J. Phys. Chem. A **2002,** *106,* 5828−5831

Homoconjugated (NH···N)$^-$ Hydrogen Bonds with Great Proton Polarizability—FTIR and NMR Studies

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Received: February 14, 2002

Nine NH acids with pK_a values between 0 and 8.57 were studied by FTIR spectroscopy in the middle and far-infrared region. In addition, NMR spectra were taken and a semiempirical AM1 analysis of the systems performed. The proton potential in the NH···N$^-$ $\rightleftharpoons$ $^-$N···HN hydrogen bonds is almost the same. The proton polarizability of these hydrogen bonds is almost independent of the pK_a of the studied *N* acids. There is no relation between the position of the hydrogen bond vibration in the far-infrared region and the pK_a of the *N* acids. Only with the pyrrol, the pyrazol, and the 4,(5)-methylimidazol systems these hydrogen bonds are linear. With all other systems these hydrogen bonds are more or less strongly bent. The position of the hydrogen bond vibrations ν_σ calculated with the AM1 procedure agrees well with the experimentally obtained values. The chemical shift of the hydrogen-bonded proton increases in proportion to the pK_a values of the *N* acids.

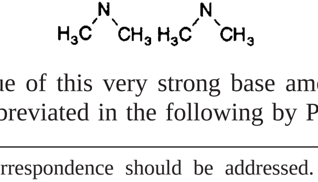
Introduction

Homoconjugated inter- and intramolecular B$^+$H···B $\rightleftharpoons$ B···H$^+$B as well as BH···B$^-$ $\rightleftharpoons$ $^-$B···HB hydrogen bonds are structurally symmetrical. A double minimum proton potential is present in these hydrogen bonds. The proton fluctuates within these hydrogen bonds. They show so-called proton polarizabilities due to shifts of the protons. These proton polarizabilities are about 2 orders of magnitude greater than the polarizabilities arising from distortion of electron systems.[1−4] When such bonds are present in systems infrared continua are observed in the spectra. Vice versa hydrogen bonds with great proton polarizability in systems are indicated by these infrared continua.[1−4] Many systems with N$^+$H···N $\rightleftharpoons$ N···H$^+$N bonds with great proton polarizability have been already studied.[5−15] In ref 14, it was shown that the infrared continua and hence the proton polarizability of the N$^+$H···N $\rightleftharpoons$ N···H$^+$N hydrogen bonds are almost independent of the pK_a of the N acceptors. Some systems with NH···N$^-$ $\rightleftharpoons$ $^-$N···HN were also already studied.[16−19] In ref 16 intermolecular and in refs 12, 17−19 intramolecular (NH···N)$^-$ bonds were investigated.

In the following, we study nine systems with NH···N$^-$ $\rightleftharpoons$ $^-$N···HN hydrogen bonds as a function of the pK_a of the N acids.

Experimental Section

We performed the deprotonation of the NH groups with the very strong *N* base 1-ethyl-2,2,4,4,4-pentakis-(dimethylamino)-2λ^5,4λ^5-catenadi-(phosphazene) shown in the formula.



The pK_a value of this very strong base amounts to 33.4.[21] This base is abbreviated in the following by P$_2$Et.

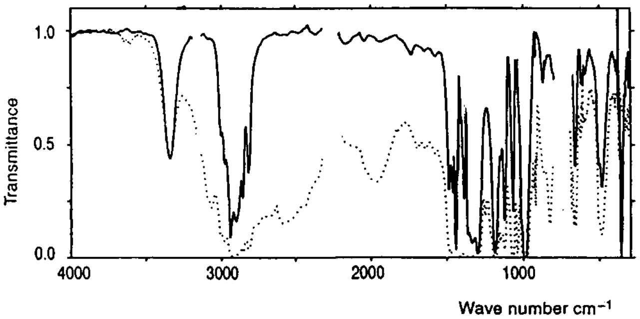


Figure 1. FTIR-spectra of the (—) 1:1 complex of the phosphazene base P$_2$-Et with HAuCl$_4$ (········) 2:1 of imidazol with the phosphazene base P$_2$Et.

To show that a complete deprotonation is reached with P$_2$Et we compared the intensity of the ν(NH) vibration of the complex imidazol − P$_2$Et with the ν(NH) vibration of P$_2$Et protonated with the strong acid HAuCl$_4$.

