particles of this size. Also, it is impossible to align "B" phase samples using microscope cover slips, as for D phase samples. This also indicates the presence of many defects in the samples (i.e., small crystallite size). Where it was possible to measure Δ values for the B phase, the values are similar to those in the D phase and do not reflect the presence of a first-order phase change. Since similar NMR behavior was observed for systems containing "B" phase (sodium octanoate, sodium octyl sulfate) and the one without a B phase (sodium octyl sulfonate) it seems likely that "B" phase is simply a continuation of D phase at high water content, and that no first-order B/D phase change exists. In the original paper,[16] Ekwall et al. concluded that the x-ray evidence for the coexistence of B + D phases was not unequivocal. The boundaries shown in Figure 4 were obtained by analysis of separated samples after prolonged centrifugation. It is possible that the gravity gradient along the centrifuge tubes caused the separation observed. Certainly it is hard to find a physical reason why lamellar phase samples with ~64 Å water layer should separate from samples with ~72 Å water layers as was observed. There appears to be a case for the reexamination of low-angle x-ray scattering on samples in the B + D two-phase region.

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Ultraviolet Photoelectron Studies of Biological Pyrimidines. The Valence Electronic Structure of Cytosine

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Abstract: UV photoelectron spectroscopy and CNDO/S molecular orbital calculations have been employed to investigate the electronic structure of cytosine (I), 1-methylcytosine (II), *N*,1-dimethylcytosine (III), *N*,*N*,1-trimethylcytosine (IV), 3-methylcytosine (V), 1,5-dimethylcytosine (VI), 1,6-dimethylcytosine (VII), 5-methylcytosine (VIII), and 6-methylcytosine (IX). The resolution of the spectra obtained for different members of this series of molecules varies markedly. Of all the molecules investigated the photoelectron bands arising from the five uppermost orbitals are well resolved only for *N*,1-dimethylcytosine. The variation in the resolution arises partially from the overlapping of bands. Furthermore, spectra obtained for molecules in which labile H atoms are replaced by methyl groups exhibit much better resolution than spectra for other molecules. This observation is probably related to hydrogen bonding effects. For cytosine the spacing of bands occurring in the spectrum is accurately reproduced in the results of CNDO/S calculations carried out on the 1(H) aminooxo tautomeric form of the molecule. In compounds II–IV and VI–IX the spacing of bands and the shifts observed in the spectra are also well predicted by calculations carried out on the aminooxo tautomers. However, for 3-methylcytosine the results indicate that an imino tautomeric form is most stable. For all compounds the CNDO/S calculations indicate that three of the five uppermost orbitals are π orbitals and that two are lone-pair orbitals. In cytosine the first and fifth bands arise from π orbitals while the fourth band arises from a lone-pair orbital. The second and third bands arise from a π and a lone-pair orbital which are strongly overlapping and their ordering remains uncertain.

Introduction

The valence molecular orbital structure of biological purines and pyrimidines plays an important role in determining the biochemical properties of these molecules.[1] Energies and electron distributions associated with the valence orbitals of these molecules influence the manner in which purines and pyrimidines participate in weak bonding interactions as well as in chemical reactions.[2-4]

