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Qualitative Analysis of the Geometry of the Hydrogen Bond in the Homoconjugated Pyridine Ion

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Abstract — A theoretical analysis of the geometry of the isolated homoconjugated ion formed by interaction of the pyridine molecule with the pyridinium cation was performed. With no *o*-substituents and no external electric field applied, the hydrogen bond is strongly asymmetric and is characterized by a low barrier to proton transfer between the two chemically equivalent structures. According to the calculations, the most probable averaged distance between the nitrogen atoms forming the hydrogen bond in such homoconjugated cations is about 2.7 ± 0.1 Å.

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The hydrogen bond geometry is sensitive both to steric effects preventing the mutual approach of the interacting molecules [1] and to the effect of an external electric field on the complex in a polar solvent [2–5]. In experimental studies of hydrogen-bonded complexes, variation of these paameters is not always possible. For example, in NMR studies of hydrogen-bonded complexes in the liquid phase, a serious experimental problem is fast (in the NMR time scale) proton and intermolecular exchange. These dynamic processes lead to averaging of the signals corresponding to complexes of different geometries, thus strongly reducing the information content of the experimental spectra. Exchange processes can be efficiently decelerated by decreasing the measurement temperature. For example, with liquefied freons, the experiments can be performed at 100–150 K [2–5]. However, at present this is the only solvent having the required properties. Thus, it is impossible to vary significantly the solvent polarity. On the other hand, variation of steric characteristics of the molecules under consideration may either require synthesis of complex, often isotopically substituted molecules or cause acceleration of the proton and intermolecular exchange.

A classical example illustrating problems with the separation of these contributions is the hydrogen bond in the homoconjugated ion formed by interaction of the 2,4,6-trimethylpyridine (collidine, Col) molecule with the 2,4,6-trimethylpyridinium (collidinium, $[ColH^+]$) cation in a mixture of liquefied freons [6] (Fig. 1). A thorough analysis made in [6] showed that the hydrogen bond under consideration is asymmetric but the proton forming this bond is involved in fast exchange between two chemically equivalent structures: $[ColH\cdots Col]^+ \rightleftarrows [Col\cdots HCol]^+$. Experimental data do not explain why the bond is asymmetric. On the one hand, relatively bulky methyl groups in the *o*-position could prevent mutual approach of the molecules to a distance required for the formation of a short hydrogen bond in which the binding proton would interact equally strongly with both nitrogen atoms forming the hydrogen bridge. On the other hand, the solvent used in the experiments has a very high dielectric permittivity at low temperatures [3], and minor fluctuations of the distribution of polar solvent molecules solvating the cation may cause its asymmetrization and determine the rate of the proton exchange between the two nitrogen atoms. Up to now, no experimental approach was found for separating the contributions under discussion. The effect of steric factors on the geometry of $[ColHCol]^+$ should be considerably weaker in the homoconjugated pyridine cation $[PyHPy]^+$. However, preliminary experiments showed that the lifetime of this cation is relatively short even at about 100 K. The extent of symmetry of the hydrogen bridge $[NH\cdots N]^+$ in such systems was examined in numerous studies [7–11]. In all the cases, only asymmetric structures of type $[NH\cdots N]^+$ were observed experimentally. It was assumed that asymmetrization of the hydrogen bridge is caused by polarization of the bond under the action of the external electric field of the solvent, whereas without electric field the bond should become symmetric [10]. This hypothesis, however, was not checked.

