Hydrogen bonding in the symmetry-equivalent $C_{2h}$ dimer of 2-pyridone in its $S_0$ and $S_2$ electronic states. Effect of deuterium substitution

Andrew Held and David W. Pratt
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 4 November 1991; accepted 19 December 1991)

The properties of the two intermolecular N-H⋯O bonds that are responsible for the formation of the cis peptide-like dimer of 2-pyridone (2PY) have been examined using deuterium substitution of the bridging hydrogen atoms as a probe. Studies of the fully resolved $S_2 - S_0$ electronic spectrum of (2PY)$_2$ in a molecular beam show that the protonated dimer has a symmetry-equivalent planar $C_{2h}$ structure in its $S_0$ ($A_g$) and $S_2$ ($B_u$) states. Analogous studies of (2PY)$_2$-$d_1$ and (2PY)$_2$-$d_2$ show that (2PY)$_2$ and (2PY)$_2$-$d_i$ are energy delocalized dimers in their $S_2$ states, with an exciton splitting of less than 20 cm$^{-1}$. Effective structures of the symmetric dimers in both states are derived from the measured rotational constants. A comparison of these structures shows that there is a distortion of the hydrogen-bonding geometry when hydrogen is replaced by deuterium, along both in-plane and out-of-plane coordinates. $\Delta R$ (N-H⋯O) = 0.008 Å, $\Delta \theta$ (C=O⋯(H)-N) = 0°, and $\Delta \phi$ (the dihedral angle) = 0.96° in $S_0$ (2PY)$_2$-$d_2$ and $\Delta R$ = 0.003 Å, $\Delta \theta$ = 0°, and $\Delta \phi$ = 0.86° in $S_2$ (2PY)$_2$-$d_2$. The implications of these findings for currently accepted models of the hydrogen bond are discussed.

INTRODUCTION

The position of an atom in a molecule often can be determined by utilizing the changes in moments of inertia that occur when the atom is replaced by another isotope of different mass. This method has been widely exploited for the determination of molecular structures by microwave spectroscopy. It also may be used to distinguish one isomer from another, and thus to probe the behavior of a molecule along an isomerization coordinate, even in different electronic states. However, there are times when the method gives ambiguous results, and this is typically because of the contributions from vibrational motions. In that event, a careful examination of the isotopically induced changes in the moments of inertia can provide valuable information about the displacements of the substituted atom. Studies of this type can provide a unique view of large amplitude motions and the anisotropy of intermolecular forces.

The hydrogen bond is an important example. Nearly all biological processes involve the making and breaking of hydrogen bonds, at some stage. In a typical hydrogen bond, the hydrogen atom serves as a bridge between two electronegative atoms, all the while executing large-amplitude motions. Therefore, if the method of isotopic substitution were used to determine the position of the bridging hydrogen atom, one might expect the method to fail. But one also might expect to gain from this measurement some important information about the forces that govern the dynamics of hydrogen-atom motion in the ubiquitous hydrogen bond.

We report the results of one experiment of this type here. The hydrogen bonds we examine are the two intermolecular N-H⋯O bonds that are found in the cis-peptide-like dimer of 2-pyridone (2PY), the keto tautomer of 2-hydroxypyridine, in its $S_0$ and $S_2$ electronic states. Two recent publications are relevant to this work. One is a study of the fluorescence excitation spectrum of the $S_1 - S_0$ electronic transition of the 2PY monomer. The rotationally resolved origin bands of 2PY, recorded in the collision-free environment of a molecular beam with a cw dye laser, exhibit intensity anomalies that were shown to result from an in-plane inertial axis reorientation that occurs on absorption of the photon. The second is a high-resolution study of a band that appears 945 cm$^{-1}$ to the blue of the first monomer origin in the fluorescence excitation spectrum of 2PY. The carrier of this band was shown to be the dimer of 2PY, (2PY)$_2$, a planar hydrogen-bonded structure in both states in which the two amine hydrogens are attracted to the carbonyl oxygens, structure I. Here, we describe the results of similar experiments on the singly deuterated dimer, (2PY)$_2$-$d_1$, and the doubly deuterated dimer, (2PY)$_2$-$d_2$. These studies show that the 2PY monomer units in the dimer are symmetry equivalent and that the $S_2 - S_0$ excitation is delocalized over both rings. We obtain information about the exciton interaction energy in the $S_2$ state from the shifts in transition energies produced by deuterium substitution. The experiments also show that replacing hydrogen by deuterium changes the vibrationally averaged position of the substituted atom. We use the mea-
measured rotational constants of $(2\text{PY})_2$ to establish an effective structure of the dimer in both electronic states. We also use the isotopically induced changes in these constants to establish how the effective structure must be modified to incorporate the effects of deuterium substitution, in both states. We thus obtain information about the potential-energy surfaces that govern the motion of the bridging hydrogen atoms in the two intermolecular hydrogen bonds, in both states. The results show that both in-plane and out-of-plane motions of these atoms are important.