The valence structure of biological purines and pyrimidines

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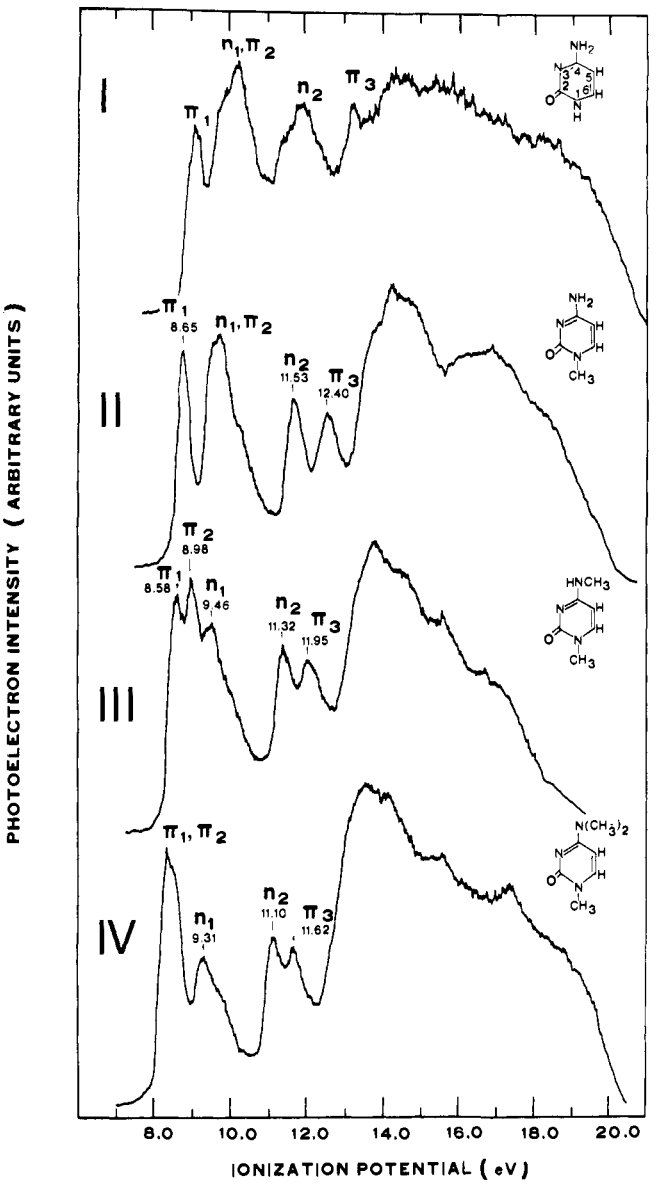

Figure 1. He(I) photoelectron spectra of cytosine, 1-methylcytosine, *N*,1-dimethylcytosine, and *N*,*N*,1-trimethylcytosine. Assignments are given for the five highest occupied molecular orbitals.

has been extensively investigated in numerous theoretical studies employing both semiempirical[5-7] and ab initio[8,9] molecular orbital calculations. All of the calculations predict the ordering and spacing of orbitals within these molecules. However, until recently there has not been much experimental data with which these predictions can be compared. Most previous experimental investigations of electronic structure in biological purines and pyrimidines have involved UV absorption spectroscopy.[10,11] The results from these studies have yielded information primarily about the first $\pi \rightarrow \pi^*$ transition. Little information has been obtained about the ground-state molecular orbital structure.

In recent studies it has been found that gas-phase UV photoelectron spectroscopy can provide a highly resolved picture of electronic structure in biological purines and pyrimidines.[2,3,12-14] Most of this work has focused on elucidating the ground-state electronic structure of uracil, thymine, and adenine. The present report gives results of a photoelectron investigation of cytosine. Previous gas-phase UV absorption studies on this molecule were hampered by decomposition problems.[11] In the present study this difficulty has been circumvented by investigating volatile methyl-substituted derivatives of cytosine.

Experimental Section

Gas-phase He(I) photoelectron spectra were measured with a Perkin-Elmer PS-18 spectrometer equipped with a heated probe for vaporizing solids. The spectra of compounds I–IX were measured at temperatures of 224, 181, 146, 127, 172, 185, 195, 195, and 205 °C, respectively. For each molecule the sample temperature was maintained constant within ±1 °C during a spectroscopic run. Ionization potentials were calibrated using the $^2P_{3/2}$ and $^2P_{1/2}$ bands of Xe and Ar. For all compounds except cytosine, spectra obtained from a single sample over a period of 1 h were identical, indicating that no decomposition occurred. For cytosine, spectra measured from a single sample over a time period of 1 h changed slightly. It was found that the resolution of the spectra decreased as the sample aged. The cytosine spectrum shown in Figure 1 was obtained for a fresh sample and was measured immediately after the electron analyzer was cleaned.

