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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamics of the Hydrogen Bonding of Nitrogen-Containing Cyclic and Aromatic Compounds with Proton Donors: The Structure–Property Relationship

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Abstract—Enthalpies of dissolution are measured at infinite dilution of nitrogen-containing cyclic (pyrrolidine, piperidine) and aromatic compounds (aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, *N*-methylimidazole, pyridine, 2-, 3-, 4-methylpyridine, pyrrole, *N*-methylpyrrole) in chloroform and dichloromethane, and vice versa ($T = 298.15$ K). The enthalpies of hydrogen bonds in the above systems are calculated. Relationships between resulting thermochemical data and the structure of nitrogen-containing cyclic and aromatic compounds are explored.

Keywords: hydrogen bonds, solvation, nitrogen-containing compounds, chloroform, dichloromethane, reorganization, enthalpy of dissolution

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INTRODUCTION

Nitrogen-containing cyclic and aromatic compounds and their fragments are widely used as dyes and pesticides; they are found in drugs and other biologically active compounds [1–3] and are components of many ionic liquids [4] with great practical value. In many respects, the properties and structures of these compounds are determined by the presence of hydrogen bonds, e.g., secondary structures in proteins, enzymes, and nucleic acids [5, 6]. In addition, the hydrogen bonds of nitrogen-containing cyclic and aromatic compounds play a great role in various physicochemical and biological processes [6, 7]. Knowledge of the energy of hydrogen bonds in nitrogen-containing compounds allows us to better understand the nature and mechanism of different phenomena in the condensed state, and to predict the properties of more complicated supramolecular systems.

The hydrogen bonds of nitrogen-containing cyclic and aromatic compounds have been studied experimentally by different physicochemical methods, e.g., the calorimetry of dissolution [19–26], IR [8–14], UV [15, 16], and NMR [16–18] spectroscopy. During these studies, special attention was paid to the self-association of nitrogen-containing compounds [8, 9] and the formation of hydrogen bonds with proton acceptors [10–12, 16, 17, 19, 21] and amphiphilic molecules [13, 14, 22, 23]. In most cases, the experimental data was obtained in inert solvents where the formation of complexes of structures that differed from real system compositions was possible.

The energies of the hydrogen bonds of nitrogen-containing cyclic and aromatic compounds with water, alcohols, and organic bases were estimated mainly via quantum chemical calculations [8, 9, 13, 14, 17]. These experimental data were obtained only for pyridine and its methyl derivatives [17, 20, 23]. At the same time, the thermodynamics of hydrogen bond formation in organic compounds remains poorly studied in media of nitrogen-containing cyclic and aromatic compounds. This due in particular to the weak C–H···N hydrogen bonds, which affect conformation stability and the packing of biomolecules [6]. It should be noted that traditional spectral methods cannot be used to study these interactions.

In this work, we study the thermodynamics of hydrogen bond formation of nitrogen-containing cyclic and aromatic compounds with C–H proton donors by means of calorimetry of dissolution. The effect of the structure of the studied compounds on the resulting thermochemical data is analyzed.

EXPERIMENTAL

All solutes and solvents were purchased from Aldrich, Alfa Aesar, and Acros Organics; compound purity was >98.0%. Nitrogen-containing compounds were distilled over CaH_2 in an inert atmosphere under reduced pressure. Chloroform and dichloromethane were purified and dried according to the standard procedures in [27]. Compound purity was monitored via gas chromatography on a KONIK 5000 chromatograph. The water content was deter-

mined by Karl Fischer titration using a C20 Mettler Toledo titrator. It was no higher than 0.02%.

Enthalpies of dissolution were measured at 298.15 K using a pseudo-adiabatic dissolution calorimeter. The measuring procedure was described in [28]. A Dewar flask was used as our calorimetric cell, the volume of solvent was 110 mL, and the weight of a dissolved sample was 0.03–0.06 g. The calorimeter was calibrated by measuring the enthalpy of potassium chloride dissolution in water. Value of $\Delta_{soln}H^{KCl/H_2O} = 17.41 \pm 0.04$ kJ/mol (298.15 K, $m = 0.0278$ mol/kg) measured in this work was in agreement with the standard value for this system: $\Delta_{soln}H^{KCl/H_2O} = 17.47 \pm 0.07$ kJ/mol [29]. Obtained enthalpies of dissolution for the investigated systems were measured at infinite dilution conditions.

