ELSEVIER Journal of Molecular Liquids 67 (1995) 217 - 234

journal of MOLECULAR LIQUIDS

NMR STUDY OF PROTON LOCATION IN STRONGLY HYDROGEN BONDED COMPLEXES OF PYRIDINE AS INFLUENCED BY SOLVENT POLARITY

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Dedicated to Prof.P.L.Huyskens

Abstract

^{1}H,^{15}N and ^{13}C NMR spectra of H-bonded complexes of ^{15}N-enriched pyridine (Y) with various strong proton donors (XH) were obtained in a range of solvents with different dielectric constant at low temperature. Chemical shifts and nuclear magnetic relaxation times, T_1, were measured. A procedure for evaluating the mean N-H distance in the complexes using T_1 values for ^{15}N and ^{13}C nuclei treated as determined by dipole-dipole coupling with nearest protons is proposed. The results point to a gradual shift of the average proton position towards the N atom, with increasing the XH acidity. For a given complex, the N-H distance falls with the ε dielectric constant of a solvent, linear correlation between r_{N-H} and the reactive field factor, $F=(\varepsilon-1)/(2\varepsilon+1)$, being observed. The analogous correlation was found for the $\Delta\delta$ values. For interpretation of the effect, an anharmonic two-dimensional model of H-bond in connection with the Onsager-Butcher potential was used. It was found that the reactive field of a solvent causes the N-H bond to shorten due to the specific feature of the dipole moment function common for nearly all XH...Y and X^-...HY^+ complexes ($\partial\mu/\partial R_{Y-H}<0$). With the required parameters taken from IR spectra, this model gives a reasonable coincidence with the experimental Δr_{NH} values.

Introduction

The question of location of the bridging proton inside complexes with a very strong hydrogen bond was intensively discussed in literature for a long time [1-5]. The transformation of a molecular complex, XH...Y, into an ionic pair, X^-...HY^+, with strengthening the acid-base interaction can be performed in two ways, namely, by smooth shift of the proton equilibrium position or by the shift of the tautomeric equilibrium between two forms of the complex,

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SSDI 0167-7322 (95) 00877-2

$$XH...Y <===> X^{-}...HY^{+} \qquad (1)$$

In the case of intermediate interaction strength, the structure of the complex can correspond to the so-called "quasi-symmetric" H-bond, $X^{\delta-}...H...Y^{\delta+}$, or tautomerism involving the reversible proton transfer. The potential energy surface of the interaction contains either one broad minimum corresponding to the central position of the proton, or two minima separated by a barrier determining the frequency of the reversible proton transfer. Some experimental evidences are available for both the types of proton location and, respectively, of potential surface evolution with strengthening the acid-base interaction to be possible [6-8]. The "symmetric" type of proton location is characteristic of extremely strong and short hydrogen bonds, like in homo-conjugated ions, e.g., FHF^- and $[H_2O...H...OH_2]^+$. Some quantum chemical calculations [9,10] show that, with increasing the internuclear R_{X-Y} distance, the only potential minimum transforms into the double potential well, with the barrier height depending on this distance. The reversible intracomplex proton transfer is thus more characteristic of comparatively long H-bonds.

The question of how the solvent polarity influences H-bond strength and the proton location in intermolecular hydrogen bonds is unclear. The calorimetric data [11] point distinctly to some decrease in the complex formation enthalpy with solvent polarity rising. The same result was obtained [12] from the measured T-dependencies of the association constants. The weakening of H-bonds by a polar medium is, however, in a sharp contradiction to some data on the changes of spectral parameters sensitive to H-bond formation. Thus, in [13-16] it was found that the low frequency shift of the stretching ν_{XH} vibration for a range of polar XH...Y complexes rises by 10-50 % upon transfer from the gaseous phase to an apolar solvent, this rising proceeds with increasing the solvent dielectric constant, ε. This effect is largest for compact highly polar complexes, like $FH...N{\equiv}CH$. Since the frequency shift (as compared to the ν_{XH} vibration in "free" XH molecules) can be correlated with the H-bond enthalpy [17], these data may indicate some "strengthening" of intermolecular H-bonds upon their transfer into a polar medium.

In Ref.[18,19] an attempt of quantitative evaluation of the frequency shifts was made for two vibrations, ν_{XH} and ν_{XY}, using a two-dimensional anharmonic model of H-bond, the medium influence being taken into account using the Onsager-Butcher potential. This approach allowed to account for the medium effects observed in IR spectra of weakly H-bonded complexes. Besides, more direct manifestations of H-bond strengthening were predicted, i.e., some decrease of the R_{X-Y} H-bond length and increase of the r_{X-H} covalent bond length due to the polarization of a complex by the reactive field of a medium. The effect must be much more considerable for strongly H-bonded complexes with high values of dipole moment, μ, and its derivatives on the R_{X-Y} and r_{X-H} coordinates.

For experimental detection of this effect, a physical method is required providing the measurement of mean internuclear distances for molecules dissolved in liquids. At present, no general technique suitable for this purpose is known. When comparing structural parameters of H-bonds in the gaseous and crystalline states [1,2,20,21], the conclusion may be drawn that the same crystalline complexes are obviously more compact. In some cases the lengthening of an X-H bond upon the gas-solid state transfer was detected. Well-known examples of this effect are the HalH-amine complexes, which, while being molecular in the gas phase, give usually typical ionic crystals [22,23]. (The only gaseous complex having a structure close to an ionic pair is probably $(CH_3)_3N...HBr$, [23,24].) The origin of this transformation may be the influence of crystalline field as well as the co-operativity effect. At any rate, the influence of surroundings on the structure of easily polarisable hydrogen bonds can be very strong.