Cytosine was obtained from the Sigma Chemical Co. Samples of compounds II and V–IX were obtained from Vega-Fox Biochemicals. The 3-methylcytosine employed in these experiments was in the hemihydrate form; the 5-methylcytosine contained some moisture. Spectra for both these molecules contain photoelectron bands arising from water. The other compounds were not hydrated.

Samples of *N*,1-dimethylcytosine and *N*,*N*,1-trimethylcytosine were synthesized employing a method involving aminolysis of alkoxyl-1-methylpyrimidine.[15] The procedure for synthesizing both *N*-methyl substituted cytosine derivatives was similar. For both compounds the starting material, 4-ethoxyl-1-methyl-2-pyrimidinol, was obtained by treating 2,4-diethoxypyrimidine (commercially obtained from the Sigma Chemical Co.) with freshly distilled methyl iodide. *N*,1-Dimethylcytosine was synthesized by adding the starting material to a solution (25% by weight) of methylamine in anhydrous methanol. In the synthesis of *N*,*N*,1-trimethylcytosine, dimethylamine was substituted for methylamine. In both syntheses the reaction mixture was heated for 18 h at 100 °C in a high-pressure bomb. The filtered solution was evaporated to dryness and the residue was recrystallized in ethyl acetate. Melting points obtained for *N*,1-dimethylcytosine and *N*,*N*,1-trimethylcytosine were 180 and 175 °C, respectively. These melting points compare well with previously reported values of 180 and 178–179 °C.[15]

Small amounts of 1,3-dimethylcytosine were synthesized from 1-methylcytosine by employing a modified procedure used by Brookes and Lawley[16] for the methylation of cytidine. A sample of 1-methylcytosine (0.25 g) was dissolved in 5 mL of dimethylformamide and 2 mL of dimethyl sulfate. After the reaction mixture was heated for 1 h at 70 °C the dimethylformamide and dimethyl sulfate were removed by vacuum distillation. The remaining solid was dissolved in 1 mL of water and extracted with 2 mL of chloroform. Petroleum ether was added to the organic layer until it became cloudy. After cooling 5 mg of product crystallized. The melting point of the product, 148 °C, is in agreement with the literature value of 145 °C.[16] The photoelectron spectrum of 1,3-dimethylcytosine was measured at 68 °C.

Results and Discussion

Figure 1 shows He(I) photoelectron spectra of compounds I–IV along with assignments for bands arising from the five uppermost orbitals. The cytosine spectrum is poorly resolved, especially for bands in the energy regions around 10.0 and 11.9 eV. In 1-methylcytosine the band around 9.6 eV is also poorly resolved but the spectrum in the region 11.5–12.5 eV is much sharper than in cytosine. The *N*,1-dimethylcytosine spectrum indicates that the 9.5–10.0 eV region of the 1-methylcytosine spectrum contains two bands. These are resolved in *N*,1-dimethylcytosine. In *N*,*N*,1-trimethylcytosine the first and second bands appearing in *N*,1-dimethylcytosine overlap.

Figure 2 shows He(I) photoelectron spectra and assignments for bands arising from the five uppermost orbitals of compounds V–IX. In all spectra the bands in the region 9.0–10.0 eV are poorly resolved owing to the superposition of the second and the third bands. The spectra for compounds V–VII are well resolved in the region between the first and second bands and in the energy region between 11.1 and 11.8 eV. The spectra for compounds VIII and IX are less well resolved in these two regions.

A preliminary assignment of bands in the photoelectron spectra of cytosine and the methyl-substituted cytosines is based on the observation that in almost all molecular orbital calculations of cytosine using both semiempirical[5-7] and ab initio[8,9] methods it is found that three of the five uppermost orbitals are π orbitals and two are lone-pair orbitals. The lone-pair orbitals are made up from in-phase and out-of-phase combinations of p electrons associated with the oxygen atom and the nitrogen atom at the 3 position.[6] The most recent of the semiempirical calculations[6,7] indicate that the ordering of the upper five orbitals in cytosine is π_1, n_1, π_2, n_2, π_3. Furthermore, the ab initio calculations[8] indicate that the energies associated with the n_1 and π_2 orbitals are nearly the same.