This result is shown in Figure 1. At 3343 cm^{-1} the band of the NH stretching vibration is observed. The intensity of this band is the same with the imidazol − P$_2$Et complex and the HAuCl$_4$ − P$_2$Et complex. Hence, we can use in the following the intensity of this band to determine the degree of the deprotonation of the NH groups of the NH acids.

Results and Discussion

Proton Polarizability of the $^-$N···HN $\rightleftharpoons$ HN···N$^-$ Hydrogen Bonds. The semideprotonated *N* bases formed in acetonitrile of the complexes are shown in Figure 2. We studied these homoconjugated complexes of nine NH acids with pK_a values between 0 and 8.57. They are summarized together with their pK_a values in Table 1.

Figure 3 shows the infrared spectra of five selected systems. In all cases intense infrared continua are found. They begin at about 3000 cm^{-1} and extend down toward smaller wavenumbers over the whole region studied. These infrared continua demonstrate that the NH···N$^-$ $\rightleftharpoons$ $^-$N···HN hydrogen bonds show great proton polarizability since the protons within these bonds

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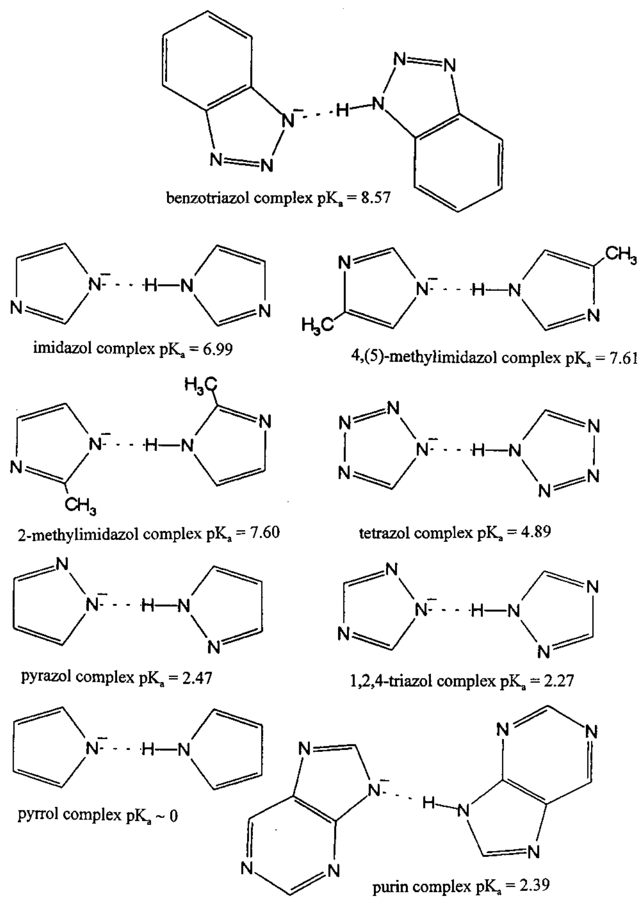

Figure 2. Structural formulas of the semideprotonated *N*-base complexes (proton limiting structure with the proton on the right-hand side).

TABLE 1: Systems Studied, the pK_a Values and the Hydrogen Bond Vibration and band at about 1940 cm^{-1}

system	pK_a	ν_σ [cm^{-1}] exper.	ν_σ [cm^{-1}] AM1	wavenumber [cm^{-1}]
benzotriazol	8.57	138	126	1919
4-(−5) methylimidazol	7.61	137	133	1948
2-methylimidazol	7.60	153	134	1948
imidazol	6.99	143	145	1948
tetrazol	4.89	155	161	1964
pyrazol	2.47	137	133	1977
purin	2.39	110	114	1893
1,2,4-triazol	2.27	138	133	
pyrrol	~0	109	114	1937