In the present paper the proton location in the complexes of ^{15}N isotopically enriched pyridine with various strong proton donors (carboxylic acids) in a range of aprotic solvents by means of different NMR techniques is studied. These very strongly H-bonded complexes are of most interest from the point of view of proton location. When considering IR spectra of the complexes with mono- and dichloroacetic acids, D.Barrow first suggested the molecular-ionic tautomerism involving reversible proton transfer [25]. This conclusion was, however, doubted by some authors [26,27] on the basis of extremely low frequency of the longitudinal proton vibration, close to that for the homo-conjugated bipyridinium ion. In Ref.[28] the so-called Evans holes were found on the broad band referred to this vibration corresponding to the frequencies of some skeleton vibrations of both XH and Y fragments, which can be considered as an indication to the symmetric type of proton location. However, the question of the structure of pyridine complexes with carboxylic acids like mono- and dichloroacetic acids is unclear so far.

In this paper an attempt is made to evaluate the mean internuclear N-H distance in dissolved complexes of pyridine. To solve this problem for the particular case of the X-H...N hydrogen bridges, the longitudinal magnetic relaxation time, T_1, for the ^{15}N nucleus can be used. This value is determined mainly by the magnetic dipole-dipole coupling of this nucleus with the nearest proton. In literature, some applications of the magnetic relaxation method to determination of internuclear distances between covalently unbound atoms and groups are available [29], although we have found no example of this method to be applied to studying geometry of hydrogen bonds in liquids.

Strong changes in the measured r_{NH} values are found with changing the solvent polarity. The results are interpreted using the model [18,19] combined with the dipole moment function proposed in [30].

Experimental

^{15}N-substituted pyridine (98.4 % isotope purity) was kindly put at our disposal by Prof. H.-H.Limbach (Freie Universitat Berlin). The solvents (dichloromethane-D_2, chloroform-D, difluorochloromethane CDF_2Cl, butyl chloride, squalane, hexachlorobutadiene, butyronitrile) from "Sigma" and

"Aldrich" were used without purification. The samples were prepared using a vacuum unit; oxygen was removed from the solutions by a conventional freezing-evacuating-thawing procedure.

NMR spectra were recorded on an AC-200 Bruker instrument (200.1 MHz for ^1H, 50.3 MHz for ^{13}C, 20.3 MHz for ^{15}N). To shift the equilibrium between the "free" molecules and the complexes, as well as to slow down intermolecular exchange processes, lowering the temperature down to 110-180 K was required, depending on the acid strength. The temperature was maintained and measured within the accuracy ±1 K using a BVT-1000 Bruker system and a special low temperature probehead. Absence of "free" pyridine molecules in solutions was verified by IR absorption spectra (an IFS 25 Bruker instrument).

As the problem of an ideal standard molecule for measuring ^{15}N chemical shifts is not yet solved, in the present research we used high long term stability of the frequency/magnetic field ratio of the instrument under the conditions of the internal deuterium lock (≤ 1 Hz/hour) which allowed to avoid using any standards. First, the absolute resonant frequency was measured for a solution containing pure pyridine (in a given solvent at 230 K). Then this frequency was measured for the same solution with an XH proton donor added. The chemical shift (ppm) due to complex formation was taken as: $\Delta\delta_N = (\delta_N - \delta_N^0)/\delta_N^0$.(This technique would correspond to using the "free" pyridine molecule as a standard in case of its NMR signals being observed separately.) The ^{13}C and ^{15}N chemical shifts were measured in the CPD regime.

The measurement of the T_1 values was performed using the conventional 180-τ-90 (INVREC) pulse sequence. The spectra were accumulated until the standard deviation upon computer processing the data becomes as low as $\Delta T_1/T_1=0.02$. The viscosity of solvents was varied by changing the temperature so that the T_1 values were found in a convenient region, 0.1 ÷ 5 s.

For measuring the mean N-H internuclear distance in the complexes, the following procedure suitable for liquid solutions is proposed. The time of longitudinal magnetic spin relaxation of nuclei with comparatively low magnetic moment, like ^{15}N and ^{13}C, in organic molecules, is determined mainly by dipole-dipole magnetic coupling with nearest protons, modulated by rotational diffusion [31]. In the "extreme narrowing limit" which holds for not very viscous liquids, the part of the relaxation rate due to the intramolecular coupling with the only proton is: $T_1^{-1}=h^2\gamma_X^2\gamma_H^2(r_{XH})^{-6}\tau_c$, where γ is the hyromagnetic ratio and τ_c - the correlation time for rotational diffusion. As far as pyridine complexes are concerned, the relaxation rate for its ^{15}N nucleus can be written as:

$$T_1^{-1}(NH)= h^2\gamma_N^2\gamma_H^2(r_{NH})^{-6}\tau_c + \mathit{T}_1^{\;-1}, \qquad (2)$$

