22	43.97
57.22	1701.47	1644.07	1669.37	0.120	0.198	0.172	1655.83	1657.60	45.64	57.40	32.10	43.86
60.07	1701.39	1643.89	1669.33	0.121	0.203	0.175	1655.66	1657.55	45.73	57.50	32.06	43.84
63.28	1701.33	1643.77	1669.30	0.121	0.202	0.174	1655.58	1657.48	45.75	57.56	32.03	43.84
66.73	1701.14	1643.35	1669.23	0.125	0.210	0.178	1655.22	1657.35	45.92	57.79	31.91	43.78
70.65	1700.99	1643.06	1669.15	0.127	0.216	0.179	1654.88	1657.32	46.11	57.93	31.84	43.66
75.06	1700.86	1642.73	1669.07	0.127	0.215	0.176	1654.58	1657.21	46.28	58.13	31.79	43.65
80.06	1700.74	1642.40	1669.01	0.122	0.209	0.169	1654.29	1657.11	46.45	58.34	31.73	46.63
85.05	1700.55	1641.80	1668.89	0.132	0.230	0.181	1653.73	1656.95	46.82	58.75	31.66	43.59
92.33	1700.35	1641.27	1668.80	0.193	0.345	0.267	1653.28	1656.78	47.07	59.08	31.55	43.56
100.00	1699.99	1640.44	1668.64	0.124	0.225	0.166	1652.41	1656.66	47.58	59.55	31.35	43.32
Δ (cm ⁻¹)	6.63	- 13.09	- 2.28				-10.97	- 4.40	-4.34	6.46	-4.35	-2.23



Fig. 12. Plot of $\nu_{ip}(C=O)_2$ for 1,3,6-trimethyluracil vs. mole% CHCl₃/CCl₄.

3.5. 1,3,6-Trimethyluracil

Table 4 lists IR data for 1,3,6-trimethyluracil (1,3,6-TMU) in 0.125 mole% CHCl₃ and/or CCl₄ solutions. The $\nu_{ip}(C=O)_2$ mode for 1,3,6-TMU occurs at 1710.84 cm⁻¹ in CCl₄ solution and at 1701.99 cm⁻¹ in CHCl₃ solution. The most intense IR band in the carbonyl stretching region for 1,3,6-TMU occurs at 1670.52 cm⁻¹ in CCl₄ solution and at 1664.48 cm^{-1} in CHCl₃ solution. The frequency difference between the band at 1670.52 cm⁻¹ (CCl₄ solution) and the band at 1664.48 cm^{-1} (CHCl₃ solution) is 6.04 cm⁻¹, and the difference for $v_{in}(C=O)_2$ for 1,3,6-TMU in CCl₄ and CHCl₃ solutions is 8.55 cm^{-1} . Based upon the Nyquist rule (NR) for the inphase $(C=O)_2$ or $(C=O)_3$ and out-of-phase $(C=O)_2$ or $(C=O)_3$ stretching modes and for the symmetric and antisymmetric stretching modes for the NO₂ and SO₂ groups, it is not reasonable to assign the IR band in the region 1664–1671 cm⁻¹ to only ν_{op} (C=O)₂. We suggest that the band in the region 1664-1671 cm^{-1} is in Fermi resonance (FR) with the band in the region 1623-1629 cm⁻¹. Both of these bands decrease in frequency as the mole% CHCl₃/CCl₄ increases, and we have calculated the unperturbed $\nu_{op}(C=O)_2$ frequency by correction for FR by the method of Langseth and Lord [31,32] for each of the CHCl₃ and/or CCl₄ solutions of 1,3,6-TMU. The frequency decrease for unperturbed $\nu_{op}(C=O)_2$ is 10.6 cm⁻¹ vs. a frequency decrease of 8.9 cm⁻¹ for $\nu_{ip}(C=O)_2$ in going from CCl₄ solution to CHCl₃ solution, and these data now fulfil the criterion for the NR. Thus, these data for 1,3,6-TMU indicate that these two bands discussed above are in FR, and unperturbed $\nu_{op}(C=O)_2$ occurs at lower frequency than the observed IR band which is in FR with the observed lower lying band which results primarily from a combination tone.

Fig. 12 shows a plot of $\nu_{ip}(C=O)_2$ for 1,3,6-TMU vs. the mole% CHCl₃/CCl₄. These data show that $\nu_{ip}(C=O)_2$ decreases in frequency as the mole% CHCl₃/CCl₄ increases. In addition, it appears as though two linear lines intersect at ca. 48 mole% CHCl₃/CCl₄. This break point suggests that the type of intermolecular hydrogen bond equilibrium association between solvents and solute changes at ca. 48 mole% CHCl₃/CCl₄.