One approach to determining the energy of hydrogen bond formation in the condensed state is to analyze the thermodynamic functions of solvation. Solvation is the transfer of dissolved molecules from ideal gas state to a solution at 298.15 K and atmospheric pressure. The enthalpy of solvation of solute A in solvent S ($\Delta_{solv}H^{A/S}$) at 298.15 K can be calculated as the difference between the experimentally measured enthalpy of dissolution of A in S ($\Delta_{soln}H^{A/S}$) and the enthalpy of vaporization of liquid solute A ($\Delta_{vap}H^{A}$):

$$\Delta_{solv}H^{A/S} = \Delta_{soln}H^{A/S} - \Delta_{vap}H^{A}. \quad (1)$$

The enthalpy of solvation indicates the strength of all the intermolecular interactions between the solute and solvent that occur in the solution. It is conventionally written as the sum of the enthalpy of nonspecific solvation ($\Delta_{solv(nonsp)}H^{A/S}$), representing the Van der Waals interactions in the solution, and the enthalpy of hydrogen bond formation of the solute A in the solvents ($\Delta_{BC}H^{A/S}$) using the equation

$$\Delta_{solv}H^{A/S} = \Delta_{solv(nonsp)}H^{A/S} + \Delta_{HB}H^{A/S}. \quad (2)$$

Based on these data, the authors of [30] developed a method for estimating the enthalpies of hydrogen bonds from the enthalpy of solvation:

$$\begin{aligned}\Delta_{HB}H^{A/S} = {} & \Delta_{solv}H^{A/S} - (\delta_{cav}h^{S} - \delta_{cav}h^{C_6H_{12}})V_X^{A} \\ & - \Delta_{solv}H^{A/C_6H_{12}} - (\delta_R + b_R(\delta_{cav}h^{S})^{1/2}) \\ & \times [(\Delta_{solv}H^{A/R} - \Delta_{solv}H^{A/C_6H_{12}}) \\ & - (\delta_{cav}h^{R} - \delta_{cav}h^{C_6H_{12}})V_X^{A}],\end{aligned} \quad (3)$$

where $\Delta_{solv}H^{A/S}$, $\Delta_{solv}H^{A/C_6H_{12}}$, $\Delta_{solv}H^{A/R}$ are the enthalpies of solvation of A in solvent S, cyclohexane (C_6H_{12}) and standard solvent R; V_X^{A} is the characteristic volume of solute molecules calculated by the additive scheme in [31]; a_R and b_R are empirical coefficients determined through regression analysis for each standard solvent R; and $\delta_{cav}h^{S}$, $\delta_{cav}h^{C_6H_{12}}$, $\delta_{cav}h^{R}$ are specific relative enthalpies of cavity formation for each solvent, calculated as

$$\delta_{cav}h^{S} = \frac{\Delta_{soln}H^{C_nH_{2n+2}/S}}{V_X^{C_nH_{2n+2}/S}}, \quad (4)$$

where $\Delta_{soln}H^{C_nH_{2n+2}/S}$ is the enthalpy of dissolution of linear alkane in solvent (S); and $V_X^{C_nH_{2n+2}/S}$ is the characteristic volume of linear alkane according to McGowan.

A solvent that is unable to form hydrogen bonds with the solute is chosen as standard solvent R. Tetrachloromethane ($a_R = 0.34$, $b_R = 0.61$) is therefore used as R for proton-donor solutes, and benzene ($a_R = 0.20$, $b_R = 0.38$) is used for proton-acceptor solutes.

The method for determining the enthalpy of hydrogen bonds on the basis of Eq. (3) was tested with a high number of solute–solvent systems in [30].

RESULTS AND DISCUSSIONS

We measured enthalpies of dissolution at limited dilutions of a range of nitrogen-containing cyclic and aromatic compounds in two C–H proton donors (e.g., dichloromethane and chloroform) at 298.15 K. Chloroform and dichloromethane do not have proton-acceptor properties and differ considerably in their proton-donating properties. On the basis of obtained experimental data, the thermodynamics of hydrogen bond formation was considered in case when nitrogen-containing cyclic and aromatic compounds are solutes and when they are solvents.