where T_1 describes additional mechanisms of magnetic relaxation (caused mainly by magnetic coupling with two ortho-protons in the molecule and intermolecular coupling with nuclei of a solvent). To eliminate the unknown values, τ_c and T_1, experimental relaxation times for the 2-^{13}C pyridine nucleus and ^{15}N nucleus in the deuterio XD...Y complexes were drawn. It seems reasonable to assume that, under the identical conditions (solvent and temperature), the additional relaxation rate of the ^{15}N nucleus is the same (T_1 = const) for both XH...Y and XD...Y complexes. Some more suppositions were made: a)the molecule is rigid and, therefore, the only correlation time is valid for all the nuclei; b)the relaxation of the 2-^{13}C nucleus is determined by magnetic coupling with the only covalently bound proton; the r_{CH} distance is independent of H-bond formation and can be taken from literature; c)geometric parameters and rotational correlation times of the XH...Y and XD...Y complexes are identical. The last supposition is not quite correct, however, our evaluations showed that neglecting the difference cannot lead to the error in measuring r_{NH} more than 0.1%. Upon writing and solving the (2) equations for three relaxation times, $T_1(^{15}NH)$, $T_1(^{15}ND)$ and $T_1(^{13}CH)$, we obtain:

$$(r_{NH})^6 = (\gamma_N/\gamma_C)^2[1-(\gamma_D/\gamma_H)^2]\,\frac{T_1^{-1}(CH)}{T_1^{-1}(NH) - T_1^{-1}(ND)}\,(r_{CH})^6 \qquad (3)$$

With the experimental standard deviation, $\Delta T_1/T_1 = 0.02$, for the accuracy in evaluating r_{NH} the (3) equation gives $\Delta r/r \approx 0.008$. Actually, the reproduci-bility of thus measured r_{NH} distances did not exceed 0.3% (0.003 A). The account of additional relaxation mechanisms by accounting the $T_1^{-1}(ND)$ member proved to be essential only for high r_{NH} distances (> 1.3 A).

To check up the stability of obtained values, for one of the complexes, pyridine-acetic acid in butyl chloride, the measurements were performed in a temperature range, T= 150÷190 K. Due to a strong temperature dependence of the solvent viscosity, the obtained T_1 times varied by one order of magnitude. Nevertheless, the calculated r_{NH} value proved to be practically constant (1.376 ± 0.003 A). For another complex (the pyridinium perchlorate salt), the value r_{NH} =0.984 ±0.003 A can be compared with that obtained by neutron diffraction technique in the crystalline state (0.98 A, [1]).

Experimental Results

In Fig.1 the ^{1}H spectra of one of the examined systems, pyridine + formic acid in CDF_2Cl at ~120 K, with an excess of both the proton donor and proton acceptor, are represented as a typical example of low temperature NMR spectra of acid-base systems (some other examples are given in [32,33]). In an excess of pyridine, the only signal of the bridging proton is observed which can be assigned to the 1:1 complex. Its doublet splitting is due to spin-spin coupling with the CH-proton of formic acid (which was proved by a double resonance experiment), no sign of spin-spin coupling with the ^{15}N nucleus is

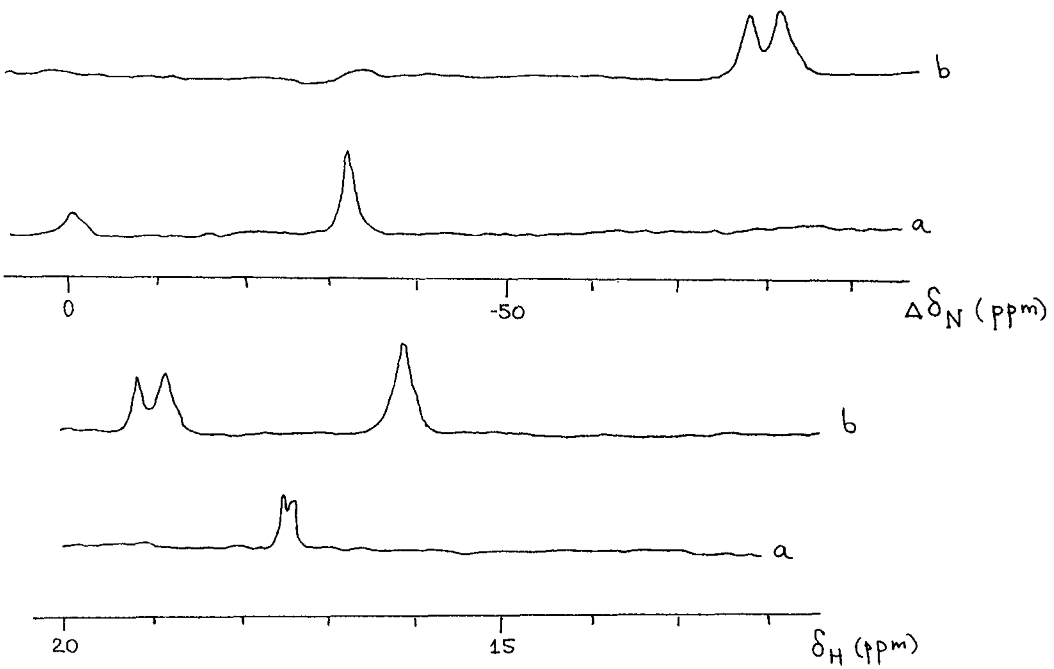

Fig. 1. ^{1}H (bottom) and ^{15}N NMR spectra (200 and 20.3 MHz, respectively) of solutions containing ^{15}N-enriched (98%) pyridine ($2 \cdot 10^{-3}$M) and formic acid ($1.7 \cdot 10^{-3}$M, (a); $4 \cdot 10^{-3}$M, (b)) in CDF_2Cl at 120 K.