Fig. 13 shows plots of the two observed IR bands for 1,3,6-TMU occurring in the region 1620-1675 cm⁻¹, and also for these two bands which have been

					•						
Mole%	$\nu_{\rm ip}(\rm C=O)_2$	$\nu_{\rm op}(\rm C=0)_2$	5	$\nu_{ip}(C=O)_2$	ដ	$v_{ip}(C=0)_2$	A[$\nu_{i_0}(C=0)_2$]	A[$\nu_{op}(C=0)_2$]	5	$A[\nu_{ib}(C=0)_2]/$	$\nu_{\rm in}(\rm C=0)_2$
CHCl₃/CCl₄	(cm^{-1})	(cm^{-1})	(cm^{-1})	minus	(cm^{-1})	(cm^{-1})				$A[\nu_{op}(C=0)_2]$	minus
				$\nu_{\rm op}(\rm C=0)_2$ (cm ⁻¹							$\nu_{\rm op}({\rm C=0})_2$
00.00	1710.84	1670.52	1628.46	1668.83	1630.14	40.32	0.16	0.264	0.011	0.48	42.00
10.74	1709.81	1668.44	1627.52	1666.30	1629.65	41.37	0.136	0.327	0.018	0.42	43.50
19.40	1708.53	1667.75	1626.88	1665.28	1629.34	40.78	0.126	0.327	0.021	0.39	43.55
26.53	1707.53	1667.21	1626.40	1664.65	1628.95	40.32	0.122	0.329	0.022	0.37	42.88
32.50	1706.70	1666.82	1626.03	1664.43	1628.41	39.88	0.117	0.322	0.020	0.36	42.27
37.57	1706.10	1666.56	1625.81	1663.75	1628.61	39.54	0.117	0.325	0.024	0.36	42.34
41.93	1705.68	1666.41	1625.41	1663.44	1628.37	39.27	0.116	0.321	0.025	0.36	42.23
45.73	1704.84	1666.13	1625.18	1662.68	1628.62	38.71	0.123	0.327	0.030	0.38	42.15
49.06	1704.96	1666.18	1625.24	1662.86	1628.55	38.78	0.120	0.318	0.028	0.38	42.09
52.00	1704.69	1666.06	1624.95	1662.77	1628.23	38.63	0.117	0.322	0.028	0.36	41.92
54.62	1704.62	1666.03	1624.97	1662.59	1628.40	38.59	0.117	0.313	0.029	0.37	42.04
57.22	1704.60	1666.02	1624.85	1662.58	1628.28	38.58	0.120	0.319	0.029	0.38	42.01
60.07	1704.40	1665.92	1624.59	1662.30	1628.20	38.48	0.118	0.313	0.030	0.38	42.09
63.28	1704.26	1665.85	1624.51	1662.04	1628.31	38.41	0.121	0.316	0.032	0.38	42.21
66.73	1704.07	1665.76	1624.34	1661.97	1628.12	38.31	0.117	0.308	0.031	0.38	42.10
70.65	1703.76	1665.61	1624.19	1661.26	1628.53	38.15	0.126	0.324	0.038	0.39	42.50
75.06	1703.36	1665.42	1623.93	1661.09	1628.25	37.94	0.120	0.309	0.036	0.39	42.27
80.06	1703.03	1665.24	1623.75	1660.91	1628.07	37.79	0.118	0.301	0.035	0.39	42.11
85.05	1702.74	1665.02	1623.60	1660.36	1628.25	37.72	0.120	0.300	0.038	0.40	42.38
92.33	1702.43	1664.78	1623.47	1659.75	1628.49	37.65	0.119	0.296	0.041	0.40	42.68
100.00	1701.99	1664.48	1623.28	1658.20	1629.55	37.51	0.126	0.306	0.055	0.41	43.79
Δ (cm ⁻¹)	- 8.85	- 6.04	-5.18	- 10.63	-0.59	- 2.81					

Table 4 IR data for 1,3,6-trimethyluracil in 0.125 mole% carbon tetrachloride and/or chloroform solutions (0.207 mm KBr cell)

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Fig. 13. Plots of $\nu_{op}(C=O)_2$ and a combination tone (CT) in Fermi resonance and the calculated unperturbed $\nu_{op}(C=O)_2$ and CT frequencies for 1,3,5-trimethyluracil vs. mole% CHCl₃/CCl₄.

corrected for FR [31,32]. Unperturbed $\nu_{op}(C=O)_2$ decreases as the mole% CHCl₃/CCl₄ increases.