**EXPERIMENT**

2-Hydroxypyridine (2HP) was purchased from Aldrich and used without further purification. Hydroxy-deuterated 2HP was prepared by exchange with $D_2O$. The isotopic purity of the $D_2O$ sample was 98 ± %. The experimental conditions used to form the 2-pyridone dimer $(2\text{PY})_2$ are the same as those used in studies of the 2PY monomer. In the low-resolution experiments, the sample was heated to ca. 400 K, seeded into 3–5 atm of helium, and expanded into a vacuum chamber through a 1 mm orifice pulsed valve (General Valve Series 9) operating at 10 Hz. The molecule was excited by a frequency-doubled dye laser pumped by a Nd$^3+ :$YAG laser, also operating at 10 Hz. The spectral resolution of the dye laser is 0.6 cm$^{-1}$. The signal was detected by a photomultiplier tube (PMT) and processed by a boxcar integrator; a MASSCOMP MCS561 data-acquisition system was used to record the data. Relative frequency calibration was performed using a solid étalon (free spectral range equal to 1.0 cm$^{-1}$ at the fundamental of the dye).

High-resolution data were obtained using our molecular-beam laser spectrometer, described elsewhere. The sample was heated to ca. 500 K, seeded in 500 Torr of argon, expanded through a 240 $\mu$m quartz nozzle, skimmed twice, and probed 110 cm downstream of the nozzle by a single frequency tunable UV laser. Fluorescence was collected using spatially selective optics, detected by a PMT and photon counting system, and processed by the MASSCOMP data-acquisition system. Under the present operating conditions, the Doppler-limited spectral resolution was about 3 MHz in the UV. Relative frequency calibration was performed using a near-confocal interferometer having a mode-matched free spectral range of 299.752 ± 0.005 MHz. The absolute transition frequencies in both the low- and high-resolution spectra were determined by comparison to the $I_1$ absorption spectrum and are accurate to + 30 MHz.

**RESULTS AND INTERPRETATION**

The low-resolution $S_1 \rightarrow S_0$ fluorescence excitation spectrum of 2HP in a supersonic jet is shown in Fig. 1. The two lower-frequency bands, at 29 831 and 29 930 cm$^{-1}$, are the electronic origins of two conformers of the 2PY monomer, differing in the degree of nonplanarity at the nitrogen atom in the $S_1$ state. The strong transition displaced 945 cm$^{-1}$ to the blue of the first monomer band belongs to the dimer of 2PY, $(2\text{PY})_2$. The spectrum exhibits significant hot-band activity probably associated with the population of low-frequency ground-state dimer modes. The electronic origin of $(2\text{PY})_2$ has not been assigned.

A ~50 cm$^{-1}$ scan of the spectrum in the vicinity of the strong dimer band at ~30 776 cm$^{-1}$ is shown in Fig. 2 (a). Only one band is observed in this region when the sample is fully protonated. Figure 2 (b) shows the excitation spectrum in this same region of a 3:1 mixture of undeuterated $(d_0)$ and amine-deuterated 2PY $(d_1)$. In this case, a second band is observed, shifted to the blue of the first band by about 10 cm$^{-1}$. The measured intensity ratio of the two bands in Fig. 2 (b) is ~9:7. Figure 2 (c) is similar to Fig. 2 (b) except that the mixture is 1:3 $d_0$ : $d_1$. In this case, two bands separated by ~10 cm$^{-1}$ are again observed but the measured intensity ratio is now ~1:15. If the dimer possesses a center of inversion, and the two monomer units are equivalent by symmetry (as shown in the $C_{2v}$ structure, structure I), then samples of isotopically mixed 2PY should contain three possible dimers, $d_0$-$d_0$, $d_0$-$d_1$, and $d_1$-$d_1$. However, only two resolved bands appear in Figs. 2(b) and 2(c) which requires an explanation.

The number of bands present and their relative intensities in the spectra of different isotopic mixtures of 2PY is characteristic not only of the structure of the dimer but also of the strength of the electronic coupling that exists between the two monomer units. In the limit where electronic coupling is very weak or nonexistent, the electronic excitation is localized on one half of the dimer, while strong electronic coupling between the two monomer units delocalizes the excitation energy over the entire dimer molecule. Localization of the excitation on one monomer unit would produce four distinct dimer bands. The four bands would correspond to electronic excitations of the type $d_0$-$d_0$, $d_0$-$d_1$, $d_0$-$d_1$, and $d_1$-$d_1$. In the 3:1 $d_0$-$d_1$ spectrum the intensity pattern for the aforementioned species would be 9:3:3:9 in the 1:3 $d_0$-$d_1$ spectrum, if deuterium substitution has no effect
on the absorption cross section or fluorescence quantum yield. However, the shift in frequency produced by single isotopic substitution of the unexcited half of the localized dimer may be too small to resolve with our jet apparatus. If this is the case, we expect the intensity patterns to follow the isotopic mixing ratios 3:1 (or 1:3) in Fig. 2(b) and 1:3 (or 3:1) in Fig. 2(c). In the limit of strong electronic coupling, where the electronic excitation is delocalized uniformly over both halves of the dimer, we expect three bands (since the \( d_0 - d^\dagger \) species would be indistinguishable) and intensity ratios of 9:6:1 and 1:6:9 in the completely resolved 3:1 and 1:3 \( d_0 - d^\dagger \) spectra. If we assume the heterodimer \( d_0 - d^\dagger \) (or \( d_0 - d^\dagger \)) lies unresolved with respect to either of the homodimers, then we would observe intensity ratios of either 15:1 or 9:7 for the 3:1 \( d_0 : d^\dagger \) mixture and ratios of either 7:9 or 1:15 for the 1:3 \( d_0 : d^\dagger \) mixture. The observed intensity ratios are 9:7 and 1:15 for the 3:1 \( d_0 : d^\dagger \) and 1:3 \( d_0 : d^\dagger \) samples, respectively. Comparing these results to our predictions, we conclude that the energy in the excited electronic state is delocalized over the entire molecule. We also conclude that the \( d_0 - d^\dagger \) and \( d^\dagger - d^\dagger \) bands are overlapping at \( \sim 0.6 \text{ cm}^{-1} \) resolution and that both are blue shifted with respect to the \( d_0 - d^\dagger \) dimer transition. The fact that the \( d_0 - d^\dagger \) band lies in the vicinity of the \( d^\dagger - d^\dagger \) band and is not centered between the \( d_0 - d^\dagger \) and \( d^\dagger - d^\dagger \) bands, as might be expected, will be discussed later.