seen. Thus, this complex must have a typical molecular structure, XH...Y. In the double excess of the acid, two low-field signals are observed, one of them coupled with the ^{15}N nucleus and the other being a broad singlet. This spectrum can be assigned to the 2:1 complex having a structure close to ionic, $XH...X^-...HY^+$. It is important that this formula cannot describe exactly the structure, as the J_{NH} value (65 Hz) is smaller than ~90-95 Hz, characteristic of the pyridinium cation [31]. Unfortunately, in this case the OH-signal broadening due to, probably, a residual intermolecular exchange deprives us of the possibility to measure another coupling constant, J_{HH}, in the homoconjugated anion, $XH...X^-$, even at 120 K. At any rate, all the spectra taken at the equimolar XH/Y ratio contain narrow well-resolved signals. This enabled us to consider spectral parameters obtained under these conditions as unaffected by any chemical exchange and assigned to the "pure" 1:1 complex. Complexes of more complicated composition will not be discussed in the present paper.

In Table 1 the measured chemical shifts of the ^{15}N nucleus, $\Delta\delta_N$, for a number of 1:1 pyridine complexes (in CD_2Cl_2 at 160 K) are presented together with the r_{N-H} mean value calculated from the equation (3) using r_{C-H} = 1.02 A. It is seen that increase of the XH acidity leads to gradual approaching the bridging proton to the nitrogen atom, from $r_{N-H} \approx 1.4$ A, which is characteristic of a strong hydrogen bond, to 0.98 A, typical for pyridinium cation with fully transferred proton. For the complex with dichloroacetic acid, an intermediate distance, r_{N-H} = 1.22 A, is found, which might be interpreted in terms of almost central proton location inside the bridge (the quasi-symmetric H-bond). However, this can be merely a result of time averaging in case of very fast ($\tau^{-1} >> \omega$, where ω is the NMR frequency) proton oscillation in a double well potential.

Fig.2 shows the dependencies of chemical shifts, $\Delta\delta_N$ and δ_H, on the mean r_{N-H} distance. With rising the XH acidity, the pyridine ^{15}N signal shifts monotonously upfield towards the value characteristic of the typical ionic salt, $PyH^+ClO_4^-$. This shift is explained by a decrease of the paramagnetic deshielding caused mainly by the contribution of an $n\pi^*$ triplet electronic state to the ground state [34]. With increasing the positive charge on the nitrogen atom, the energy difference between these levels rises. Thus, the ^{15}N upfield shift is determined by the "degree of proton transfer" and its correlation with the mean N-H distance is quite comprehensible.

As far as the bridging proton signal is concerned, its chemical shift goes through maximum (δ_H > 20 ppm). Analogous dependencies of various parameters characterizing H-bond strength, on another value characterizing the full interaction strength (e.g., ΔpK_a) were found in a number of papers [e.g.,4,6,17,27] and interpreted as gradual strengthening the hydrogen bond until the "quasi-symmetric" limit is reached. Subsequent increase of the acid strength results in weakening the H-bond, which is now formed by a conjugated acid-base pair, the PyH^+ and X^- ions. However, an alternative explanation involving the tautomeric equilibrium (1) cannot be rejected. In this

Table 1. Measured values of mean N-H internuclear distance, r_{NH}, and chemical shifts of the ^{15}N nucleus and the bridging proton for the 1:1; complexes of pyridine with different acids, XH, in CD_2Cl_2 at 160 K.

XH	r_{NH}, A	$-\Delta\delta_N$, ppm	δ_H, ppm
CH_3COOH	1.38	25.1	16.0
HCOOH	1.30	32.0	17.5
$CH_2ClCOOH$	1.28	36.3	18.5
$CHCl_2COOH$	1.22	59.2	20.5
CCl_3COOH	1.10	80.6	20.3
CF_3COOH	1.05	98.1	19.0
HCl	1.02	104.0	15.3
$HClO_4$	0.98	108.4	12.2