Fig. 14 shows plots of unperturbed $\nu_{op}(C=O)_2$ and perturbed $\nu_{op}(C=O)$ in FR with a combination tone

vs. $\nu_{ip}(C=0)_2$ for 1,3,6-TMU in CCl₄ and/or CHCl₃ solutions. These plots illustrate that both modes decrease in frequency as the mole% CHCl₃/CCl₄ increases.



Fig. 14. Plots of perturbed $\nu_{op}(C=O)_2$ and $\nu_{op}(C=O)_2$ corrected for Fermi resonance vs. $\nu_{ip}(C=O)_2$ for 1,3,6-trimethyluracil in CCl₄ and/or CHCl₃ solutions.

Та	ble	5						
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Infrared data for 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione in 0.125% CHCl₃/CCl₄ solutions (0.207 mm KBr cell)

Mole%	$\nu_{ip}(C=0)_2$	СТ	$v_{op}(C=0)_2$	Unperturbed	Unperturbed	In Fermi r	esonance		
CHCl ₃ /CCl ₄	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	$A[v_{op}(C=O)_2]$ (cm ⁻¹)	CT (cm ⁻¹)	$\frac{A[\nu_{ip}]}{(C=0)_2}$	$A (\sim 1671 \text{ cm}^{-1})$	$A (\sim 1657 \text{ cm}^{-1})$	$\nu_{ip}(C=O)_2$ minus unperturbed (cm ⁻¹)
00.00	1711.63	1672.84	1662.68	1667.00	1668.51	0.155	0.196	0.264	44.62
10.74	1710.14	1671.85	1660.83	1664.71	1667.96	0.139	0.149	0.274	45.43
19.40	1709.72	1671.87	1660.54	1664.35	1668.05	0.137	0.141	0.278	45.37
26.53	1708.11	1671.88	1659.16	1662.75	1668.28	0.127	0.111	0.282	45.36
32.50	1707.19	1671.57	1658.57	1662.03	1668.10	0.122	0.101	0.278	45.16
37.57	1706.80	1672.16	1658.29	1661.76	1668.68	0.122	0.093	0.278	45.03
41.93	1706.41	1671.87	1657.96	1661.36	1668.46	0.120	0.089	0.275	45.06
45.73	1706.16	1671.57	1657.75	1661.04	1668.27	0.120	0.085	0.272	45.12
49.06	1705.90	1669.96	1657.52	1660.40	1667.07	0.119	0.082	0.272	45.50
52.00	1705.72	1669.96	1657.34	1660.25	1667.04	0.118	0.081	0.270	45.65
54.62	1705.59	1669.96	1657.20	1660.13	1667.02	0.118	0.081	0.271	45.47
57.22	1705.40	1670.35	1656.98	1659.95	1667.37	0.116	0.076	0.265	45.44
60.07	1705.31	1669.96	1656.88	1659.81	1667.02	0.116	0.076	0.263	45.50
63.28	1705.07	1670.24	1656.57	1659.67	1667.13	0.116	0.077	0.262	45.40
66.73	1704.90	1670.35	1656.37	1659.35	1667.36	0.115	0.071	0.262	45.55
70.65	1704.72	1670.13	1656.01	1659.17	1666.96	0.115	0.073	0.253	45.55
75.06	1704.64	1670.74	1655.84	1659.01	1667.56	0.116	0.070	0.259	45.47
80.06	1704.37	1670.35	1655.30	1658.28	1667.36	0.114	0.066	0.267	45.36
85.05	1704.29	1669.57	1655.16	1658.02	1666.70	0.111	0.062	0.250	46.27
92.33	1704.04	1669.96	1654.70	1657.80	1666.85	0.114	0.065	0.254	46.23
100.00	1703.73	1670.70	1654.23	1657.40	1667.52	0.105	0.057	0.239	46.33
Δ (cm ⁻¹)	- 7.9	-2.14	-8.45	- 9.60	-0.99				



Fig. 15. Plot of $v_{ip}(C=0)_2$ for 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione vs. mole% CHCl₃/CCl₄.