Semiempirical molecular orbital calculations employing the CNDO/S method[17] were used to confirm the assignment of these spectra. Cytosine coordinates employed in the calculation were obtained from crystallographic data.[18] The geometries for compounds II-IV and VI-IX were obtained by combining the coordinates for cytosine with the coordinates for the methyl groups in 1-methylthymine.[19] The C-CH_3 bond distance used in the calculations was 1.497 Å. The N-CH_3 bond distance for the ring nitrogen atom was 1.470 Å. The CH_3 geometry used for the methylamino groups in *N*-methylcytosines was taken from the crystal structure of *N,N*-dimethylguanosine.[20] In the amino group the N-CH_3 bond distances were 1.462 and 1.453 Å.

In recent UV absorption studies of 3-methylcytosine[21] it was found that an imino tautomer (shown in the structural drawing in Figure 2) is the most stable form in nonpolar solvents. In order to examine the possibility that this is also the most stable form in the gas phase, the photoelectron spectrum of 3-methylcytosine was compared with results obtained from a CNDO/S calculation on the imino tautomer. The geometry of the ring structure of 3-methylcytosine used in the calculation was obtained from the crystal structure of 1,5-dimethyl-N^4-hydroxycytosine.[22] The imine, C=N, bond distance was 1.288 Å.[22] It was found that reducing the C=N bond distance to as little as 1.275 Å did not alter the calculated energy levels significantly.

Panel A of Figure 3 shows vertical ionization potentials for molecules I-IX which were obtained from the photoelectron spectra. Panel B shows energy levels which were obtained when results from CNDO/S calculations were used in conjunction with Koopmans' theorem.[23] An examination of the results in Figure 2 indicates that the order and spacing of energy levels predicted by the calculation are in remarkable agreement with the results from the photoelectron spectra.

It is particularly interesting to note that the overlap between the photoelectron bands associated with the n_1 and π_2 orbitals in most of the molecules studied is consistent with results from the calculation. Furthermore, the high sensitivity of the π_2 and π_3 orbitals to methyl substitution at the amino group which is observed in the spectra also appears in the results from the calculation. A result similar to this has been observed in other aromatic amines. In adenine the π_1 and π_3 orbitals are highly sensitive to methyl substitution at the amino group.[3] In aniline the π_1 and π_3 orbitals exhibit the same behavior.[24]

Figure 4 shows electron density maps for the three uppermost π orbitals of 1-methylcytosine. The maps were obtained from results of the CNDO/S calculation and were constructed in a manner which has been described previously.[14] An examination of the maps suggests that the sensitivity of the π_2 and π_3 orbital energies to methyl substitution of the amino group is related to the significant contribution to these orbitals from what are normally considered to be the nitrogen "lone pair" electrons of the amino group. The maps also predict that these nitrogen electrons do not contribute to the π_1 orbital. This conclusion is consistent with the low sensitivity of this orbital to methyl substitution at the amino group.