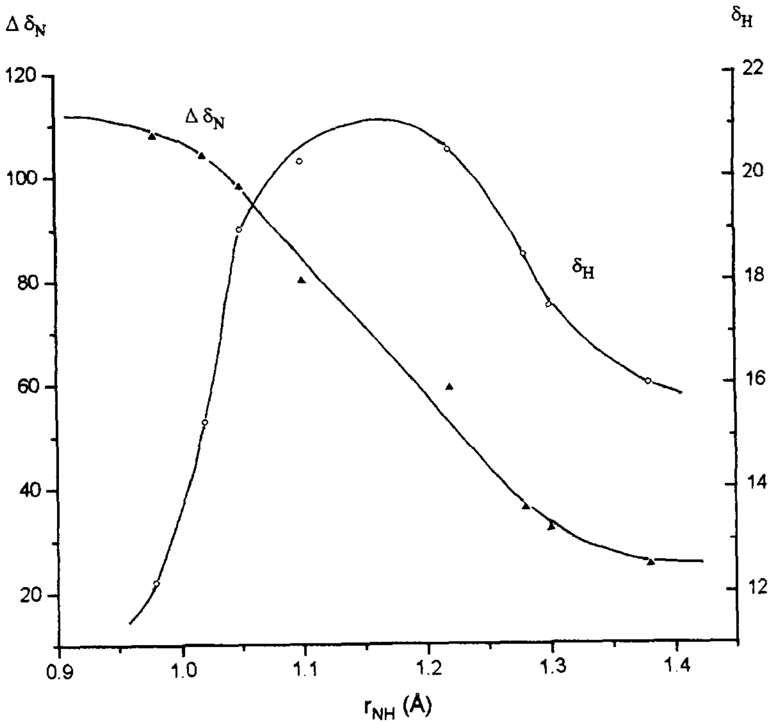

Fig.2. Dependencies of the chemical shifts of ^{15}N and the bridging proton in H-bonded complexes of pyridine on the mean N-H distance.

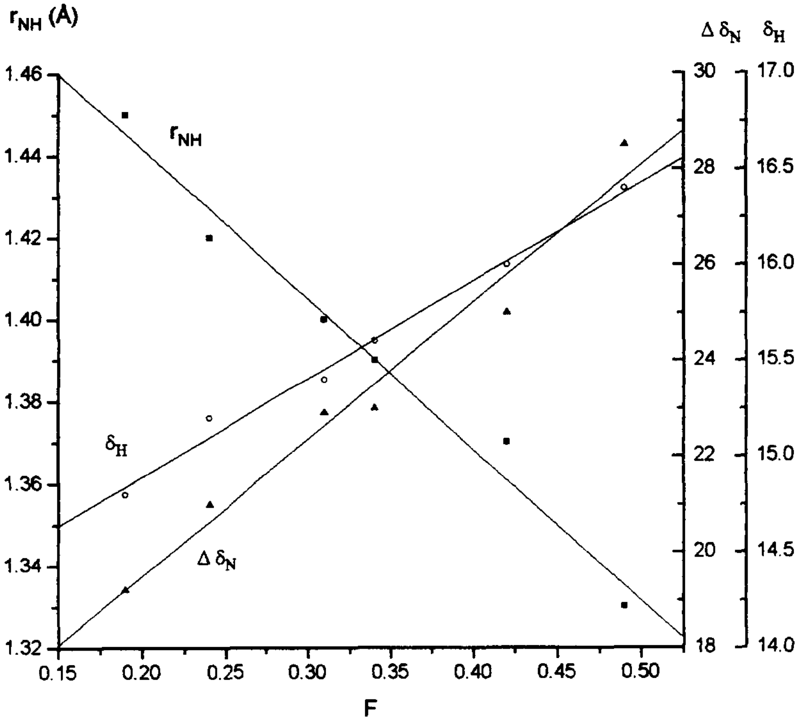

Fig.3. Dependencies of the mean N-H distance and the δ_H, $\Delta\delta N$ chemical shifts for the pyridine-acetic acid complex on the reactive field factor, ΔF, of a solvent.

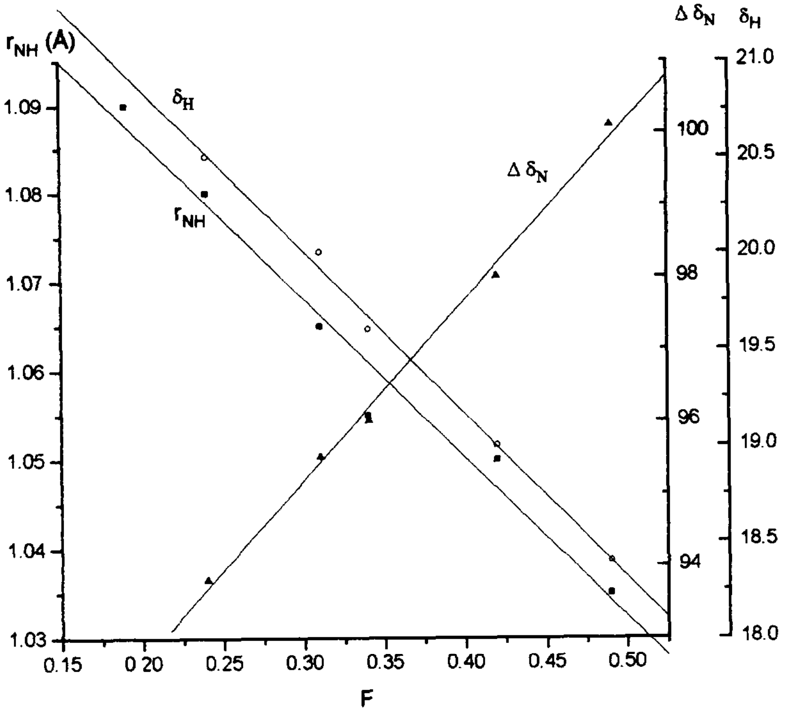

Fig.4. Dependencies of the mean N-H distance and the δ_H, $\Delta\delta_N$ chemical shifts for the pyridine-trifluoroacetic acid complex on the reactive field factor, ΔF, of a solvent.

case, the observed δ_H value is averaged between those belonging to the two forms, molecular and ionic, and determined both by the chemical shifts of individual forms and the equilibrium position. The above data on the average internuclear distances and chemical shifts are insufficient to distinguish between the two models, the "quasi-symmetric" and "tautomeric". It would be useful to attract experimental data concerning the J_{NH} coupling constant as well as spectroscopic effects caused by the H/D isotope substitution. Our preliminary data showed that these values are not characteristic of a system, XH...Y, but depend strongly on experimental conditions (temperature, solvent and concentration). The results of the systematic investigation will be reported in the following communication.