3.6. 1,3-Dimethyl-2,4-(1H,3H)-quinazolinedione

Table 5 lists IR data for 1,3-dimethyl-2,4-(1*H*,3*H*)-quinazolinedione (**V**) as well as the unperturbed $v_{op}(C=O)_2$ and the unperturbed CT which have been corrected for FR. Fig. 15 shows a plot of $v_{ip}(C=O)_2$ for **V** vs. mole% CHCl₃/CCl₄. This plot shows that $v_{ip}(C=O)_2$ decreases in frequency as the mole% CHCl₃/CCl₄ increases. Fig. 16 shows plots of the perturbed and unperturbed CT and $v_{op}(C=O)_2$ frequencies vs. mole% CHCl₃/CCl₄. The filled circles represent unperturbed $v_{op}(C=O)_2$, and the filled diamonds represent unperturbed CT.

The frequency separation between $\nu_{ip}(C=O)_2$ and unperturbed $\nu_{op}(C=O)_2$ varies between 44.62 cm⁻¹ in CCl₄ solution and 46.33 cm⁻¹ in CHCl₃ solution for V. These frequency separations are similar to those exhibited by 1,3,5-TMU and caffeine. In addition, unperturbed $\nu_{op}(C=O)_2$ decreases more in frequency (9.60 cm⁻¹) than $\nu_{ip}(C=O)_2$ (7.9 cm⁻¹) in going from solution in CCl₄ to solution in CHCl₃. Both sets of data are consistent for six-membered cyclic imide type compounds (see Scheme 7).

It is interesting to compare the $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ frequencies for isocaffeine and caffeine. The $\nu_{ip}(C=O)_2$ modes for isocaffeine and caffeine at 10.74 mole% CHCl₃/CCl₄ occur at 1716.65 and 1710.17 cm⁻¹, respectively. In CHCl₃ solution, the



 $\nu_{ip}(C=O)_2$ modes for isocaffeine and caffeine occur at 1711.33 and 1707.85 cm⁻¹, respectively. The $\nu_{op}(C=O)_2$ mode for isocaffeine and caffeine at 10.74 mole% CHCl₃/CCl₄ occur at 1673.18 and 1663.49 cm⁻¹, respectively. The $\nu_{op}(C=O)_2$ mode for isocaffeine and caffeine occur at 1663.95 and 1658.36 cm⁻¹ in CHCl₃ solution. Thus, in all cases the $\nu(C=O)_2$ modes for isocaffeine occur at higher frequency than those for caffeine, and the only difference in the structure of the two compounds is the position of the N-CH₃ and C=N groups.

We suggest that there is a field effect between the lone pair of electrons of the 7-N atom and the 6-C=O group that causes both ν (C=O)₂ modes of isocaffeine to occur at higher frequency than the corresponding modes for caffeine. An example of the field



Fig. 16. Plots of perturbed $\nu_{op}(C=O)_2$ and the perturbed combination tone (CT) and $\nu_{op}(C=O)_2$ and CT corrected for Fermi resonance for 1,3-dimethyl-2,4-(1H,3H)-quinazolinedione vs. mole% CHCl₃/CCl₄.

Ta	ble 6						
IR	data	for	uracils	in	the	solid	state

Uracil	$\nu_{ip}(C=0)_2$ (cm ⁻¹)	$ \nu_{op}(C=0)_2 (cm^{-1}) $	$A[\nu_{\rm ip}(\rm C=O)_2]$	$A[\nu_{\rm op}(\rm C=O)_2]$	$ \nu_{ip}(C=O)_2 \text{ minus} $ $ \nu_{op}(C=O)_2 $ $ (cm^{-1}) $
5-Fluoro	1710	1661	0.48	0.95	49
5-Amino	1750	1670	М	S	80
5-Methyl	1745	1675	1.27	0.30	70
5-Bromo	1704	1680	S	M S	24
5-Chloro	1718	1695	S	Μ	23
5-Nitro	1719	1695	WM	S	24
5-Acetyl	1730	1704	М	S	26
6-Methyl	1720	1685	1.74	1.15	35
1,3-Dimethyl	1710	1658	Μ	S	52
1,3-Dimethyl (VP	(1733)	(1699)	(M)	(S)	(34)
1,3-Dimethyl-5-(morpholinecarbonyl)	1709	1659	Μ	S	50
1,3-Dimethyl-5-nitro	17020	1668	М	S	52
1,6-Dimethyl-3-(<i>p</i> -chloro- phenyl)-5-Br	1700	1648	М	S	52
1,3-bis-(2-Aminoethyl-2HCl)	1701	1659	М	S	42
1,3,5-Trimethyl	1701	1667	Μ	S	34
1,3,6-Trimethyl	1689	1652	М	S	37
Range	1689-1750	1652-1704			23-80

Vapor phase data (at 260°C in a 7.6 cm KBr cell) shown in parentheses are obtained from the Sadtler standard collection. M = medium.