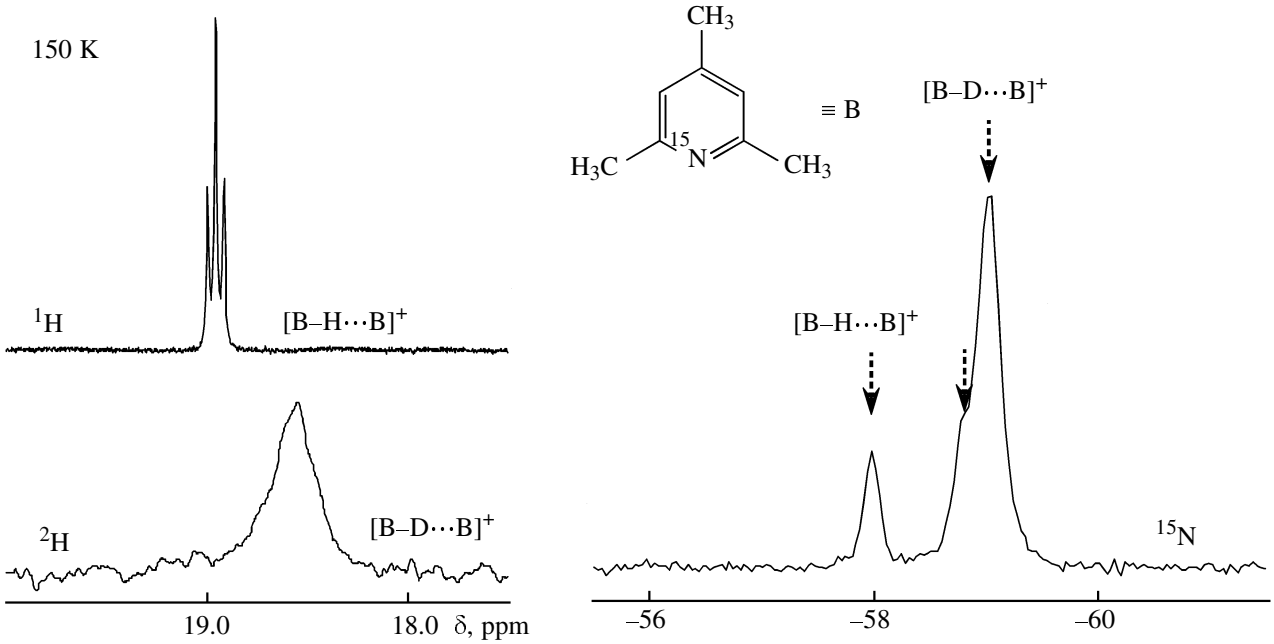

Fig. 1. NMR spectra of homoconjugated cations $[ColHCol]^+$ and $[ColDCol]^+$ in a mixture of liquefied freons CDF_3/CDF_2Cl at 150 K [6].

The main goal of this study was theoretical analysis of the geometry of the hydrogen bond in the homoconjugated ion formed by interaction of the pyridine (Py) molecule with the pyridinium ($[PyH]^+$) cation and of the mechanism responsible for the fast transfer of the binding proton in the case when this hydrogen bond is asymmetric. Additionally we examined the possibility of estimating the effect of a polar solvent and bulky *o*-substituents on the geometry of the homoconjugated cation.

The main goal was accomplished as follows. First we determined the structure of the hydrogen-bonded complex, optimal for the gas phase. For this geometry, we calculated the energy of the complex. Then the N···N bond length was varied, and for its fixed values the geometry of the complex was optimized, i.e., the energetically most favorable position of the binding proton was found, and the corresponding variation of the energy of the complex was determined. Finally, for several N···N bond lengths we determined how the energy of the complex changes when the binding proton is localized in the center of the hydrogen bridge. The validity of this approach for describing the geometry of hydrogen-bonded complexes with proton transfer was confirmed previously [12, 13]. The additional goal was accomplished as follows. For the optimized geometries of the perturbed complex with a fixed N···N bond length, we calculated the ^{15}N [δ(*N*H···N) and δ(NH···*N*)] and ^{1}H [δ(N*H*···N] chemical shifts for the nuclei directly involved in the formation of the hydrogen bridge; the calculated values were compared with the available experimental data.

The geometry of the complexes was optimized within the framework of the density functional theory (DFT) using the B3LYP/6-311++G(d, p) basis set, and the vibration frequencies for this geometry were analyzed to determine whether this geometry corresponds to the equilibrium state. The chemical shifts were calculated by the GIAO (Gauge-Invariant Atomic Orbital) method on the B3LYP/6-311++G(d, p) level. All the calculations were performed using the GAUSSIAN 98 package [14].