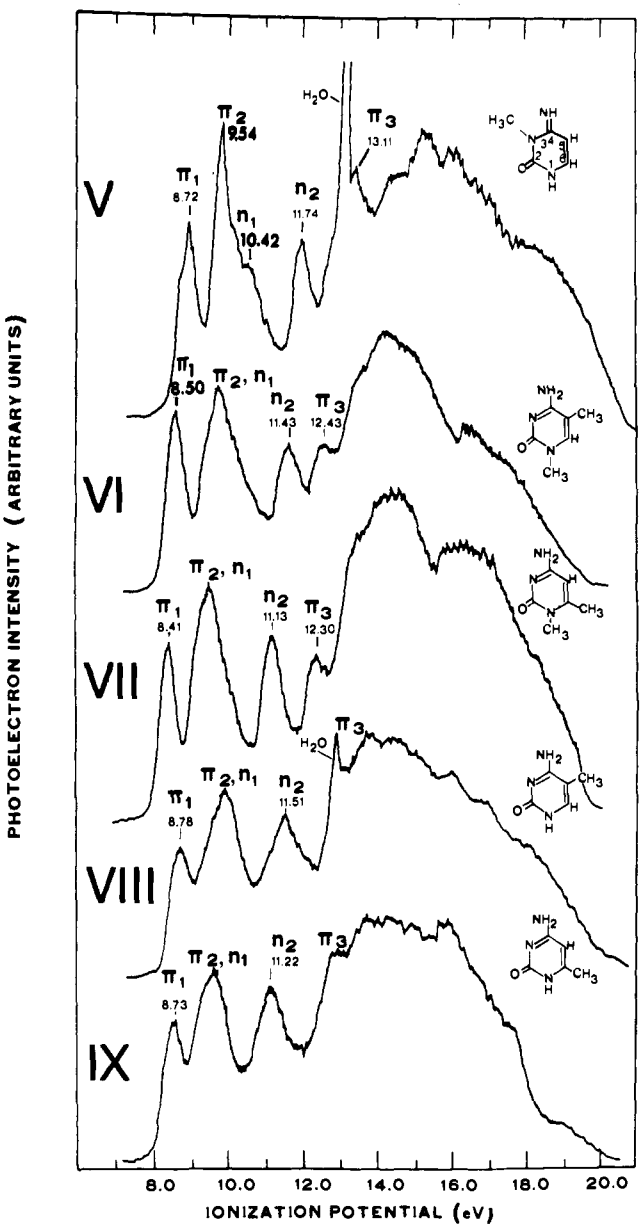

Figure 2. He(I) photoelectron spectra of 3-methylcytosine, 1,5-dimethylcytosine, 1,6-dimethylcytosine, 5-methylcytosine, and 6-methylcytosine.

The good agreement between experimental ionization potentials and the spacing of energy levels predicted by the CNDO/S calculations for the imino form of 3-methylcytosine strongly suggests that this tautomer is the most common one under the present experimental conditions. When calculations were carried out on the amino form of 3-methylcytosine it was found that there is no longer good agreement between the spectroscopic results and the theoretical energy levels. For example, a calculation on the amino tautomer predicts that the splitting between the π_1 and π_2 energy levels is greater than 2.5 eV.

In order to further confirm that the imino form of 3-methylcytosine is the most stable tautomeric form of the molecule the spectrum of 3-methylcytosine was compared with that obtained for 1,3-dimethylcytosine. This latter molecule exists only in the imino form.[21] It was found that the spectrum for 1,3-dimethylcytosine is very similar to that for 3-methylcytosine. In particular the sharpness associated with the π_2 band of 3-methylcytosine and the high intensity of this band relative to the π_1 band are also characteristic of the spectrum of 1,3-dimethylcytosine.

