his assistance with the torsion angle calculations.

Supplementary Material Available: Description of the X-ray diffraction experiment and tables of experimental data, atomic coordinates, thermal parameters, interatomic distances, and bond angles (5 pages); listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

The 2-Pyridone Dimer, a Model Cis Peptide. Gas-Phase Structure from High-Resolution Laser Spectroscopy

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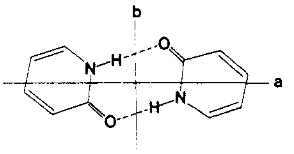
One of the criteria for the formation of a satisfactory polypeptide configuration is that each carbonyl and imino group be involved in the formation of a hydrogen bond with the N—H···O distance approximately 2.8 Å and with the oxygen atom nearly on the N–H axis.[1] This requirement is met by many proteins, including those containing the rare cis amide linkage.[2] Linkages of this type also are exploited widely in molecular recognition.[3] In this report, we show that at least one precursor to such structures also exists in the gas phase, that it is planar or nearly so, and that its ground-state geometry is very similar to that determined by X-ray crystallography.

The model cis peptide is the 2-pyridone dimer I, formed in the gas phase by expansion of a supersonic jet seeded with 2-hydroxypyridine (2-HP). Figure 1A shows a portion of the $S_1 \leftarrow S_0$ fluorescence excitation spectrum (FES) of the resulting gas-phase mixture, probed ~15 mm downstream of the nozzle with a tunable pulsed dye laser operating in the ultraviolet. There are three prominent bands in this spectrum at a resolution of ~1 cm^{-1}. The two lower frequency bands, at 29 831 and 29 930 cm^{-1}, are the electronic origins of two conformers of the 2-pyridone monomer (2-PY, the lactam form of 2-HP), differing in the degree of nonplanarity at the nitrogen atom.[4,5] The higher frequency band, displaced 945 cm^{-1} to the blue of the first monomer origin, belongs to the 2-PY dimer, $(2\text{-PY})_2$.



I

Proof that this high-frequency band is that of $(2\text{-PY})_2$ was provided by examining it at higher resolution, sufficiently high to expose the underlying rotational structure of the band so that the inertial parameters of the molecule (in both its S_0 and S_1 states) could be measured. A molecular beam CW laser spectrometer[6] was employed for this purpose. Figure 1, spectra B and C, shows the rotationally resolved FES of the high-frequency band. The entire spectrum of this band (Figure 1B) spans ~90 GHz (3 cm^{-1}) and exhibits more than 1500 resolved lines. The lifetime-limited line width (fwhm) of single lines (Figure 1C) is 18 MHz (~0.0006 cm^{-1}). Notably, these lines exhibit spacings that are significantly