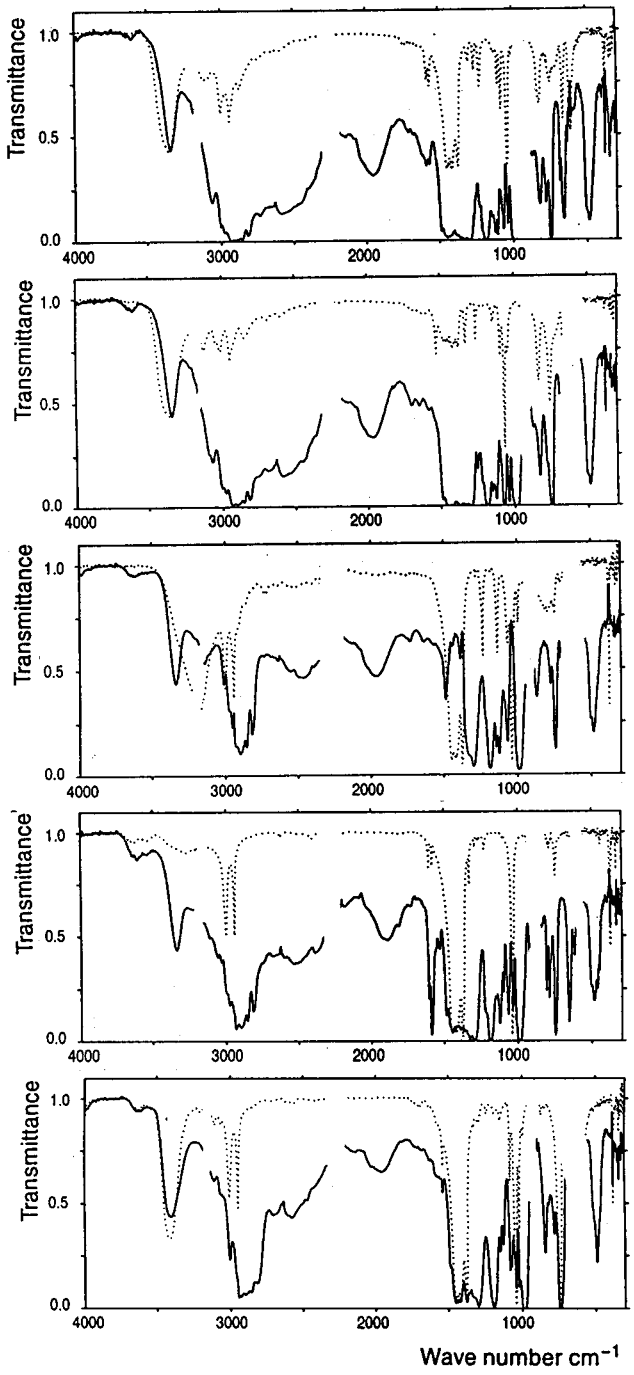

Figure 3. FTIR-spectra of the(—) complex, (········) *N* acid. 4-(5)-methylimidazol: P$_2$Et-base, 2:1, pK_a = 7.61 imidazol: P$_2$Et-base, 2:1, pK_a = 6.99 tetrazol: P$_2$Et-base, 2:1, pK_a = 4.89 purin: P$_2$Et-base, 2:1, pK_a = 2.39 pyrrol: P$_2$Et-base, 2:1, pK_a ≈ 0.

fluctuate and can easily be shifted. The observed wavenumber dependent intensity distributions of these continua are almost the same with all systems. They are independent of the respective *N* bases. Thus, the proton potential and the proton polarizability of the NH···N$^-$ $\rightleftharpoons$ $^-$N···HN bonds are almost independent of the pK_a of the *N* bases studied.

Hydrogen Bond Vibration in the Far-Infrared. Figure 4 shows the hydrogen bond vibration in the far-infrared region for six selected examples. In Table 1, in column 5 the wavenumber values of this band are summarized. This table shows that there is no relation between the pK_a value and the position of the hydrogen bond vibration.

To clarify whether these hydrogen bonds are linear or bent, we plotted the reciprocal square of the reduced mass

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

over the wavenumber (Figure 5). If the hydrogen bonds are linear the points are on a straight line because the center of gravity of these molecules is on the hydrogen bond axis. This is true only in the cases of the pyrrol, the 4,(5)-methylimidazol and the pyrazol systems. With all other systems the NH···N$^-$ $\rightleftharpoons$ $^-$N···HN hydrogen bonds are more or less strongly bent.

Semiempirical AM1-Analysis. The geometry of the complexes was optimized using the semiempirical AM1-procedure. These results confirm the experimental finding that only if the center of gravity of the mass is on the hydrogen bond axis the energy becomes minimal with a hydrogen bond angle of 180° in the complexes. All other hydrogen bonds are more or less bent.