Proof that \((2\text{PY})_2\) is a symmetry-equivalent dimer in both electronic states was provided by a high-resolution study of the lower-frequency band in Fig. 2. Figure 3(a) shows the high-resolution spectrum of the lower-frequency band in Fig. 2(b). [The corresponding spectrum of the band in Fig. 2(a) is identical.] Under our experimental conditions, this band spans \( \sim 3 \text{ cm}^{-1} \). There are over 1500 lines in the spectrum, each of which exhibits a lifetime-limited linewidth [full width at half maximum (FWHM)] of \( 18 \pm 2 \text{ MHz} \), corresponding to a fluorescence lifetime of...
about 9 ns. The frequency-determined lifetime of \((2PY)_2\) is the same, within experimental error, as that of the 2PY monomer.\(^4\) Employing Watson's asymmetric rotor Hamiltonian\(^7\) and previously described fitting strategies,\(^8\) we obtained a fit to the observed dimer spectrum with a standard deviation of about 9 MHz, significantly less than the experimental linewidth. Centrifugal distortion terms were added but improved the standard deviation of the fit by less than 1 MHz. Figure 3(b) shows a portion of Fig. 3(a) at full experimental resolution along with the corresponding calculated simulation, demonstrating the quality of the fit. As discussed elsewhere,\(^5\) there is excellent agreement between the rotational constants obtained from this fit and those calculated from the \textit{ab initio} equilibrium geometry for structure I,\(^9\) with two bridging hydrogen atoms. From this agreement, we conclude that the species responsible for the lower-frequency band in Fig. 2 is the planar, symmetry-equivalent \(C_{2h}\) dimer of 2PY, \(d_0-d_0\). Notably, no further splittings are observed in its fully resolved electronic spectrum.

Proof that \((2PY)_2\) is an energy-delocalized dimer in its excited state was provided by a high-resolution study of the higher-frequency band in Fig. 2. The rotationally resolved spectrum of the higher-frequency band in Fig. 2(b) is shown in Fig. 4. [The corresponding spectrum of the higher-frequency band in Fig. 2(c) is identical.] In contrast to the results for the lower-frequency band, we find that the higher-frequency band in Fig. 2 consists of two closely overlapping bands, whose origins are separated by 0.635 ± 0.002 cm\(^{-1}\). These two bands were fit separately. Again, adding first-order centrifugal distortion terms improved the standard deviations in both bands. However, the improvement was significant (~8 MHz) only for the highest-frequency band. We also compared the sum of these two bands, the "simulated" spectrum in Fig. 4, with experiment. The agreement is excellent, again confirming the existence of two closely overlapping bands. Finally, from the derived inertial parameters, we assigned these two bands to the \(d_0-d_1\) and \(d_1-d_1\) dimers, with the \(d_0-d_1\) band lying at higher frequency. Both dimers exhibit linewidths that are the same as that of the \(d_0-d_0\) dimer, 18 ± 2 MHz. No intensity anomalies were observed in any of the dimer bands, showing that the inertial axes of \((2PY)_2\) in the two electronic states are coincident. This is consistent with a \(C_{2h}\) geometry for both states.

The existence of one \(d_0-d_0\) dimer band at full rotational resolution unambiguously demonstrates that the energy in the excited electronic state of the symmetry-equivalent \(C_{2h}\) dimer of \((2PY)_2\) is delocalized. Two \(d_0-d_1\) dimer bands would be observed if this were not the case. It is thus appropriate to require that the electronic wave functions of \((2PY)_2\) be eigenfunctions of the point group of the molecule as a whole. In \(C_{2h}\), the ground state is \(A_g\) and the two lowest excited states are \(A_u\) and \(B_u\). The transition from the ground state to the excited \(A_u\) state of the dimer is symmetry forbidden by one-photon selection rules. The transition to the excited \(B_u\) state is allowed, with \(a\) or \(b\) axis polarization. We find, experimentally, that all three dimer bands are polarized entirely (>95%) along the \(b\) axis of \((2PY)_2\); cf. structure II, in accord with the

$$\text{B}_u$$ assignment. Now, it is known that the transition moment in the monomer makes an angle of either ± 51° with respect to its \(a\) axis.\(^4\) Projecting this moment onto the inertial axes of the dimer, we see (II) that bringing the two monomer units into a symmetric \(C_{2h}\) configuration results in a dimer transition moment that lies along either its \(a\) or \(b\) axis. Since the observed polarization is \(b\), the transition moment in the monomer must make an angle of − 51° with respect to its \(a\) axis. Clearly, the transition that is allowed in the dimer \((1B_u - X 1A_u)\) must involve an in-phase excitation of the two monomer units. We do not know, at this juncture, whether the symmetry-forbidden excited \(1A_u\) state lies at lower or higher energy than the allowed excited \(1B_u\) state, since the former state was not observed. However, simple exciton theory\(^10,11\) suggests that the observed \(1B_u\) state lies at higher
energy than the excited $^1A_g$ state and is, in fact, the $S_2$ state of the dimer, as discussed more fully below.