To account for a procedure for simulating the effect of various factors (solvent reactive field, steric effects) on the geometry of hydrogen-bonded complexes, it is necessary to consider general properties of such complexes, discussed previously [2–4]. Let us consider for simplicity the linear bridge N–H···N. The $r_{N–H}$ and $r_{N···H}$ distances are mutually dependent. Therefore, the effect of external factors can be simulated by forced variation of the r_{NN} distance, with optimization of the $r_{N–H}$ distance and of the geometry of the complex as a whole for each fixed r_{NN} distance. The linear geometry of the hydrogen bridge is forced if necessary.

Geometry of the N–H···N hydrogen bond in [PyHPy]$^+$. The geometric parameters and energy of the N–H···N hydrogen bond in $[PyHPy]^+$ at the equi-

Table 1. Geometric parameters and energies of the complex $[PyHPy]^+$ calculated for the equilibrium geometry, a series of fixed N···N distances, and selected transition states

$R_{N\cdots N}$, Å	r_{N-H}, Å	$r_{H\cdots N}$, Å	ΔE_e, kJ mol^{-1}	$R_{N\cdots N}$, Å	r_{N-H}, Å	$r_{H\cdots N}$, Å	ΔE_e, kJ mol^{-1}
10.0	1.016	8.984	98.25	2.686 [a]	1.109	1.577	0
4.0	1.026	2.974	56.27	2.686 [b]	1.343	1.343	9.67
3.5	1.037	2.463	36.08	2.65	1.118	1.532	0.22
3.0	1.063	1.937	9.70	2.6	1.137	1.463	1.27
2.85	1.078	1.772	3.18	2.6 [b]	1.3	1.3	3.58
2.85 [b]	1.425	1.425	33.17	2.5	1.25	1.25	6.86
2.75	1.094	1.656	0.56				
2.72 [c]	1.1	1.62	7.65				

[a] Equilibrium geometry. [b] Transition state. [c] Aromatic rings of pyridine molecules were forced in coplanar position.

librium geometry and at various fixed N···N distances are given in Table 1. At the equilibrium geometry, the N–H···N hydrogen bridge is asymmetric and the planes of the aromatic rings of the interacting pyridine molecules are mutually perpendicular. Despite this fact, the bond strength is about 98 kJ mol^{-1}, which is comparable in energy with the strength of the symmetric hydrogen bond in the $[ClHCl]^-$ anion [15, 16]. Fixation of the aromatic rings in the coplanar position causes the N···N distance to increase by 0.034 Å and the energy of the complex, by 7.65 kJ mol^{-1}. At the same time, if the planes of the aromatic rings of the interacting pyridine molecules are mutually perpendicular, the same increase in the energy is observed when the N···N distance is increased by approximately 0.3 Å relative to the equilibrium configuration. Shortening of the N···N distance by 0.19 Å leads to the shift of the binding proton to the center of the bridge but is accompanied by an increase in the energy of the complex by approximately 7 kJ mol^{-1}. However, the shift of the proton to the bridge center at the fixed N···N distance corresponding to the equilibrium configuration requires larger energy: 9.7 kJ mol^{-1}. The energetically preferable mechanism of proton transfer involves certain shortening of the N···N distance, e.g., to 2.6 Å, followed by the proton transfer; the barrier to this transformation is about 3.6 kJ mol^{-1} (Table 1).