VM = weak medium.

MS = medium strong.

S = strong.

effect upon carbonyl stretching frequencies is illustrated by methyl 5-chloro-6-methyl-2-picolinate which exists as rotational isomers in solution. The carbonyl band in rotational isomer IX (see Scheme 8) occurs at a ca. 23 cm⁻¹ higher frequency than the carbonyl band in rotational isomer X, and ν (C=O) for rotational isomer X occurs at a frequency essentially identical to that exhibited by methyl benzoate XI (1730 cm⁻¹). The relatively high ν (C=O) frequency exhibited by rotational isomer IX we attribute to a field effect between the C=O group and the free pair of electrons on the N atom. The structure X is assigned on the basis that ν (C=O) occurs at a frequency comparable to that exhibited by XI.

3.7. Solid phase data for uracils and hydantoins

Table 6 lists $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ frequencies for a series of uracils in the solid phase (also listed are the frequencies for 1,3-dimethyluracil in the vapor phase). The frequencies listed in Table 6 were read visually from either Sadtler standard spectra or from the Dow standard reference spectra, and these are approximated frequencies ($\pm 2 \text{ cm}^{-1}$).

The 5- and 6-substituted uracils XII (Scheme 9) contain two N-H groups and in the solid phase these compounds are intermolecularly hydrogen bonded such as XIII (Scheme 10).

Therefore, the $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ frequencies for the 5- and 6-substituted uracils listed in Table 6 are for the intermolecularly hydrogen bonded species. For the 5- and 6-uracils studied intermolecularly hydrogen bonded $\nu_{ip}(C=O)_2$ occurs in the region 1704–1750 cm⁻¹ and intermolecularly hydrogen bonded $\nu_{op}(C=O)_2$ occurs in the region 1661–1704 cm⁻¹. The frequency separation between intermolecularly hydrogen bonded $\nu_{op}(C=O)_2$ and $\nu_{op}(C=O)_2$ varies between 23 and 80 cm⁻¹. This variance most likely results from the strength of the intermolecular hydrogen bond and the crystal structure of the 5- and 6-substituted uracil in the solid phase.

In the solid phase 1,3-dimethyluracil exhibits $\nu_{ip}(C=O)_2$ at 1710 cm⁻¹ and $\nu_{op}(C=O)_2$ at 1658 cm⁻¹ while in the vapor phase $\nu_{ip}(C=O)_2$ occurs at 1733 cm⁻¹ and $\nu_{op}(C=O)_2$ at 1699 cm⁻¹. Thus, $\nu_{ip}(C=O)_2$ decreases in frequency by ca. 23 cm⁻¹



while $\nu_{on}(C=O)_2$ decreases by ca. 41 cm⁻¹ in going from the vapor phase to the solid phase. There are no N-H groups in the case of 1.3-dimethyluracil, and the lower frequencies observed for both $\nu_{in}(C=O)_2$ and $v_{on}(C=O)_2$ in the solid phase compared to the vapor phase cannot be attributed to intermolecular hydrogen bonding. The decrease in frequency we suggest results from dipolar interaction between molecules in the solid phase, and also from the crystalline structure. The uracils which contain 1.3-dimethyl groups or are substituted in the 1,3-positions studied in the sold phase exhibit $v_{in}(C=O)_2$ in the region 1689-1710 cm⁻¹ and $\nu_{op}(C=O)_2$ in the region 1652–1667 cm⁻¹. The ν_{op} (C=O)₂ mode has a strong band intensity and the $\nu_{in}(C=O)_2$ mode has a medium band intensity in the case of 1,3-dimethyl substituted uracils. In contrast, the IR band intensity for v_{in} - $(C=O)_2$ and $\nu_{op}(C=O)_2$ for the 5- and 6-substituted uracils varies, since $\nu_{op}(C=O)_2$ does not consistently have a higher band intensity than $v_{in}(C=O)_2$.