Summarized in Table I are the inertial parameters of the three isotopically labeled (2PY)$_2$ dimers in their $S_0$ and $S_2$ states. The inertial defects of both states of the $d_0$-$d_0$ and $d_1$-$d_1$ dimers are both small and negative, as expected for a $C_{2h}$ planar molecule. The inertial defect of the $d_0$-$d_1$ dimer is small but positive in the $S_2$ state. Focusing on the results for the ground vibronic levels, we see that the rotational constants (which are accurate to $\pm 0.1$ MHz) decrease with deuterium substitution. These decreases are expected since rotational constants are inversely proportional to moments of inertia. However, we further expect that sequential replacement of the two bridging hydrogens by deuterium in the $C_{2h}$ dimer should bring about two equal decreases in the rotational constants. From the data in Table I we see that this is not the case. The change in the ground-state B constant, for example, on going from the parent $d_0$-$d_0$ molecule to the $d_0$-$d_1$ molecule ($-0.3$ MHz) differs significantly from that observed on going from the $d_0$-$d_1$ molecule to the $d_1$-$d_1$ molecule ($-0.8$ MHz). In the excited state, single isotopic substitution of the parent dimer molecule actually causes an increase in the $B$ rotational constant, producing the positive inertial defect.

Now, we know from model potential calculations that there is very little change in the vibrationally averaged position of the hydrogen atom when a hydrogen bond is formed. In (2PY)$_2$, the rotational constants themselves also are not very sensitive functions of these positions. (Displacing a hydrogen atom by $\pm 0.1$ Å along R produces a change of only $\pm 0.05$ MHz in the ground-state B value.) So the anomalies in the rotational constants are, at first sight, surprising. However, the hydrogen atoms also participate in the large-amplitude, low-frequency intermolecular vibrational modes of the dimer, and the amplitudes of these do change when hydrogen is replaced by deuterium. This is the effect that gives rise to the changes in the rotational constants, since the effect of deuterium substitution is to change the vibrationally averaged position of the atom. So, in what follows, we use these changes to probe the motions along these coordinates, in both electronic states, thus exposing features of the potential-energy surface that governs hydrogen-bond formation.

Table I

<table>
<thead>
<tr>
<th>$d_0$-$d_0$</th>
<th>$d_1$-$d_1$</th>
<th>$d_0$-$d_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^*$ (MHz)$^a$</td>
<td>2 010.4</td>
<td>2 004.0</td>
</tr>
<tr>
<td>$B^*$ (MHz)$^a$</td>
<td>319.4</td>
<td>319.1</td>
</tr>
<tr>
<td>$C^*$ (MHz)$^a$</td>
<td>275.8</td>
<td>275.5</td>
</tr>
<tr>
<td>$A^*$ (MHz)$^a$</td>
<td>2 010.5</td>
<td>2 004.7</td>
</tr>
<tr>
<td>$B^*$ (MHz)$^a$</td>
<td>310.3</td>
<td>311.5</td>
</tr>
<tr>
<td>$C^*$ (MHz)$^a$</td>
<td>269.2</td>
<td>269.1</td>
</tr>
<tr>
<td>$\Delta I^*$ (amu Å$^2$)$^b$</td>
<td>- 1.299</td>
<td>- 1.416</td>
</tr>
<tr>
<td>$\Delta I^*$ (amu Å$^2$)$^b$</td>
<td>- 3.029</td>
<td>+ 3.448</td>
</tr>
<tr>
<td>$\kappa^*$</td>
<td>- 0.950</td>
<td>- 0.950</td>
</tr>
<tr>
<td>$\kappa^*$</td>
<td>- 0.953</td>
<td>- 0.951</td>
</tr>
<tr>
<td>Origin (cm$^{-1}$)$^c$</td>
<td>30 776.479</td>
<td>30 787.336</td>
</tr>
</tbody>
</table>

$^a$ $\pm 0.1$ MHz

$^b$ Inertial defects, $\pm 0.001$ amu Å$^2$.

$^c$ $\pm 0.002$ cm$^{-1}$.