Now consider the question of the influence of solvent polarity on the proton location. Since in the case of intermediate acid-base interaction this influence might consist in the (1) equilibrium shift and have nothing to do with the actual geometry of a complex, in this paper only complexes with no sign of the tautomerism in IR spectra were studied quantitatively. A typical molecular complex (with CH_3COOH, $J_{NH}=0$) and a typical ionic pair (with CF_3COOH, $J_{NH}\approx 85$ Hz) were chosen. It was found that increasing the dielectric constant, ε, leads to a shortening of the N-H bond which exceeds considerably the experimental error of the method described above. Figures.3,4 represent the dependencies of the $r_{N\text{-}H}$ distance as well as the chemical shifts, δ_N and δ_H, on one of model parameters, characterizing solvent polarity, namely, the reactive field factor, $F = (\varepsilon-1)/(2\varepsilon+1)$. All the dependencies can be approximated by straight lines of different slope. It should be noted that these dependencies are "self-consistent". Taking from Fig.2 the derivatives, $d\delta_N/dr_{NH}$ and $d\delta_H/dr_{NH}$, at the points corresponding to the two complexes, with acetic and trifluoroacetic acids, we obtain a reasonable coincidence of the values, $d\delta/dF = (d\delta/dr_{NH})(dr_{NH}/dF)$, with the experimental slopes. If the chemical shift of the bridging proton is accepted as a measure of the strength of an H-bond, the following conclusion may be drawn: the reactive field causes an increase in the H-bond strength for the molecular complex and a decrease for the ionic pair. In the both cases, the mean N-H distance decreases with the solvent polarity. This is in qualitative agreement with the IR results referred in [16].

Discussion

1.Description of the model

For interpretation of the found effect of bond length changing in an XH...Y hydrogen bridge under the influence of a solvent, consider a linear three-mass model characterized by three normal vibrations. Only stretching vibrations, the high frequency $\nu_1 \approx \nu_{XH}$ and the low-frequency $\nu_3 \approx \nu_{XY}$, will be taken into account. The potential energy can be written as:

$$V = V_0 + V_1 + U \qquad (4)$$

where $V_0= 1/2\omega_1 q_1^2 + 1/2\omega_3 q_3^2$ is the harmonic part of the potential; $V_1 = =\alpha_{111}q_1^3 + \alpha_{113}q_1^2 q_3 + \alpha_{133}q_1 q_2^2 + \alpha_{333}q_3^3$ - its cubic anharmonic part; $U = =U_0 + U'_1 q_1 + U'_3 q_3 + 1/2U''_{11}q_1^2 + U''_{13}q_1 q_2 + 1/2U''_{33}q_3^2$ is an expansion of the energy of interaction with a solvent with respect to the intramolecular dimensionless normal coordinates. In the first approximation, $q_1= (\gamma_1)^{1/2}Q_1$, $q_3= (\gamma_3)^{1/2}Q_3$; $Q_1=\Delta r_{XH}$, $Q_3=\Delta R_{XY}$; $\Delta r_{YH} = Q_3 - Q_1$; $\gamma_i = 4\pi^2\omega_i c\mu_i/h$, where ω_i and μ_i are the harmonic frequency and reduced mass for both the vibrations. (For ionic complexes, $X^-...HY^+$, $\Delta r_{YH} = Q_1$)

In order to obtain expressions for the changes of the equilibrium bond lengths, $\Delta r_{XH} = \Delta Q_1$ and $\Delta R_{XY} = \Delta Q_3$, wave functions in the 1st and 2nd orders of the perturbation theory were used with $V_1 + U$ as a perturbation [18,19]. The relation, $\omega_1 >> \omega_3$, was accounted (the adiabatic approximation), a part of small members being neglected. Due to this approximation, the obtained expressions are not fully symmetric with respect to the permutation of the 1,3 subscripts:

$$\Delta q_1 = -\frac{U'_1}{\omega_1}[1-\frac{1}{2}\frac{U''_{11}}{\omega_1}-\frac{U''_{13}U'_3}{U'_1\omega_3}-(\frac{U''_{11}3\alpha_{111}}{U'_1\omega_1}+\frac{U''_{13}\alpha_{113}}{U'_1\omega_3})(V_1+\frac{1}{2})- \tag{5}$$

$$-(\frac{1}{2}\frac{U''_{11}\alpha_{133}}{U'_1\omega_1}+\frac{1}{2}\frac{U''_{13}3\alpha_{333}}{U'_1\omega_3}+\frac{1}{2}\frac{U''_{33}\alpha_{133}}{U'_1\omega_3})(V_3+\frac{1}{2})]$$

$$\Delta q_3 = -\frac{U'_3}{\omega_3}[1-\frac{1}{2}\frac{U''_{33}}{\omega_3}-\frac{U''_{13}U'_1}{U'_3\omega_1}-(\frac{1}{2}\frac{U''_{33}\alpha_{133}}{U'_3\omega_3}+\frac{U''_{13}3\alpha_{111}}{U'_3\omega_1}+\frac{1}{2}\frac{U'_{11}\alpha_{113}}{U'_3\omega_1})(V_1+\frac{1}{2})-$$

$$-(\frac{u''_{33}3\alpha_{333}}{u'_3\omega_3}+\frac{u''_{13}\alpha_{133}}{u'_3\omega_1})(v_3+\frac{1}{2})] \tag{6}$$