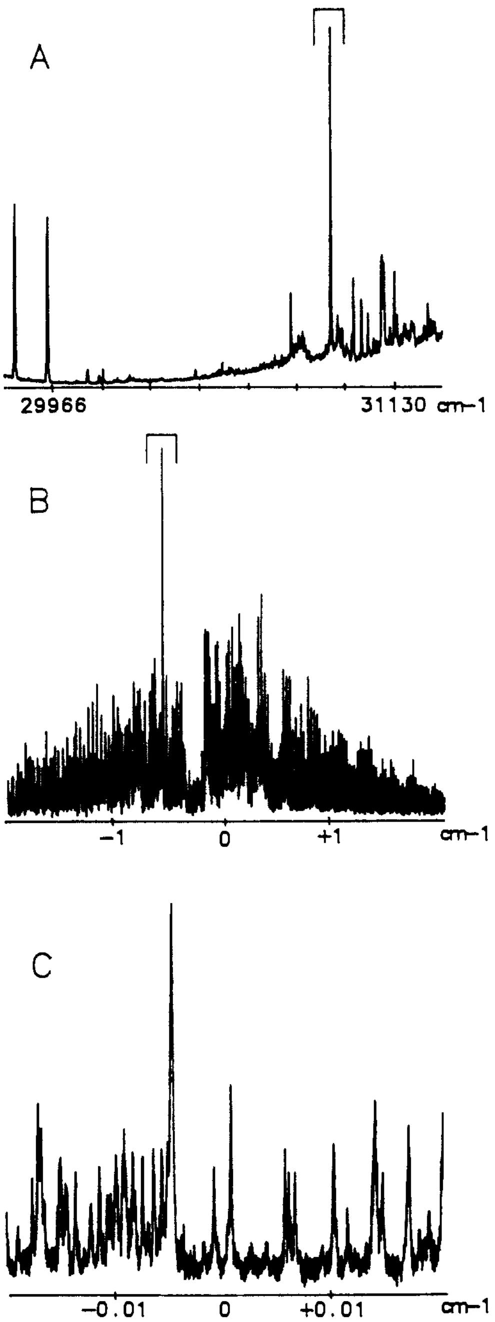


Figure 1. (A) A portion of the vibrationally resolved fluorescence excitation spectrum (FES) of 2-hydroxypyridine (2-HP) in a supersonic jet. The heated sample of 2-HP (at ~120 °C) was seeded in 5 atm of He, expanded through a 2 mm diameter pulsed nozzle, and probed 15 mm downstream by a frequency-doubled pulsed dye laser. The two strong lower frequency bands are the $S_1 \leftarrow S_0$ origins of the 2-HP tautomer 2-pyridone (2-PY); the strong high-frequency band is a $S_1 \leftarrow S_0$ vibronic transition of the model cis peptide, 2-pyridone dimer $[(2\text{-PY})_2]$. (B) The rotationally resolved FES of the $(2\text{-PY})_2$ $S_1 \leftarrow S_0$ vibronic band, recorded in the collision-free environment of a molecular beam. In this case, 2-HP was heated to ~200 °C, seeded in 300 Torr of Ar, expanded through a 240-μm quartz nozzle, skimmed twice, and probed 100 cm downstream by a tunable CW laser operating in the UV. The resulting FES, detected with a photon counter, was calibrated with use of a mode-matched confocal interferometer and the I_2 absorption spectrum. All data were processed and analyzed with a Concurrent computer system and specially designed software. (C) A portion of spectrum B illustrating the resolved rotational lines of $(2\text{-PY})_2$. In spectra A and B, brackets denote the piece of the spectrum that is expanded in spectra B and C, respectively.

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Table I. Inertial Parameters of the 1-Pyridone Dimer in Its Ground Electronic State[a,b]

parameter	S_0(exptl)	S_0(3-21G)[c]
A'', MHz	2010.3 ± 0.1	2077.9
B'', MHz	319.4 ± 0.1	319.2
C'', MHz	275.9 ± 0.1	276.7
κ''	−0.950	−0.953
$\Delta I''$,[d] amu Å^2	−1.7 ± 0.8	0.0

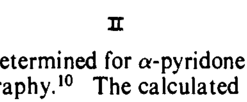
[a] Fits of the spectrum were made with use of the derivative approximation and a standard least-squares analysis. The standard deviation of the fit to a rigid-rotor Hamiltonian for both states is 9.0 MHz, significantly less than the experimental line width. Adding centrifugal distortion terms improved the standard derivation, but by less than 1 MHz, so they are neglected here. [b] The rotational constants obtained from the least-squares analysis are A'' = 2010.261 ± 0.005, B'' = 319.429 ± 0.003, and C'' = 275.888 ± 0.003. However, the precision of the measurement is reduced to ±0.1 MHz by systematic errors in the experiment (ref 6). [c] Theoretical inertial parameters calculated from the ab initio geometry of Field and Hillier (ref 9). [d] Inertial defects. $\Delta I = I_c - I_b - I_a$.

less than the corresponding spacings in the high-resolution spectra of the monomer bands, suggesting that the carrier of the high-frequency band is an aggregate structure.