We first calculate an effective structure of (2PY)$_2$ in both electronic states from the observed rotational constants of the unsubstituted dimer. In this calculation, bond distances and angles for the two pyridone rings were fixed at the values determined for $\alpha$-pyridone by Penfold using X-ray crystallography. The remaining three geometrical parameters; the intermolecular heavy-atom separation $R(N-H\cdots O)$ (see structure III), the angle $\theta$ between $R$ and the C-O bonds (structure III), and the dihedral angle $\phi$ of the two rings (not shown in structure III), were then fit to the observed rotational constants. The resulting ground-state values are $R(N-H\cdots O) = 2.77 \pm 0.03$ Å and $\theta[C=O\cdots (H)-N] = 121.8 \pm 0.5^\circ$. On electronic excitation to the $S_2$ state of (2PY)$_2$, $R$ increases by 0.10 Å relative to $S_0$, while $\theta$ remains approximately the same. The out-of-plane angle, $\phi$, was determined to be zero (to within $\pm 0.5^\circ$) for both states. The increase in $R(N-H\cdots O)$ on electronic excitation shows that the hydrogen-bonding strength decreases in the $S_2$ state, relative to the $S_0$ state. This is consistent with the large blue shift of the dimer $S_2$ - $S_0$ band relative to the origin bands of the monomer. (The slight differences in the geometrical parameters reported here and those reported earlier are a result of optimizations using different restricted geometries. The two sets of data are, however, the same within the reported errors).

Listed in Table II are the $S_0$ and $S_2$ coordinates of the amine hydrogens determined from the effective structures of (2PY)$_2$ described above. Also listed in Table II are the amine hydrogen coordinates of the $S_0$ and $S_2$ states of (2PY)$_2$, calculated from Kraitchman's equations. Three sets of these substitution coordinates were derived, based on comparisons of the rotational constants of the $d_0$-$d_0$ and $d_0$-$d_1$ dimers, the $d_0$-$d_1$ and $d_1$-$d_1$ dimers, and the $d_0$-$d_0$ and $d_1$-$d_1$ dimers. Comparing the results, we see that the substitution structures have much larger x and z values. An increase in x (i.e., a decrease in the length of the N-H bond; see structure I) is an unreasonable result of hydrogen-bond formation. We also see that the three different sets of substitution coordinates are different from each other.

To account for these results, we then postulate that $R$, $\theta$, and $\phi$ change when hydrogen is replaced by deuterium. Estimates of these changes in both electronic states were determined by modifying the effective structure of (2PY)$_2$ until its rotational constants agreed with those of the effective structure of (2PY)$_2$, with the two hydrogens replaced...
TABLE II. Amine hydrogen atom coordinates in the $S_0$ and $S_1$ electronic states of the 2-pyridone dimer.

<table>
<thead>
<tr>
<th>Type of coordinate</th>
<th>State</th>
<th>$x$ (Å)</th>
<th>$y$ (Å)</th>
<th>$z$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective*</td>
<td>$S_0$</td>
<td>0.76 ± 0.02</td>
<td>0.91 ± 0.02</td>
<td>0.00 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>0.79 ± 0.07</td>
<td>0.86 ± 0.07</td>
<td>0.00 ± 0.02</td>
</tr>
<tr>
<td>Substitution, $d_0$</td>
<td>$S_0$</td>
<td>1.37 ± 0.22</td>
<td>0.83 ± 0.34</td>
<td>0.24 ± 1.55</td>
</tr>
<tr>
<td>$d_0-d_1/d_0+d_1$</td>
<td>$S_2$</td>
<td>1.56 ± 0.21</td>
<td>2.01 ± 0.15</td>
<td>1.82 ± 0.17</td>
</tr>
<tr>
<td>Substitution,</td>
<td>$S_0$</td>
<td>1.39 ± 0.22</td>
<td>0.88 ± 0.35</td>
<td>0.63 ± 0.41</td>
</tr>
<tr>
<td>$d_0-d_1/d_0+d_1$</td>
<td>$S_2$</td>
<td>2.15 ± 0.15</td>
<td>1.58 ± 0.21</td>
<td>1.90 ± 0.17</td>
</tr>
<tr>
<td>Substitution,</td>
<td>$S_0$</td>
<td>1.38 ± 0.23</td>
<td>0.84 ± 0.34</td>
<td>0.69 ± 0.40</td>
</tr>
<tr>
<td>$d_0-d_1/d_0+d_1$</td>
<td>$S_2$</td>
<td>1.02 ± 0.18</td>
<td>0.82 ± 0.36</td>
<td>0.67 ± 0.40</td>
</tr>
<tr>
<td>Adjusted*</td>
<td>$S_0$</td>
<td>0.76 ± 0.02</td>
<td>0.91 ± 0.02</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>0.79 ± 0.07</td>
<td>0.86 ± 0.07</td>
<td>0.00 ± 0.02</td>
</tr>
</tbody>
</table>

*Effective coordinates determined from the rotational constants. See text.
Substitution coordinates determined from Kraitchman’s equations for single isotopic substitution of a nonplanar asymmetric top molecule (Ref. 1).
Substitution coordinates determined from Kraitchman’s equations for a disubstituted molecule belonging to the $C_2$ point group (Ref. 1).
Adjusted effective coordinates determined from the modified structure described in the text.

by deuterium. It is found that $\Delta R = 0.008 \pm 0.002$ Å, $\Delta \theta = 0 \pm 0.3^\circ$, and $\Delta \phi = 0.96 \pm 0.03^\circ$ in the ground state, and that $\Delta R = 0.003 \pm 0.002$ Å, $\Delta \theta = 0 \pm 0.3^\circ$, and $\Delta \phi = 0.86 \pm 0.03^\circ$ in the excited state. Thus, we conclude that deuterium substitution increases the intermolecular heavy-atom distance and out-of-plane angle, but has little or no effect on the heavy-atom in-plane angle. Stated differently, the average positions of the bridging hydrogen atoms change when hydrogen is replaced by deuterium because of vibrational motions along these two coordinates. Notably, the observed isotopically induced structural changes in the effective structure are smaller in the excited state, which has the weaker hydrogen bonds.