Enthalpies of Hydrogen Bond Formation for Nitrogen-Containing Cyclic and Aromatic Compounds in Proton Donors

Table 1 presents the characteristic volumes (according to McGowan, V_X^{A}) of pyrrole; *N*-methylpyrrole; aniline; *N*-methylaniline; *N*,*N*-dimethylaniline; *N*-methylimidazole; pyrrolidine; piperidine; pyridine; and 2-, 3-, and 4-methylpyridines, calculated according to [30], along with the enthalpies of their dissolution at limited dilution in cyclohexane ($\Delta_{soln}H^{A/C_6H_{12}}$), standard solvents ($\Delta_{soln}H^{A/R}$), chloroform ($\Delta_{soln}H^{A/CHCl_3}$), and dichloromethane ($\Delta_{soln}H^{A/CH_2Cl_2}$). Tetrachloromethane was used as the standard solvent (R) for pyrrole, aniline, and *N*-methylaniline. Benzene was used for *N*,*N*-dimethylaniline, *N*-methylpyrrole, *N*-methylimidazole, piperidine, pyrrolidine, pyridine, and picolines.

Using the data in Table 1 and specific relative enthalpies of cavity formation in chloroform (3.42×10^2 kJ/cm^3 [30]) and dichloromethane (7.43×10^2 kJ/cm^3 [30]), we measured the enthalpies of hydrogen bonds for nitrogen-containing cyclic and

Table 1. Characteristic volumes (according to MvGowan, V_X^A) of nitrogen-containing cyclic and aromatic compounds (A) and their enthalpies of dissolution in cyclohexane ($\Delta_{soln}H^{A/C_6H_{12}}$), standard solvents ($\Delta_{soln}H^{A/R}$), chloroform ($\Delta_{soln}H^{A/CHCl_3}$), and dichloromethane ($\Delta_{soln}H^{A/CH_2Cl_2}$). $T = 298.15$ K

A	$V_X^A \times 10^{-2}$, cm^3/mol	$\Delta_{soln}H^{A/R}$, kJ/mol	$\Delta_{soln}H^{A/C_6H_{12}}$, kJ/mol	$\Delta_{soln}H^{A/CHCl_3}$, kJ/mol	$\Delta_{soln}H^{A/CH_2Cl_2}$, kJ/mol
Aniline	0.8160	8.66 ± 0.04, [30]	15.56 ± 0.54, [30]	0.83 ± 0.03	3.03 ± 0.05, [25]
N-Methylaniline	0.9571	5.61 ± 0.00, [30]	11.59 ± 0.17, [30]	−1.55 ± 0.12, [19]	2.31 ± 0.05, [25]
N,*N*-Dimethylaniline	1.0980	0.66 ± 0.50	6.44 ± 0.12, [30]	−5.43 ± 0.08, [19]	−1.17 ± 0.02, [25]
N-Methylimidazole	0.6772	3.56 ± 0.10, [30]	15.8 ± 0.50, [28]	−9.37 ± 0.58, [33]	−3.89 ± 0.19, [25]
Pyrrole	0.5770	9.29 ± 0.08, [30]	15.65 ± 0.54, [30]	1.38 ± 0.08, [21]	2.95 ± 0.03, [25]
N-Methylpyrrole	0.7183	0.69 ± 0.02, [30]	7.90 ± 0.35, [30]	−6.15 ± 0.08, [21]	−2.66 ± 0.07, [25]
Pyrrolidine	0.6634	2.15 ± 0.03	5.72 ± 0.19	−8.60 ± 0.07	−1.00 ± 0.02, [25]
Piperidine	0.8043	1.80 ± 0.04, [24]	4.48 ± 0.09, [24]	−9.05 ± 0.16	−1.20 ± 0.02, [25]
Pyridine	0.6753	0.00 ± 0.01, [28]	8.20 ± 0.20, [28]	−8.16 ± 0.05, [34]	−3.10 ± 0.02
2-Methylpyridine	0.8162	−0.54 ± 0.08, [28]	6.57 ± 0.04, [28]	−10.50 ± 0.05	−3.71 ± 0.02
3-Methylpyridine	0.8162	0.44 ± 0.05, [28]	8.44 ± 0.20, [28]	−10.65 ± 0.07	−3.19 ± 0.01
4-Methylpyridine	0.8162	−0.09 ± 0.03, [22]	7.82 ± 0.03, [22]	−11.01 ± 0.02	−3.24 ± 0.02

Tetrachloromethane was used as our standard solvent (R) for aniline, *N*-methylaniline, and pyrrole; benzene was used for *N*,*N*-dimethylaniline, *N*-methylimidazole, pyrrolidine, piperidine, pyridine, 2-, 3-, and 4-methylpyridines.

aromatic compounds in chloroform and dichloromethane according to Eq. (3), Table 2.