The second order members in (5,6) depend on the quantum numbers, v_1 and v_3. For T>0, the thermal population of excited vibrational levels must be accounted:

$$\overline{(V_i+\frac{1}{2})} = \frac{\exp(-hc\omega_i/kT)}{1-\exp(-hc\omega_i/kT)}+\frac{1}{2} \tag{7}$$

For the high frequency vibration, $\omega_1 >> kT/hc$, and $<v_1+1/2> \approx 1/2$. As to the ω_3 vibration, its frequency is of the same order of magnitude as kT/hc, and the account of its population can contribute noticeably to the result.

2. Potential of interaction with solvent

For highly polar H-bonded complexes (μ=5÷10 D), the main contribution to the interaction energy can be written as [35]:

$$U = -\mu[\mu \frac{1}{a^3}\frac{\varepsilon_\upsilon - 1}{2\varepsilon_\upsilon + 1} - \mu_e \frac{2}{a^3}(\frac{\varepsilon - 1}{2\varepsilon - 1} - \frac{\varepsilon_\upsilon - 1}{2\varepsilon_\upsilon - 1})] = -\mu[\mu A + 2\mu_e(B - A)] \qquad (8)$$

where μ is the dipole moment depending on vibrational coordinates; μ_e - the static dipole moment of a complex; a - the Onsager radius; ε - the static dielectric constant of a medium; ε_v - the dielectric constant for vibrational frequencies. Upon differentiation, at the equilibrium point ($\mu=\mu_e$) we obtain:

$$U'_{1(3)} = -2\mu_e\mu'_{1(3)}B \qquad (B = \frac{1}{a^3}\frac{\varepsilon - 1}{2\varepsilon + 1}) \qquad (9)$$

$$U''_{11(33)} = -2(\mu'_1)^2 A - 2\mu_e\mu''_{11}B \qquad (A = \frac{1}{a^3}\frac{\varepsilon_\upsilon - 1}{2\varepsilon_\upsilon + 1}) \qquad (10)$$

$$U''_{13} = -2\mu'_1\mu'_3 A - 2\mu_e\mu''_{13}B \qquad (11)$$

To calculate the derivatives, the model dipole moment function [30] was used:

$$\mu = \mu_\infty + \mu_{XH} + \mu_Y + \mu_{ind} \qquad (12)$$

$$\mu_{ind} = \mu^0_{ind}(\frac{r}{r_e})^n \exp[-b(R - R_e)]; \quad \text{at } r=r_e, \quad R=R_e, \quad \mu_{ind}=\mu^0_{ind}$$

where μ_{XH} and μ_Y refer to the monomer molecules; μ_∞=0 for molecular complexes, but μ_∞= eR for ionic pairs; μ_{ind} is the dipole moment induced by complex formation; μ_0, n and b are parameters. After differentiation with respect to q_1 and q_3 we have:

$$\mu'_1 = \mu'_{1(mon)} + n\mu_0 / \sqrt{\gamma_1 r_e} \qquad (13)$$

$$\mu'_3 = -\mu_0 b / \sqrt{\gamma_3} = -\mu'_{1(ind)}\frac{b\sqrt{\gamma_1 r_e}}{n\sqrt{\gamma_3}} \qquad (14)$$

(for ionic pairs, μ'_3= (e -μ_ob)/$\sqrt{\gamma_3}$)

$$\mu''_{11(ind)} = n(n-1)\mu_0 / \gamma_1 r_e = \mu'_{1(ind)} b / \sqrt{\gamma_3} \qquad (15)$$

$$\mu''_{13} = -n\mu_0 b / \sqrt{\gamma_1\gamma_3 r_e} \qquad (16)$$

$$\mu''_{33} = \mu_0 b^2 / \sqrt{\gamma_3} \qquad (17)$$

3. Quantitative evaluations for the pyridine-acetic acid complex.

The above formulae allow to calculate alterations of the average bond length in hydrogen bridges as a result of its transfer from vacuum into a solvent. In order to describe our experimental data on liquid solutions, it is permissible to neglect changes in high-frequency dielectric constant ($\varepsilon_v \approx$ const = 2). In order to compare the results with our experiment as well as to evaluate relative contribution of different terms in (5,6) to the resulting value, Δr_{NH}, let us consider the effect of transferring the pyridine-acetic acid from an apolar ($F \approx 0.2$) to a strongly polar ($F \approx 0.5$) solvent. For this complex, the following parameters can be taken: $\mu_e \approx 7$ D [36]; $(a_{XH...Y})^3 = (a_{XH})^3 + (a_y)^3 \approx 60$ $A^{3.}$ Spectroscopic data required for the estimation are presented in Table 2 [36,37]. The parameters of the induced dipole moment function derived from these data are: $(\partial\mu/\partial Q_1)_{ind}$ =5.4 D/A; $(\partial\mu/\partial q_1)_{ind}$ = 0.63 D. Taking n = 2 [30], r_e =1A, we have: $(\mu_o)_{ind}$ = 2.7D; b = 2.7 A^{-1}.The derivatives of the dipole moment function calculated with n=2 are also given in Table 2.