The differences between the calculated rotational constants of the disubstituted dimer with and without the corrected geometry can be applied as a correction to the experimental rotational constants. These corrected experimental rotational constants were used in Kraitchman’s equations to demonstrate the validity of our procedure. The resulting adjusted experimental amine hydrogen coordinates also are compared to the substitution and effective coordinates in Table II. As expected, there is poor agreement between the substitution and the adjusted coordinates, and excellent agreement between the effective and adjusted coordinates. Obviously, small changes in the effective geometry of the dimer produce large displacements of the substituted atom, in both electronic states. It is this sensitivity that we have exploited to determine the coordinates along which the averaging occurs.

**DISCUSSION**

The 2-pyridone dimer has a nearly ideal geometry for the formation of strong intermolecular hydrogen bonds. The ground-state values of $R = 2.77$ Å (2.87 Å in $S_1$) and $\theta = 121.8^\circ$ are very similar to those found in a wide variety of systems. For example, the gas-phase value of $R$ for (2PY), in the ground state lies within 1Å of the distribution found for 1357 intermolecular hydrogen bonds in a recent survey of 889 organic crystal structures. The N–H⋯O distance also is nearly the same as that found for cyclic dimers of carboxylic acids and amides by microwave spectroscopy. Additionally, the C–O⋯(H–N) angle conforms nicely to the HOMO–LUMO, covalent model of hydrogen bonding developed by Klemperer and co-workers. In this model, the hydrogen bond is viewed as an electron donor–acceptor complex in which a pair of electrons from the highest occupied molecular orbital of the Lewis base is donated to the lowest unoccupied molecular orbital of the Lewis acid. In (2PY)$_2$, the oxygens of the C–O groups are the Lewis bases and the N–H groups are the Lewis acids. Maximal overlap between the HOMO and the LUMO would result if the oxygen lone pairs were sp$^2$ hybridized and the acceptor orbitals are axially symmetric about the N–H bonds, giving an angle $\theta = 120^\circ$. The observed values of $R$ and $\theta$ also conform to the electrostatically based rules of VSEPR theory. The data for (2PY)$_2$ in the gas phase thus demonstrate that the environment plays a minor role in determining the geometry of an intermolecular hydrogen bond when the connected units can adopt a configuration that meets the criteria for strong bond formation, including those originally proposed by Pauling and Corey.

We may understand the effect of deuterium substitution on the properties of these bonds in the following way. Shown in Fig. 5 are cross sections of the Lippincott–Schroeder potential for N–H⋯O hydrogen bonds for two values of $R$, $R = 2.77$ Å (as a model for the $S_0$ surface) and $R = 2.87$ Å (for the $S_1$ surface). Each potential exhibits two minima when plotted as a function of the N–H distance. The inner minimum corresponds to the covalent structure N–H–O and the outer minimum corresponds to the ionic, proton-transferred structure N$^+$⋯O$^-$· O$. The existence of the outer minimum creates an anharmonicity in the potential of the more stable covalent form. This anharmonicity, in turn, is responsible for the increase in the heavy-atom distance $R$ when deuterium is substituted for hydrogen. Thus, the smaller amplitude zero-point vibration of the heavier deuterium atom results in a smaller average N–H(D) distance. This decreases the orbital overlap in the hydrogen bond and produces an increase in $R$. Model calculations show that this increase can be as large as 0.01 Å for $R$ values of order 2.8 Å. This value of $\Delta R$ is consistent with the value observed for $S_0$ (2PY)$_2$, $\Delta R = 0.008$ Å. Moreover, Fig. 5 shows that the anharmonicity decreases as the heavy-atom separation increases, in weaker hydrogen bonds. Smaller values of $\Delta R$ are then expected when hydrogen is replaced by deuterium. The value $\Delta R = 0.003$ Å for the $S_1$ state is again consistent with these expectations, since $R$ is 0.10 Å larger in this state. These increases in $R$, in both states of (2PY)$_2$, cannot be explained by a purely electrostatic model of the hydrogen bond. The smaller average N–D distance would decrease the intermolecular repulsive forces between the two monomer units, and thus decrease $R$. The two minima in Fig. 5 owe their origin to the two...
Limiting positions of attachment of a proton to the two basic sites. In general, both the covalent N-H···O and the ionic N-···H-O structures are important contributors to the properties of hydrogen bonds. However, in the case of (2PY)$_2$, the covalent structure is the dominant one in both electronic states. Its importance increases on excitation to the excited states, which have the weaker hydrogen bonds. The magnitude of $\Delta I$ is larger for the $d_0$-$d_1$ dimer. These results suggest that the dimer executes larger-amplitude out-of-plane vibrational motions when $R$ is increased, either by electronic excitation or by deuterium substitution. In other words, the in-plane and out-of-plane modes are coupled. A full description of the hydrogen bond will require the inclusion of both types of motion.