Using this optimized geometry the wavenumber values of

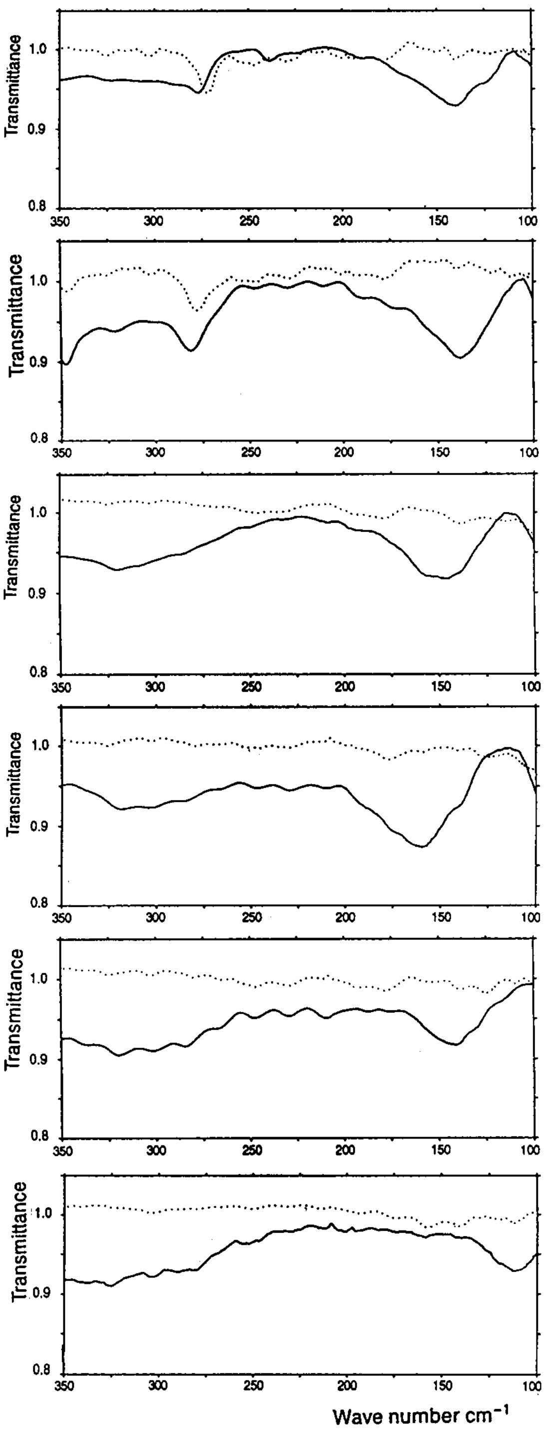

Figure 4. Far-infrared region of the FTIR spectra of:benztriazol: P_2Et-base, 2:1, pK_a = 8.57 4-(5)-methylimidazol: P_2Et-base, 2:1, pK_a = 7.60 imidazol: P_2Et-base, 2:1, pK_a = 6.99 tetrazol: P_2Et-base, 2:1, pK_a = 4.89 1.2.4-triazol: P_2Et-base, 2:1, pK_a = 2.27 pyrrol: P_2Et-base, 2:1, pK_a ≈ 0.