Infrared data for hydantoins (III) in the solid phase are listed in Table 7. Hydantoins contain a fivemembered ring cyclic imide $[N-(C=O)_2]$ type structure and a cyclic urea type structure. In compounds such as hydantoin it is possible for the two carbonyl



groups to couple forming an in-phase $(C=O)_2$ stretching mode, $\nu_{ip}(C=O)_2$, and an out-of-phase $(C=O)_2$ stretching mode, $\nu_{op}(C=O)_2$ rather than cyclic urea and cyclic amide type carbonyl stretching modes. The data presented below shows that hydan-toins exhibit $\nu_{in}(C=O)_2$ and $\nu_{on}(C=O)_2$ modes.

Hydantoin (III) exhibits IR bands at 1825 and 1785 cm^{-1} in the vapor phase and at 1783 and 1717 cm^{-1} in the solid phase. The band intensity ratio $A(1825 \text{ cm}^{-1})/A(1785 \text{ cm}^{-1})$ is 0.1 in the vapor phase and in the solid phase the band intensity ratio $A(1783 \text{ cm}^{-1})/A(1717 \text{ cm}^{-1})$ is 0.56. The higher frequency band in each set we assign as $v_{ip}(C=O)_2$ and the lower frequency band as $\nu_{on}(C=O)_2$. We note that the frequency separation between $\nu_{ip}(C=O)_2$ and $v_{op}(C=O)_2$ for hydantoin is 40 cm⁻¹ in the vapor phase and 66 cm^{-1} in the solid phase. Thus, there is a considerable change in the $\nu_{in}(C=O)_2$ and ν_{on} - $(C=O)_2$ modes in going from the solid state to the vapor state. In the vapor phase a band can be observed at 3495 cm^{-1} for hydantoin which we assign to a non-hydrogen bonded N-H stretching mode, $\nu_{\rm NH}$. However, in the solid phase IR bands are noted at 3150 and 3260 cm^{-1} for hydantoin, which we assign as hydrogen bonded $\nu(NH)$ modes. Thus, the $v_{in}(C=O)_2$ and $v_{on}(C=O)_2$ modes occur at lower frequency in the solid state than they occur in the vapor state due to intermolecular hydrogen bonding between C=O and N-H groups (C=O:H-N) in the solid phase, while in the vapor state at elevated temperature the hydantoin molecules are not intermolec-



Hydantoin				ν(NH) (cm ^{- 1})	A[µ(NH)]	$\nu_{\rm ip}({\rm C=0})_2$ (cm ⁻¹)	$v_{\rm op}({\rm C=0})_2$ (cm ⁻¹)	$A[\nu_{\rm ip}{\rm C=0}_2]$	$A[\nu_{\rm op}({\rm C=0})_2]$	$A[\nu_{\rm ip}(\rm C=0)_2]/$ $A[\nu_{\rm op}(\rm C=0)_2]$	$\frac{\nu_{\rm ip}(\rm C=O)_2}{\min}$ minus $\nu_{\rm op}(\rm C=O)_2$) (cm ⁻¹)
1-	3-	5-	5-								
H	Н	H	H	(3495)	(0.082)	(1825)	(1785)	(0.13)	(1.27)	(0.10)	(40)
Н	Н	Н	Н	3262	0.250	1783	1717	0.705	1.25	0.56	99
				3150	0.260						
Н	Н	CH3	CH ₃	3210	0.310	1779	1744	0.540	1.46	0.37	35
							1716		1.46		63
Н	Н	$C_{3}H_{7}$	$C_{3}H_{7}$	3200	0.312	1766	1717	0.622	1.30	0.48	49
Н	Н	C ₆ H ₁₁	C ₆ H ₁₁	3180	0.200	1755	1702	0.400	1.07	0.37	53
Н	Н	CH	$C_{3}H_{7}$	3215	0.271	1761	1707	0.415	1.17	0.35	54
Н	Н	CH ₃	C_3H_7	(3485)	(0.234)	(1809)	(1774)	(0.613)	(1.24)	(0.49)	(35)
Н	Н	CH3	$iso-C_3H_7$	3205	0.530	1770	1712	0.873	1.30	0.67	59
Н	Н	CH3	$iso-C_3H_7$	(3485)	(0.224)	(1808)	(1774)	(0690)	(1 26)	(5s)	(34)
Н	Н	СH	iso-C₄H ₉	3180	0.345	1780	1718	0.650	1.25	0.52	62
Н	Η	CH3	iso-C₄H₀	(3485)	(0.210)	(6081)	(1774)	(0.55)	(1.25)	(0.44)	(35)
Н	Н	CH,	C ₆ H ₅	3270	0.470	1758	1720	0.640	1.24	0.52	38
				3200	0.520	1709			0.96	0.67	49
Н	Н	CH3	p-ClC ₆ H₄	3250	0.130	1777	1727	0.300	0.00	0.33	50
				3185	0.150	1720			0.80	0.38	57
Н	Н	$C_{3}H_{5}$	C ₃ H ₅	3300	0.160	1781	1720	0.190	1.14	0.17	61
				3165	0.080	1761		0.150		0.13	41
C ₆ H ₅	C ₆ H ₅	Н	Н	I	I	1782	1720	0.230	0.86	0.27	62
C_2H_5	CH,	C ₆ H ₅	C ₆ H ₅	ł	Ι	1778	1721	0.200	0.95	0.21	57
						1771		0.210	0.22		50
$iso-C_3H_7$	CH3	C ₆ H ₅	С6Н5	I	1	1770	1711	0.490	1.00	0.49	59
iso-C ₄ H ₉	CH3	C ₆ H ₅	С6Н5	ţ	I	1774	1720	0.390	1.05	0.37	54
iso-C ₅ H ₁₁	CH_3	C ₆ H ₅	C ₆ H ₅	I	I	1779	1723	0.370	1.19	0.31	56
Range				3150-		1755-	1702-				35-66
				3300		1783	1744				
				(3485-		(1808–	(1774–				(34–40)
				3495)		1825)	1785)				