A still more sensitive probe of the properties of the hydrogen bonds in (2PY)$_2$ is provided by the single isotopic substitution experiment. We find, in (2PY)$_2$-$d_1$, that the inertial defect of the $S_0$ state has the same sign and is only slightly larger in magnitude than that of the $S_0$ state of (2PY)$_2$, $-1.416$ vs $-1.299$ amu Å$^2$. However, $S_2$ (2PY)$_2$-$d_1$ has $\Delta I = 3.448$ amu Å$^2$, compared to values of $-3.029$ and $-3.924$ amu Å$^2$ for (2PY)$_2$ and (2PY)$_2$-$d_2$, in their $S_2$ states. Now, the structural changes that are produced by replacement of one hydrogen by deuterium need not be symmetric about the center of mass. Suppose we assume that only one N-H···O bond increases in length, the one that is deuterium substituted. Several other types of simultaneous motion may occur. One is an expansion of the second N-H···O bond. A second is an in-plane rotation of one pyridone ring with respect to the other. This motion could bring the remaining hydrogen into a more favorable position with respect to the oxygen lone pair, possibly increasing the strength of at least one hydrogen bond. Our rotational constant data for the $S_0$ state are most consistent with this possibility. A third possibility is an out-of-plane rotation of one pyridone ring with respect to the other. Our data for the $S_2$ state, which show a positive inertial defect, are most consistent with this possibility, which could result in a decrease in the strength of at least one hydrogen bond. Motions of this type may explain why distortion terms improve the fit to the rotational structure of the $d_0$-$d_1$ band.

Possible changes in bond strength with single isotopic substitution could explain the anomalous isotope shifts of the $S_1$-$S_0$ band origins in (2PY)$_2$. In the delocalized excitation limit, the shift produced by single isotopic substitution should be exactly half of that produced by double isotopic substitution of the symmetric dimer. We find that the $d_0$-$d_1$ dimer is shifted 0.635 cm$^{-1}$ to the blue of the $d_1$-$d_1$ dimer, which in turn is shifted 10.122 cm$^{-1}$ to the blue of the $d_0$-$d_0$ dimer. One way to account for the former result is to postulate that the force constants associated with the six intermolecular vibrational modes are affected differently by single and double isotopic substitution. A blue shift of the $d_0$-$d_1$ dimer with respect to the $d_1$-$d_1$ dimer could, for example, be explained by an increase in one bond strength. If hydrogen is replaced by deuterium. These displacements are not large. Thus, the dihedral angle $\phi$ is zero in the protonated dimer in both electronic states, and increases to 0.96° in $S_0$ (2PY)$_2$-$d_1$ and 0.86° in $S_2$ (2PY)$_2$-$d_2$. We believe that the equilibrium geometry of both states of (2PY)$_2$-$d_2$ is still planar; i.e., that the small, nonzero values of $\phi$ reflect increasing amplitudes of vibration along one or more out-of-plane coordinates. This view is consistent with the signs of the observed inertial defects, which are negative in both cases. However, the magnitudes of $\Delta I$ are larger in the excited states, which have the weaker hydrogen bonds. The magnitude of $\Delta I$ also is larger for the $d_1$-$d_1$ dimer. These results suggest that the dimer executes larger-amplitude out-of-plane vibrational motions when $R$ is increased, either by electronic excitation or by deuterium substitution. In other words, the in-plane and out-of-plane modes are coupled. A full description of the hydrogen bond will require the inclusion of both types of motion.

A still more sensitive probe of the properties of the hydrogen bonds in (2PY)$_2$ is provided by the single isotopic substitution experiment. We find, in (2PY)$_2$-$d_1$, that the inertial defect of the $S_0$ state has the same sign and is only slightly larger in magnitude than that of the $S_0$ state of (2PY)$_2$, $-1.416$ vs $-1.299$ amu Å$^2$. However, $S_2$ (2PY)$_2$-$d_1$ has $\Delta I = 3.448$ amu Å$^2$, compared to values of $-3.029$ and $-3.924$ amu Å$^2$ for (2PY)$_2$ and (2PY)$_2$-$d_2$, in their $S_2$ states. Now, the structural changes that are produced by replacement of one hydrogen by deuterium need not be symmetric about the center of mass. Suppose we assume that only one N-H···O bond increases in length, the one that is deuterium substituted. Several other types of simultaneous motion may occur. One is an expansion of the second N-H···O bond. A second is an in-plane rotation of one pyridone ring with respect to the other. This motion could bring the remaining hydrogen into a more favorable position with respect to the oxygen lone pair, possibly increasing the strength of at least one hydrogen bond. Our rotational constant data for the $S_0$ state are most consistent with this possibility. A third possibility is an out-of-plane rotation of one pyridone ring with respect to the other. Our data for the $S_2$ state, which show a positive inertial defect, are most consistent with this possibility, which could result in a decrease in the strength of at least one hydrogen bond. Motions of this type may explain why distortion terms improve the fit to the rotational structure of the $d_0$-$d_1$ band.