We employed Watson's asymmetric rotor Hamiltonian[7] and previously described fitting strategies[8] to analyze the observed rotational structure of this band. The results for the S_0 state are given in Table I. We also list in this table the rotational constants that would be exhibited by a 2-PY dimer whose geometry is identical with that of the equilibrium structure calculated by ab initio methods.[9] The agreement between these calculated values and those measured for the electronic ground state of the carrier of the high-frequency band is good. (Typical errors in such calculations are of order 2%.) We conclude, therefore, that the aggregate structure is $(2\text{-PY})_2$. The small, negative inertial defect shows further that the ground-state dimer is planar, or nearly so. Additionally, we find that the high-frequency band is a perpendicular-type transition polarized entirely (≥95%) along the *b* inertial axis of $(2\text{-PY})_2$ (cf. I). This result is consistent with the polarization properties of the two lower frequency monomer bands.[5]

The inertial parameters of the excited-state vibronic level accessed in this experiment are very similar to those of the ground-state vibronic level. We find ΔA $(=A' - A'')$ = 0.1, ΔB = −9.1, ΔC = −6.6 ± 0.1 MHz, κ' = −0.953, and $\Delta I'$ = −3.2 ± 1.2 amu Å^2. Increased vibrational amplitude along out-of-plane coordinate(s) would explain the larger magnitude of $\Delta I'$. The origin of the high-frequency band is at 30776.479 ± 0.002 cm^{-1}.

Three rotational constants are clearly insufficient to fully characterize the structure of any electronic state of such a complex molecule. Recognizing this, we have used the experimental values of these constants to optimize two geometrical properties of the dimer, the separation of the centers of mass of the two monomer units (R), and the angle (θ) between R and the C=O bond(s) (II). Bond distances and angles for the two pyridone rings were fixed at the values determined for α-pyridone by Penfold with use of X-ray crystallography.[10] The calculated rotational constants converged to within 0.15% of the experimental values for both the S_0 and S_1 states, with $R(S_0)$ = 5.30 ± 0.03 Å, $\theta(S_0)$ = 43 ± 2°, $R(S_1)$ = 5.39 ± 0.03 Å, and $\theta(S_1)$ = 43 ± 2°. The ground-state values of R and θ yield the hydrogen bond parameters r(N—H···O) = 2.75 ± 0.03 Å and ϕ[C=O···(H)—N] = 122 ± 2°. (Insufficient information is available, at present, to determine whether or not the hydrogen atom lies exactly on the N···O axis.) The corresponding solid-state values are r = 2.77 ± 0.03 Å and ϕ = 136 ± 2°.[10] Also, the gas-phase value of r lies within 1σ of the distribution found for 1357 intermolecular hydrogen bonds in a recent survey of 889 organic crystal structures.[11] On S_1 excitation of $(2\text{-PY})_2$, r increases by 0.08 Å relative to S_0 while ϕ remains approximately the same, a result that suggests a decrease in hydrogen-bonding strength on excitation and is consistent with the large blue shift of the dimer $S_1 \leftarrow S_0$ band relative to those of the monomer.



II

Intermolecular forces, particularly hydrogen bonds, lie at the heart of many chemical and biochemical phenomena. There has been much speculation about the role of the environment in determining the magnitudes of these forces. Thus, the finding that r(N—H···O) in $(2\text{-PY})_2$ is the same in both the gas phase and the condensed phase is significant. Beyond this, the high-resolution FES technique offers distinct advantages over other methods for the study of hydrogen-bonded species. Structures like I have no permanent dipole moments and so have no microwave spectrum. Additionally, isotopic substitution may be used to determine the center-of-mass coordinates of any atom in the molecule (including hydrogen atoms),[12] making possible determinations of structure and studies of tunneling and energy transfer dynamics in both ground and electronically excited states. Other degrees of freedom may be accessed at other laser wavelengths. Finally, water molecules may be attached during the expansion to probe the effect of solvent on a wide variety of structures. Work along several of these lines is in progress.

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Hydrogen Bonding in a Family of Triamides: Conformation-Directing Effects in Solution vs the Solid State

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The ability of hydrogen bonds to influence molecular conformation and to orchestrate intermolecular association is a topic of considerable current interest.[1] Our own experiments in this area are designed to elucidate the interplay among noncovalent forces that leads to discrete molecular folding patterns, with greater insight on the origins of protein tertiary structural stability as an ultimate goal.[2] We recently reported that triamide **1** experiences dramatic temperature-dependent conformational changes in a nonpolar solvent, involving the rearrangement of intramolecular hydrogen bonds.[2b] We now describe crystal structures of **1** and

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