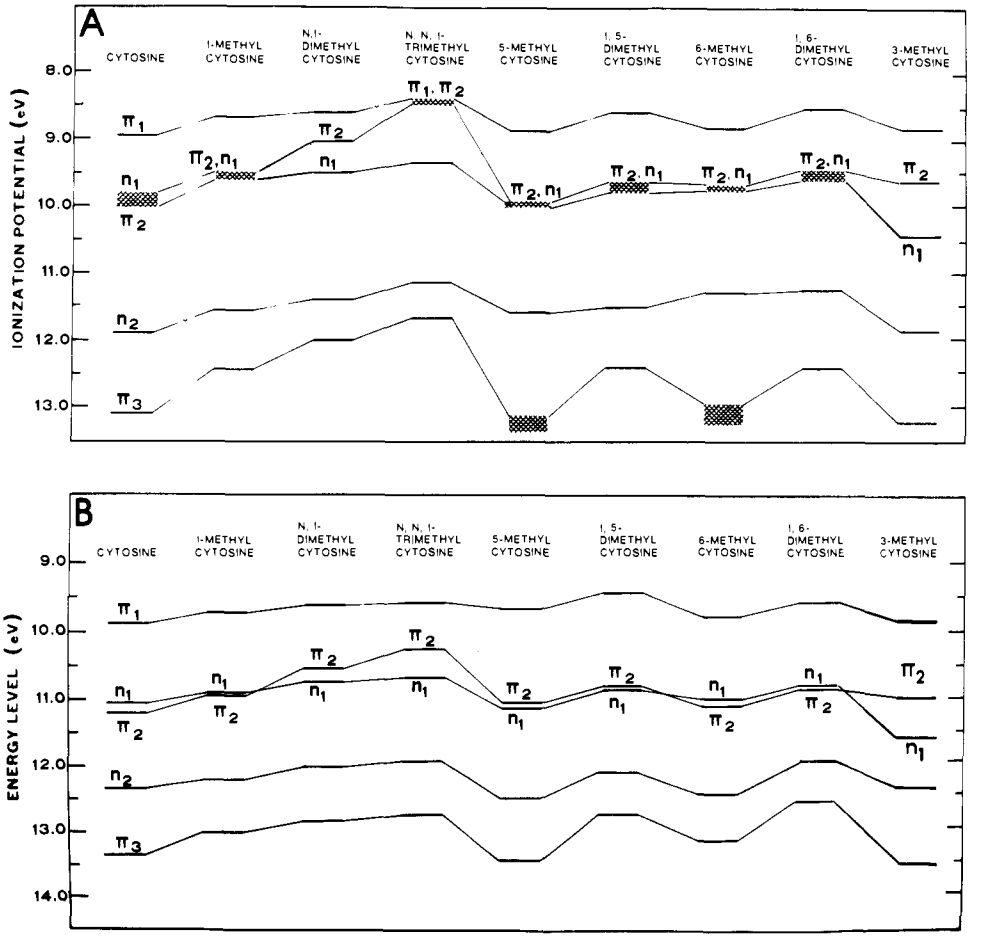

Figure 3. Energy level diagrams showing the five highest occupied molecular orbitals in cytosine and methyl-substituted cytosines. Panel A shows experimental results obtained from vertical ionization potentials. The hatched areas show regions in which there is an overlap of photoelectron bands and for which the precise ordering of the bands is uncertain. Panel B shows energy levels obtained from CNDO/S molecular orbital calculations.

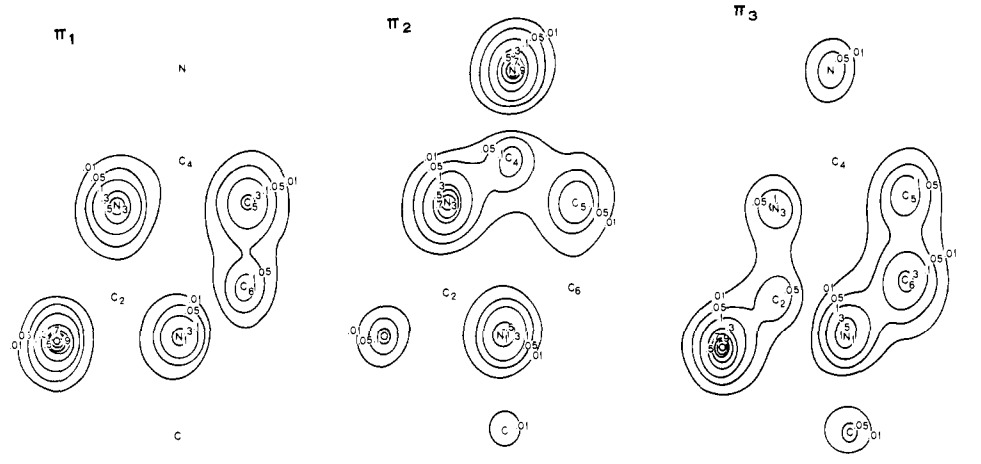

Figure 4. Electron density maps showing electron distribution in the three highest π orbitals of 1-methylcytosine as determined from CNDO/S calculations. The maps show electron density 0.25 Å above the plane of the molecule. Values of electron density, denoted on the contours, are normalized to the maximum density in each of the orbitals. The relative magnitude for the maximum density occurring in each of the orbitals is 1.3, 1.2, and 1.0 for the π_1, π_2, and π_3 orbitals, respectively.