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Table 7 Infrared data for hydantions in the solid phase

Vapor phase data (280°C in a 7.6 cm KBr cell) shown in parentheses are obtained from the Sadtler standard collection. * Allyl.

ularly hydrogen bonded. It is obvious that intermolecular hydrogen bonding affects $\nu_{ip}(C=O)_2$ differently than $\nu_{op}(C=O)_2$, since their frequency separation changes from 66 cm⁻¹ in the solid phase to 40 cm⁻¹ in the vapor phase.

In the solid phase hydantoins substituted only in the 5,5-positions with alkyl or aryl groups exhibit $\nu_{ip}(C=O)_2$ in the region 1755–1781 cm⁻¹ and $\nu_{op}(C=O)_2$ in the region 1702–1744 cm⁻¹. In the vapor phase both modes occur at significantly higher frequency than they occur in the solid phase, and $\nu_{ip}(C=O)_2$ occurs near 1809 cm⁻¹ and $\nu_{op}(C=O)_2$ near 1774 cm⁻¹ in the vapor phase. Again, intermolecular hydrogen bonding between C=O and N–H groups (C=O)₂ modes, since their frequency separation is 54–62 cm⁻¹ in the solid phase and 34–35 cm⁻¹ in the vapor phase.

The shift of $\nu_{op}(C=O)_2$ relative to $\nu_{ip}(C=O)_2$ in going from the vapor phase to the solid phase in the case of hydantoin is exactly that predicted by the Nyquist rule for systems undergoing increasing solvent association.

In the solid phase, the hydantoins substituted in the 1,3-positions with alkyl or aryl groups exhibit $\nu_{ip}(C=O)_2$ in the region 1770–1782 cm⁻¹ and $\nu_{op}(C=O)_2$ in the region 1711–1723 cm⁻¹. In these cases the C=O groups are not intermolecularly hydrogen bonded, and they do not exhibit ν (NH) absorption bands.

It is interesting to compare the $\nu_{in}(C=O)_2$ frequencies for uracils and hydantoins. In the solid phase the uracils and hydantoins exhibit $\nu_{ip}(C=O)_2$ in the region 1689-1750 cm⁻¹ (six-membered ring) and in the region 1755-1783 cm⁻¹ (five-membered ring), respectively, while uracils and hydantoins in the solid phase exhibit $v_{op}(C=O)_2$ in the region 1652–1704 cm^{-1} (six-membered ring) and in the region 1702-1744 cm⁻¹ (5-membered ring), respectively. Both $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ occur at higher frequencies for hydantoins than the corresponding ν_{ip} - $(C=O)_2$ and $\nu_{op}(C=O)_2$ uracils, and this we attribute to ring strain of the five-membered ring. The ring strain causes changes in the carbonyl bond angles which make it more difficult for $\nu_{in}(C=O)_2$ and $v_{on}(C=O)_2$ to vibrate. The ring bond angles are smaller in the case of hydantoins than in the case of uracils, thus, $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ frequencies

for hydantoins occur at higher frequency than the corresponding modes exhibited by uracils.