Our results (Table 2) showed that the enthalpies of hydrogen bonds in aniline, *N*-metthylaniline, *N*,*N*-dimethylaniline, pyrrole, and *N*-methylpyrrole with C–H proton donors coincided within the error of measurement. Consequently, these molecules have equal proton-acceptor properties. It should be noted that the $\Delta_{HB}H^{A/CHCl_3}$ values measured in this work for aniline and *N*-methylaniline were in agreement with literature data: −7.1 and −7.5 kJ/mol, respectively [12]. The strength of hydrogen bonds in complexes of pyrrolidine, piperidine, pyridine, and isomeric methylpyridines with chloroform and dichloroform was higher than in those of anilines and pyrroles (Table 2). Since adding methyl groups to pyridine rings strengthens hydrogen bonds with C–H proton donors. The $\Delta_{HB}H^{A/CHCl_3}$ and $\Delta_{HB}H^{A/CH_2Cl_2}$ values for *N*-methylimidazole were found to be the ones most exothermic, due to the molecules of *N*-methylimidazole (which have two atoms of nitrogen) forming complexes with two molecules of solvent in a 1 : 2 ratio.

The nitrogen atoms in *N*-methylimidazole are known to be nonequivalent. One is related to pyridine-type nitrogen; the other, to nitrogen of the pyrrole type, as was confirmed by the thermochemical data obtained in this work. The sum of the enthalpies of pyrrole and pyridine hydrogen bonds with chloroform is −13.6 kJ/mol, which coincides with the $\Delta_{HB}H^{A/CHCl_3}$ value (−13.3 kJ/mol) of *N*-methylimidazole. A similar result was obtained for dichloromethane.

Table 2. Hydrogen bond enthalpies of nitrogen-containing cyclic and aromatic compounds (A) in chloroform ($\Delta_{HB}H^{A/CHCl_3}$) and dichloromethane ($\Delta_{HB}H^{A/CH_2Cl_2}$), $T = 298.15$ K

A	$-\Delta_{HB}H^{A/CHCl_3}$, kJ/mol	$-\Delta_{HB}H^{A/CH_2Cl_2}$, kJ/mol	β
Pyrrole	5.6	2.9	0.29
N-Methylpyrrole	5.6, [30]	2.8	0.31
Aniline	5.7 (7.1, [12])	2.8	0.41
N,*N*-Dimethylaniline	5.4, [34]	2.2	0.41
N-Methylaniline	5.6 (7.5, [12])	2.1	0.43
Pyridine	8.2 (10.0, [35])	2.3	0.52
3-Methylpyridine	10.8	3.0	0.54
4-Methylpyridine	10.8	2.8	0.54
2-Methylpyridine	9.7	2.8	0.58
Pyrrolidine	10.3	3.3	0.63
Piperidine	10.2	3.6	0.69
N-Methylimidazole	13.3	5.6	0.80

Table 3. Specific relative enthalpies of cavity formation for nitrogen-containing cyclic and aromatic compounds ($\delta_{cav}h^S$) and enthalpies of dissolution for chloroform and dichloromethane in nitrogen-containing cyclic and aromatic compounds, cyclohexane, and tetrachloromethane. $T = 298.15$ K, (**S**, solvents)

S	$\delta_{cav}h^S \times 10^2$, kJ/cm^3	$\Delta_{soln}H^{CHCl_3/S}$, kJ/mol	$\Delta_{soln}H^{CH_2Cl_2/S}$, kJ/mol
Aniline	10.23, [34]	0.69 ± 0.02, [34]	1.22 ± 0.11
N-Methylaniline	6.53	−2.11 ± 0.02	−0.48 ± 0.22
N,*N*-Dimethylaniline	4.11	−4.01 ± 0.03	−1.10 ± 0.08
N-Methylimidazole	8.33, [28]	−6.31 ± 0.06	−1.96 ± 0.01
Pyrrole	6.60	2.50 ± 0.02	8.60 ± 0.21
N-Methylpyrrole	6.25	−4.44 ± 0.01	−2.00 ± 0.10
Pyrrolidine	4.05	−10.01 ± 0.12	−3.65 ± 0.02
Piperidine	4.91	−9.80 ± 0.08	−3.43 ± 0.02
Pyridine	6.66, [22]	−7.30 ± 0.01	−1.93 ± 0.01
2-Methylpyridine	4.66, [22]	−9.70 ± 0.06	−2.41 ± 0.10
3-Methylpyridine	4.98, [22]	−10.00 ± 0.09	−2.42 ± 0.11
4-Methylpyridine	4.58, [22]	−9.93 ± 0.09	−2.31 ± 0.06
Tetrachloromethane	1.91, [30]	0.92 ± 0.01, [36]	1.97 ± 0.03
Cyclohexane	1.40, [30]	2.87 ± 0.08, [37]	5.35 ± 0.10, [37]

The resulting hydrogen bond enthalpies could be considered as a qualitative measure of the proton-donating abilities of nitrogen-containing cyclic and aromatic solutes. In Table 2, these values are compared to the widely used parameter of the basicity of organic compounds (β) [32], developed on the basis of spectral data. Some agreement can be seen between them.