The results obtained allow us to offer a qualitative description of the geometry of $[PyHPy]^+$ in a polar solvent and of the mechanism of fast proton exchange $[PyH\cdots Py]^+ \rightleftarrows [Py\cdots HPy]^+$. The equilibrium geometry of the cation is characterized by asymmetry of the hydrogen bond. Fluctuations of the electric field of the solvent, caused by reorientation of the molecules solvating the cation, will cause the proton transfer from one pyridine molecule to another. The proton transfer is apparently impossible without simultaneous mutual approach of the pyridine molecules, because this transfer pathway requires lower energy consumption. Analysis of the energies of the complex suggests that the mean distance between the nitrogen atom in $[PyHPy]^+$ should be about 2.7 ± 0.1 Å. The results of our calculations are well consistent with the crystallographic data. In a solid, the $[PyHPy]^+$ cation also forms an asymmetric hydrogen bridge [7, 9] whose geometry is slightly perturbed by the interaction with the anion. Indeed, the aromatic ring planes are turned relative to each other by 86.6°, and the bond is nonlinear (N–H···N angle about 172°) [9]. As a result, the N···N distance increases to 2.737(2) [9] or 2.755(5) Å [7] depending on the counterion.

Homoconjugated $[ColHCol]^+$ ion in a polar solvent. Is it possible to analyze the effect of a polar solvent and bulky *o*-substituents on the geometry of homoconjugated cations of substituted pyridines? The following general algorithm of solving such problems can be suggested. The shifts δ(*N*H···N), δ(NH···*N*), and δ(N*H*···N) are calculated for fixed values of the N···N bond length. The resulting values are compared with the available experimental data, which allows estimation of this distance for the complex in solution provided that the chemical shifts are strongly dependent on the N···N distance. In so doing, it would be desirable to use the ^{15}N chemical shifts, which are strongly dependent on the N–H distance [1, 12]. Optimization of the geometry of pyridines containing bulky substituents requires much time. However, it was shown that a decrease in the ^{15}N chemical shift with a decrease in the N–H distance is essentially the same for collidine and pyridine [17, 18]. This means that, to a first approximation, the problem can be solved with $[PyHPy]^+$ as example.

The ^{15}N and ^1H NMR chemical shifts calculated for certain fixed N···N distances are given in Table 2 and Fig. 2. Instead of the shielding constants σ(^{15}N) and σ(^1H) used in the theoretical calculations, we

present the chemical shifts relative to the free base (zero chemical shift) for ^{15}N and, as commonly accepted, relative to TMS for ^{1}H: $\delta(^{1}H) \equiv \sigma_{TMS}(^{1}H) - \sigma(^{1}H)$, $\sigma_{TMS}(^{1}H) = 31.97$ ppm.

As already noted, δ(*N*H···N) and δ(NH···*N*) strongly depend on the geometry of the hydrogen bridge, and the range of variation of these quantities for the free and protonated base covers 130 ppm [1, 17]. It is seen from the table that the calculated ^{15}N chemical shift in the pyridinium cation, –147 ppm, is close to the value of –130 ppm given by extrapolation of the experimental data [1, 5]. The wide range and monotonicity of variation of the chemical shift allow its dependence on the interatomic distance to be used for estimating the hydrogen bond lengths in various complex systems [18]. However, in the system under consideration the proton transfer is very fast in the NMR time scale, resulting in averaging of the observed ^{15}N chemical shifts: δ(*N*H*N*) = [δ(*N*H···N) + δ(NH···*N*)]/2. All the three quantities are plotted in Fig. 2. It is seen that the averaged chemical shift δ(*N*H*N*) only slightly depends on the N···N distance and cannot be used for solving the problem under discussion. Furthermore, the calculated averaged ^{15}N chemical shift is –85 ppm, whereas in the complex $[ColHCol]^+$ its experimental value is about –60 ppm [6]. We believe that the major cause of this discrepancy is a strong dependence of the chemical shifts of heavy nuclei on transverse vibrations of the binding proton [19], which was not taken into account in our calculations. At the same time, theoretical calculations predict a noticeable dependence of the averaged chemical shift on the N···N distance in the range 2.5–3.0 Å, in agreement with the experimental data. Recall that the secondary isotope effect, $^{1}\Delta N(D) = \delta(NDN) - \delta(NHN)$, cased by deuteration of the hydrogen bridge in $[ColH(D)Col]^+$, was –0.7 ppm [6]. However, analysis of so weak effects requires fundamentally different calculation procedures.