The compound 5,5-dimethylhydantoin in the solid phase exhibits three IR bands in the region expected for $\nu_{ip}(C=O)_2$ and $\nu_{op}(C=O)_2$ while only two IR bands are expected. The band at 1779 cm⁻¹ is assigned to the $\nu_{ip}(C=O)_2$ mode. The IR bands at 1716 and 1744 cm⁻¹ have approximately equal intensity. These two bands most likely result from the combination tone (795 cm⁻¹ + 929 cm⁻¹ = 1724 cm⁻¹) in Fermi resonance with $\nu_{op}(C=O)_2$.

The compounds 5-methyl-5-phenylhydantoin and 5-methyl-5-chlorophenylhydantoin in the solid phase exhibit $\nu_{ip}(C=O)_2$ at 1758 and 1777 cm⁻¹, respectively. Both of these compounds exhibit two IR bands in the region expected for $\nu_{op}(C=O)_2$. These strong IR bands occur at 1709 and 1720 cm⁻¹ for 5methyl-5-phenylhydantoin and at 1720 and 1727 cm⁻¹ for 5-methyl-5-chlorophenylhydantoin. These two IR bands may result from $\nu_{op}(C=O)_2$ in Fermi resonance with a combination tone.

The hydantoins in the solid phase in Table 7 exhibit v(NH) in the region 3150-3300 cm⁻¹, $v_{in}(C=O)_2$ in the region 1755-1783 cm⁻¹, and $v_{on}(C=O)_2$ in the region 1702–1744 cm⁻¹. In some cases $\nu_{on}(C=O)_2$ occurs as a doublet most likely the result of being in Fermi resonance with a combination tone. The hydantoins in the vapor phase listed in Table 7 exhibit ν (NH) in the region 3485–3495 cm^{-1} , $v_{in}(C=O)_2$ in the region 1808–1825 cm⁻¹, and $v_{00}(C=0)_2$ in the region 1774–1785 cm⁻¹. These frequency differences are due to the fact that the hydantoins are intermolecularly hydrogen bonded in the solid phase, but are not intermolecularly hydrogen bonded in the vapor phase. The frequency separation between $\nu_{in}(C=O)_2$ and $\nu_{on}(C=O)_2$ is larger in the solid phase than in the vapor phase. In summary, the group frequencies listed in Table 7 should aid in the identification of hydantoins by application of IR spectroscopy.

Appendix 1

The Nyquist rule (NR)

The difference in the frequency behavior of normal vibrations originating within the same functional group of chemical compounds containing functional groups such as $O(C=O)_2$, $N(C=O)_2$, NO_2 , SO_2 or NH_2 with change in the physical environment of the compound (e.g., solution, liquid, solid or vapor state) apparently follow a rule. This rule was developed by Nyquist and is defined below.

The NR states that the frequency shift of antisymmetric stretching vibration is larger than that for the symmetric vibration or the frequency shift of out-ofphase stretching vibration is larger than that for the in-phase vibrations for the functional groups of chemicals whose vibrational spectra have been recorded in two or more physical states. For example, during an $\nu_{op}(C=O)_2$ mode for a compound in dilute solution, one C=O bond expands toward neighboring solvent molecules while the other C=O bond contracts from neighboring solvent molecules. Thus, there is an equal alternating solute-solvent interaction (either dipolar or intermolecular hydrogen bonding) during a cycle of $v_{on}(C=O)_2$. The net result is that the amount of energy required during half of the vibrational cycle is equal to the amount of energy required for the other half of the vibrational cycle due to the solute-solvent interaction. In the case of $\nu_{in}(C=O)_2$ both C=O bonds expand or contract from neighboring solvent molecules in-phase during a cycle of this molecular vibration. Thus, there is an alternating in-phase solute-solvent interaction of the two C=O bonds with surrounding solvent molecules during a cycle of $\nu_{in}(C=O)_2$. It follows that more energy is required for the two C=O bonds to contract away or expand toward solvent molecules during a cycle of $\nu_{in}(C=O)_2$ than it does for the alternating expansion and contraction of two C=O bonds during a cycle of $\nu_{op}(C=O)_2$. Consequently, the $v_{ip}(C=O)_2$ frequency does not decrease as much as the $v_{on}(C=O)_2$ frequency when induced with dipolar or hydrogen bonding interactions with neighboring molecules [33].

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