The difference in resolution observed in the spectra of cytosine and different methyl-substituted cytosines has also been investigated. Spectra obtained from molecules which contain methyl groups at the 1 or 3 positions are more highly resolved than spectra obtained from molecules in which these positions are unsubstituted. This fact is demonstrated by a comparison of spectra in Figure 2. Here the region between the π_1 and the second band and the region surrounding the n_2 band is much better resolved in 3-methylcytosine, 1,5-dimethylcytosine, and 1,6-dimethylcytosine than in 5-methylcytosine or 6-methylcytosine.

Two explanations of this observation have been considered. The first involves the possibility that for molecules in which there is no methyl substitution at the 1 or 3 positions more than one tautomeric form of cytosine contributes to the observed spectra. The two most stable tautomers of cytosine are generally considered to be the 1(H) and the 3(H) aminooxo forms of the molecule.[25,26] However, in cytosine crystals only the

1(H) form occurs[18] and according to most investigators this is more stable than the 3(H) form of the molecule.[27]

In aqueous solutions at a temperature of 25 °C, temperature jump experiments indicate that the ratio of the concentrations of the 3(H) tautomer to that of the 1(H) tautomer is 2.5×10^{-3}.[21] The ratio determined from pK_a measurements at 25 °C is 1×10^{-3}.[28] Different theoretical estimates of the energy difference between the two tautomeric forms of the isolated molecules yield conflicting results. According to one study[25] the tautomerization enthalpy is 0.7 kcal/mol; a more recent study[26] yielded a value of 6 kcal/mol. According to these two investigations the ratios of the concentration of the 3(H) tautomer to the 1(H) tautomer under the present experimental conditions are 0.4 and 0.001, respectively. Although the possibility that more than one tautomeric form of compounds I, VIII, and IX contribute significantly to the photoelectron spectra cannot be eliminated, there is little direct evidence which suggests that this is the case.

Another possible reason for variation in resolution of the spectra of methyl-substituted cytosines is associated with the varying volatility of these molecules. This second possibility presently appears very likely. Cytosine is an extremely active hydrogen-bonding partner. The possible hydrogen-bonding sites include the H atoms on the amino group and on the N atom at the 1 position. In anhydrous cytosine crystals all of these sites participate in hydrogen bonding.[18] In molecules where methyl substitution has reduced the number of labile H atoms the degree of hydrogen bonding will be decreased.

In the present experiments, the occurrence of weakly bound dimers in the gas phase may be expected to alter the spectra and could account for the loss of resolution observed in molecules which are not substituted at the hydrogen bonding sites. The fact that the resolution is good in previously reported spectra of adenine,[3] uracil,[2] and thymine[14] suggests that the degree of hydrogen bonding in these molecules is less than in cytosine. In crystals of adenine,[29] uracil,[30] and thymine[31] each molecule participates in two, one, and two hydrogen bonds, respectively. In cytosine crystals each molecule participates in three hydrogen bonds.[18]

Another observation which suggests that hydrogen bonding effects are important is that higher probe temperatures were required to measure cytosine spectra than were required to measure spectra of uracil (177 °C), thymine (152 °C), and adenine (185 °C). Furthermore, higher temperatures were generally required to measure spectra of cytosine, 5-methylcytosine, and 6-methylcytosine than were required for compounds II–VII.

The higher temperatures required to obtain photoelectron spectra of cytosines in which hydrogen-bonding positions are not substituted may also give rise to partial decomposition. This is suggested by the change in resolution which was observed when multiple spectra were measured from a single sample of cytosine. As mentioned above, such decomposition has also been observed in gas-phase UV absorption studies of cytosine.[11]

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