As far as the anharmonic cubic constants are concerned, we have not found their values for the particular complex in literature. Typical are, however, the following approximations [38]: $\alpha_{111}/\omega_1 \approx \alpha_{333}/\omega_3 \approx 0.1$; $\alpha_{113}/\omega_3 \approx 1$; $\alpha_{113}/\omega_1 < 0.01$; $\alpha_{133}/\omega_1 < 0.01$. Neglecting the members containing the last two factors, upon putting the required parameters from the Table 2 into (5,6), at T = 200 K , the following result is obtained:

$\Delta q_1 = 0.15$, $\Delta q_3 = -1.12$; $\Delta r_{XH} = 0.012$ A, $\Delta R_{XY} = -0.08$ A;
$\Delta r_{YH} = \Delta R_{XY} - \Delta r_{XH} = -0.092$ A. (The experimental value: $\Delta r_{YH} = 0.11$ A.) It should be noted that the very simple and approximate model gives a satisfactory agreement with experiment. This coincidence depends, however, on the choice of parameters.

The contributions of the terms depending on cubic force constants, α_{iij}, into this estimation are 8%; accounting second derivatives of dipole moment, U''_{ij}, increases the evaluated Δr_{YH} by ~ 35%. Population of the low frequency v_3 vibration caused by the temperature rising from 0 up to 200 K decreases the effect by 12%. Thus, the observed shortening of the N-H bond by the reactive field is determined mainly by the first terms in the equations (5,6).

4. General discussion

In order to discuss the main features of the solvent polarity effect, we limit ourselves by the first terms in (5,6):

$$\Delta q_i = -\omega_i^{-1} \Delta U'_i = \omega_i^{-1} a^{-3} \mu_e \mu'_i \Delta F \qquad (18)$$

It is seen that the effect must be zero for non-polar complexes (μ_e=0). Indeed, in [15,16] it was mentioned that IR spectra of non-polar cyclic dimers (trimers) are practically insensitive to alteration of medium. The sign of medium influence on different bond lengths is determined by the relative sign of dipole moment of a complex and its derivative, μ'_i. For most molecular complexes, as

Table 2. IR spectroscopic parameters and calculated parameters of the dipole moment function of the pyridine-acetic acid complex [36,37]; derivatives of the interaction potential energy, U, calculated for an extremely polar solvent ($F = 0.5$).

Parameter	$\nu_1(XH)$	$\nu_1(XH...Y)$	$\nu_3(XH...Y)$
ν (cm^{-1})	3500	2500	170
$A \cdot 10^6$ (cm^2/s)	30	1000	25
μ'_i (D)	0.12	0.80	-0.48
$\gamma_i^{1/2}$ (A^{-1})	10.2	8.56	~12
$\partial\mu/\partial Q_i$ (D/A)	1.2	6.8	-5.8
$(\mu_0)_{ind}$ (D)		2.7	
μ'_1		0.80	
μ'_3		-0.48	
μ''_{11}		0.08	
μ''_{13}		-0.13	
μ''_{33}		0.08	
U'_1 (cm^{-1})		460	
U'_3		280	
U''_{11}		46	
U''_{13}		75	
U''_{33}		46	

a rule, the induced dipole moment increases the "intrinsic" moment, $\mu^0_{ind} > 0$. Since, $\mu'_1 > 0$; $\mu'_3 < 0$; $\Delta r_{XH} > 0$; $\Delta R_{XY} < 0$; $\Delta r_{YH} = \Delta(R_{XY} - r_{XH}) < 0$. Thus, polar solvent must cause hydrogen bond to shorten (strengthen) and the covalent, X-H, bond to lengthen. In the case of an ionic pair, the main part of its dipole moment is determined by a large value, eR. The induced moment decreases this value due to some "charge transfer" from anion to cation, $\mu^0_{ind} < 0$. Therefore, $\mu'_1 < 0$; $\mu'_3 > 0$; $\Delta r_{YH} < 0$; $\Delta R_{XY} > 0$; $\Delta r_{XH} > 0$. (It is worth reminding that the Y-H bond length is now described by the q_1 normal coordinate). Thus, in this case a polar medium makes hydrogen bond longer (weaker), which is revealed in upfield shifting the δ_H signal. In both cases, the medium effect on the Y-H distance is negative, which is in accordance with experiment. It should be noted that numerous experimental facts concerning the main features of the medium effect on IR spectra of H-bonded complexes referred in [15,16] can be treated in terms of our model. The intermediate case of quasi-symmetric hydrogen bonds requires a special examination and theoretical consideration. The model used in this paper predicts a sudden sharp change in the sign of the effect upon passing through some critical r_{YH} point, which can hardly be true.

Acknowledgement

This work was performed with a financial support from the Russian Foundation for Fundamental Researches.

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