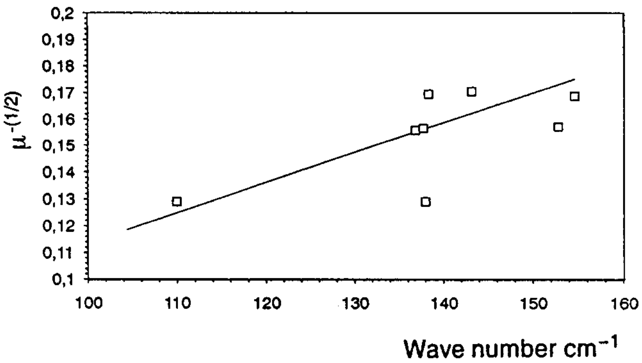

Figure 5. Square of the reduced mass, $\mu^{-1/2}$ over the wavenumber

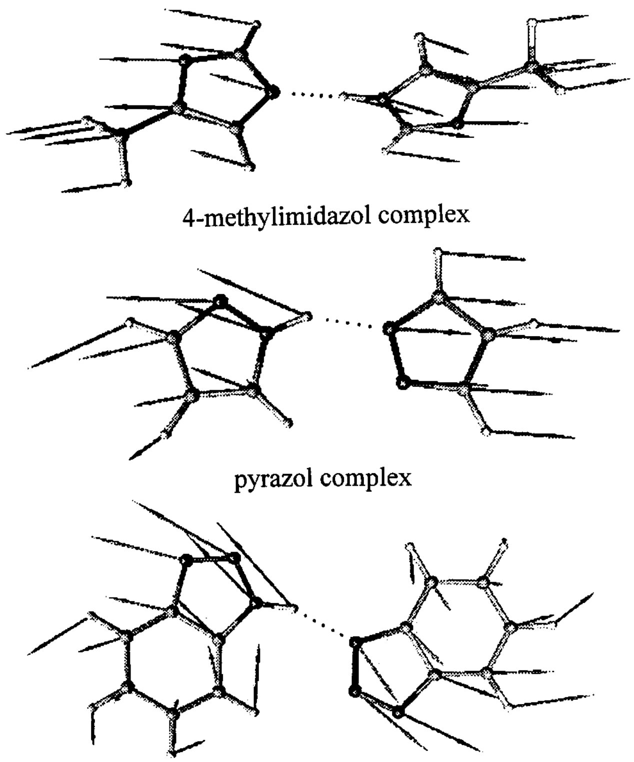

Figure 6. Hydrogen bond vibration of three complexes.

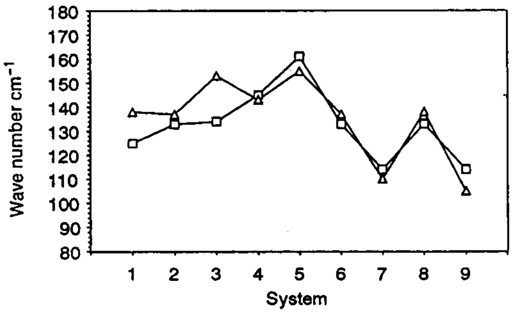

Figure 7. Comparison of the experimentally obtained with the calculated wavenumber values.

the hydrogen bond vibrations were calculated using the AM1-procedure. Three examples are shown in Figure 6. The geometry of the vibrations in Figure 6 confirms the experimental result that the complexes cannot be described by a point mass model.

The comparison of the theoretical with the experimental ν_σ values in Table 1 and Figure 7 shows that there is a good agreement with exception of the benztriazol and 2-methylimidazol systems.

In Figure 8, for some selected systems the chemical shift is shown as a function of the pK_a of the *N* acids. The chemical shift increases with increasing pK_a of the *N* acids. Hence, with increasing pK_a of the *N* acids the hydrogen-bonded proton becomes more and more deshielded.

Conclusions

With the nine semideprotonated *N* bases investigated the infrared continuum and hence the proton potential and the proton

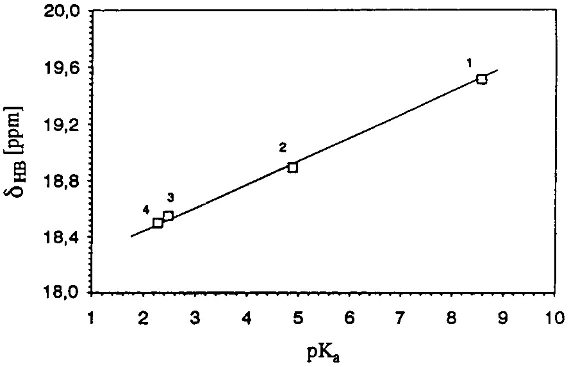

Figure 8. Chemical shift as a function of the pK_a of the *N* acids. 1, the benztriazol; 2, the tetrazol; 3, the pyrazol; and 4, the 1.2.4-triazol systems.

polarizability of the NH···N$^-$ ⇌ $^-$N···HN hydrogen bonds are almost independent of the pK_a of the *N* bases studied (pK_a range 8.5−0).

There is no relation between the pK_a of the *N* acids and the position of the hydrogen bond vibration observed in the far-infrared region. Only with the pyrrol, the 4,(5)-methylimidazol and the pyrazol systems the NH···N$^-$ ⇌ $^-$N···HN bonds are linear. With all other systems the hydrogen bonds are more or less strongly bent.

The positions of the hydrogen bond vibrations ν_σ calculated with the AM1-procedure agree well with the experimentally obtained values. This is true for all systems with exception of the benztriazol and the 2-methylimidazol systems. The chemical shift of the hydrogen-bonded proton increases in proportion to the pK_a values of the *N* bases. This result indicates a deshielding of the hydrogen-bonded proton with increasing pK_a value of the *N* acids.

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