Possible changes in bond strength with single isotopic substitution could explain the anomalous isotope shifts of the $S_1$-$S_0$ band origins in (2PY)$_2$. In the delocalized excitation limit, the shift produced by single isotopic substitution should be exactly half of that produced by double isotopic substitution of the symmetric dimer. We find that the $d_0$-$d_1$ dimer is shifted 0.635 cm$^{-1}$ to the blue of the $d_1$-$d_1$ dimer, which in turn is shifted 10.122 cm$^{-1}$ to the blue of the $d_0$-$d_0$ dimer. One way to account for the former result is to postulate that the force constants associated with the six intermolecular vibrational modes are affected differently by single and double isotopic substitution. A blue shift of the $d_0$-$d_1$ dimer with respect to the $d_1$-$d_1$ dimer could, for example, be explained by an increase in one bond strength.
(relative to the $d_1$--$d_1$ dimer) and/or a decrease in one bond strength in $S_1$ (again, relative to the $d_1$--$d_1$ dimer), changes that are consistent with the observed rotational constants.

At least three factors contribute to the blueshift of $\sim 10$ cm$^{-1}$ in the energy of the $S_2$ $\rightarrow$ $S_0$ transition of the $d_1$--$d_1$ dimer relative to that of the $d_0$--$d_0$ dimer. One is the change in zero-point energies ($ZPE$'s) of the $S_0$ and $S_2$ states. Now, the dimer formation energy of 2-pyridone in its $S_0$ state has been estimated to lie in the range 65.3--68.2 kJ mol$^{-1}$ by NMR spectroscopy and CNDO/2 calculations. Thus, the $S_0$ state of the $d_0$--$d_0$ dimer lies $\sim 5500$ cm$^{-1}$ below that of the $S_0$ state of the monomer. The blue shift of the $d_0$--$d_0$ dimer band relative to that of the monomer is $\sim 1000$ cm$^{-1}$, so the dimer formation energy of 2-pyridone in its $S_2$ state is of order $\sim 4500$ cm$^{-1}$. Taking 10% of these energies as upper limit values of the changes in $ZPE$'s of the two states, this factor produces a blue shift of the $d_1$--$d_1$ band of $\sim 100$ cm$^{-1}$ or less. A second factor is the change in hydrogen-bond energy with deuterium substitution, due to bond expansion. Increasing the heavy atom separation by 0.01 Å produces a decrease in the energy of a single hydrogen bond of $\sim 85$ cm$^{-1}$ since $R$ increases more in the ground state of ($2PY$)$_2$ than in ($2PY$)$_2$, this produces a red shift of the $d_1$--$d_1$ band. We calculate a value of $\sim 70$ cm$^{-1}$ for this shift based on the measured $\Delta R$ values of the two bonds in the two electronic states.

There also is a shift in the energies of the $S_1$ $\rightarrow$ $S_0$ transition of the symmetric dimers due to exciton interactions. As noted earlier, the delocalized excited states of ($2PY$)$_2$ may be described by symmetric and antisymmetric linear combinations of localized excited states, on one monomer unit or the other, split by some interaction energy $\Delta E$. In simple exciton theory, $\Delta E$ is the energy of interaction of two transition charge densities ($\mu$), one for each monomer unit, which depends on the inverse cube of their separation $\rho$ and an orientation factor. In ($2PY$)$_2$, the orientation of the transition moments is such that $\Delta E = 2\mu^2/\rho^3$, with the symmetric linear combination ($\mu^2$ state) lying higher in energy. Deuterium substitution increases $\rho$, reducing $\Delta E$. This produces a red shift of the $d_1$--$d_1$ band relative to the $d_0$--$d_0$ band. Comparing the observed blue shift of $\sim 10$ cm$^{-1}$ to the estimated magnitudes and directions of the shifts due to $ZPE$ effects and bond expansion, we see that the value of $\Delta E$ in ($2PY$)$_2$ cannot exceed $20$ cm$^{-1}$. Notably, all previous estimates of this exciton interaction energy, or Davydov splitting, by isotopic substitution methods have neglected the expansion of bonds that occurs when a light isotope is replaced by a heavier one. This "correction" is very large, much larger than the Davydov splitting in ($2PY$)$_2$.

**Summarizing,** we have used deuterium atom substitution, and its effect on the fully resolved $S_1$ $\rightarrow$ $S_0$ electronic spectrum of the cis-peptide-like 2-pyridone dimer, to probe the properties of the two intramolecular N--H $\cdots$ O hydrogen bonds that link the two monomer units together, in both electronic states of the isolated molecule. We find that deuterium substitution produces an expansion of the two bonds in the $C_{2h}$ symmetric ($2PY$)$_2$--$d_2$ dimer. Additionally, replacing one or two hydrogens with deuterium produces significant displacement(s) along one or more out-of-plane vibrational coordinate(s). Quantitative estimates of these structural changes (from the spectral data) and the resulting changes in the hydrogen-bonding energy (from the Lippincott--Schroeder potential) have been made. From these comparisons we deduce that the barrier to proton transfer increases on electronic excitation. We also find that the symmetric dimer is an energy delocalized dimer in its $S_2$ state, and that the deuterium-induced changes in structure produces changes in the $S_1$ $\rightarrow$ $S_0$ transition energy that are larger than the Davydov splitting. An estimate of this interaction energy, $\Delta E \leq 20$ cm$^{-1}$, is provided.

**ACKNOWLEDGMENTS**

This work has been supported by the NSF. Structure calculations were performed on the Departmental FPS-500 vector processor machine and on the Cray Y/MP at the Pittsburgh Supercomputing Center. We thank D. F. Plusquellec for helpful discussions.