On the contrary, the effect of the transverse vibration of the binding proton on its chemical shift is considerably weaker [19]. The ^{1}H chemical shift in the $[ColHCol]^+$ cation is 19.9 ppm [6], which is somewhat lower than the theoretical value for $[PyHPy]^+$, about 21 ppm (Table 1). This difference is quite expected, because the geometry of the $[ColHCol]^+$ cation should be affected by the steric interactions of the bulky *o*-substituents. Theoretical calculations show that the mean distance between the nitrogen atoms should be about 2.7 Å in $[PyHPy]^+$ and about 2.8 Å in $[ColHCol]^+$.

Thus, we examined the geometry of the hydrogen bond in the homoconjugated ion $[PyHPy]^+$. We found

Table 2. ^{15}N and ^{1}H NMR chemical shifts calculated for the equilibrium geometry of the complex $[PyHPy]^+$ and for certain fixed N···N distances

$R_{N\cdots N}$, Å	δ(^{15}NH···N), ppm	δ(NH···^{15}N), ppm	δ(^{15}NH^{15}N), ppm	δ(N^{1}HN), ppm
10.00	–146.6	0	–73.3	10.5
5.00	–144.9	–12.9	–78.9	11.0
4.00	–141.6	–22.9	–82.3	12.0
3.50	–137.0	–31.5	–84.3	13.3
3.00	–126.5	–44.5	–85.5	16.6
2.85	–120.8	–49.9	–85.4	18.4
2.75	–115.6	–54.3	–85.0	19.9
2.686	–111.2	–57.8	–84.5	21.1
2.50	–82.7	–82.7	–82.7	25.5

that the N–H···N hydrogen bridge in this complex is strongly asymmetric: $r_{N-H} \approx 1.1$ Å, $r_{H\cdots N} \approx 1.6$ Å. Direct proton transfer in the equilibrium configuration of the complex is hardly probable as requiring considerable activation energy. The activation energy appreciably decreases at small shortening of the N···N distance (by less than 0.1 Å) accompanied by only a minor increase in the energy of the complex. Most probably, this mechanism is responsible for the fast proton exchange observed experimentally in the homoconjugated $[ColHCol]^+$ ion in a polar solvent [6].

Our analysis shows that the hydrogen bond in homoconjugated ions formed by pyridine or its more basic derivatives can be symmetric neither in the gas phase nor in a polar solvent. Paradoxical as it may

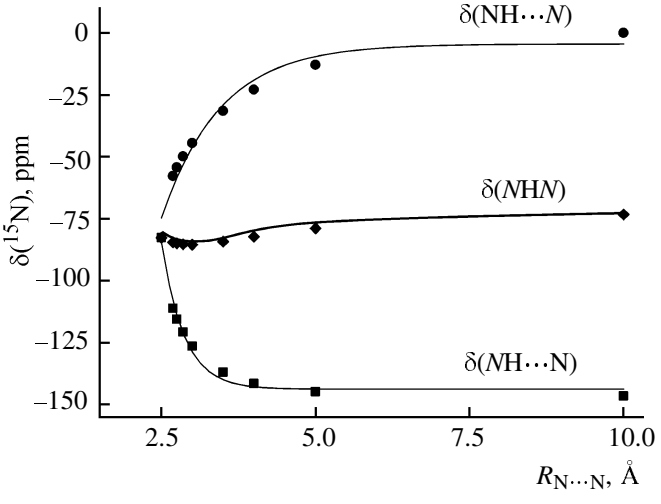

Fig. 2. ^{15}N NMR chemical shifts calculated for certain fixed N···N distances. The chemical shifts are given relative to the free base for which δ(^{15}N) is taken as zero.

seem, a symmetric hydrogen bond can probably be formed by weakly basic pyridine derivatives. In such complexes, the amplitude of vibrations of the binding proton may be sufficient for ensuring equally strong interaction of the proton with nitrogen atoms even at an N···N distance of the order of 2.7–2.8 Å.

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