Enthalpies of Hydrogen Bond Formation for Proton Donors in Nitrogen-Containing Cyclic and Aromatic Compounds

Table 3 shows the literature values for the enthalpies of dissolution of chloroform and dichloromethane at limited dilution in a medium of nitrogen-containing cyclic and aromatic compounds, along with those obtained in this work.

Using the measured enthalpies of dissolution, we determined the enthalpies of hydrogen bonds for chloroform and dichloromethane in media of pyrrole, *N*-methylpyrrole, aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, *N*-methylimidazole, pyrrolidine, piperidine, pyridine, 2-, 3-, and 4-methylpyridines according to Eq. (3). In our calculations, we used characteristic volumes of chloroform (0.6167×10^{-2} cm^3/mol) and dichloromethane (0.4943×10^{-2} cm^3/mol); the enthalpies of dissolution for chloroform and dichloromethane in cyclohexane and tetrachloromethane (Table 3); and the specific relative enthalpies of cavity formation ($\delta_{cav}h^S$) for nitrogen-containing cyclic and aromatic compounds (Table 3), obtained using Eq. (4) and the experimental data. Our hydrogen bond enthalpies are given in Table 4.

It follows from Table 4 that the strongest complexes are formed when chloroform and dichloromethane are dissolved in media of pyridines, pyrrolidine, and piperidine. The hydrogen bond enthalpies of chloroform ($\Delta_{BC}H^{CHCl_3/S}$) and dichloromethane ($\Delta_{BC}H^{CH_2Cl_2/S}$) in these solvents are close, even though pyridines are related to aromatic compounds, while pyrrolidine and piperidine are related to aliphatic compounds and have different cycle sizes. The hydrogen bond enthalpies for aniline and pyrrole were found to be positive and close to zero.

The figure compares the hydrogen bond enthalpies of nitrogen-containing cyclic and aromatic compounds in chloroform and dichloromethane to those of hydrogen bonds in an inverse system: proton donors in a medium of nitrogen-containing cyclic and aromatic compounds. The line in the figure corresponds to the equality of values of y and x. Our comparison shows that the hydrogen bond enthalpies for pyridines, pyrrolidine, piperidine, *N*-methylpyrrole, and *N*,*N*-dimethylaniline are located on that line. The proton-acceptor abilities of these molecules thus do not change whether they are solutes or solvents; at the same time, complexes of 1 : 1 ratio are formed.

The hydrogen bond enthalpies of *N*-methylimidazole with chloroform and dichloromethane deviate considerably from line $y = x$ (figure), due to formation of complexes of 1 : 1 ratio in a medium of amine during the dissolution of donors at limited dilution. At the same time, complexes of 1 : 2 ratio are formed then

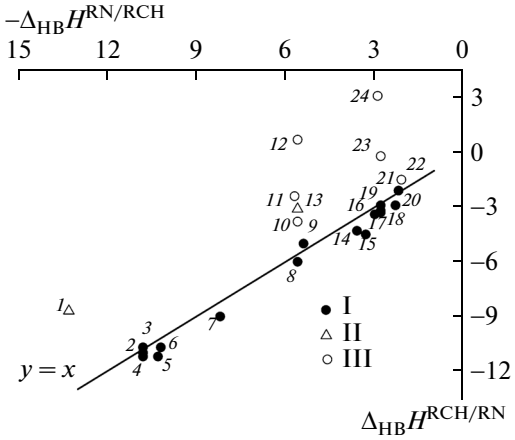
Table 4. Hydrogen bond enthalpies of chloroform ($\Delta_{HB}H^{CHCl_3/S}$) and dichloromethane ($\Delta_{HB}H^{CH_2Cl_2/S}$) in nitrogen-containing cyclic and aromatic compounds (S) (kJ/mol; $T = 298.15$ K)

N	S	$\Delta_{HB}H^{CHCl_3/S}$, kJ/mol	*N*	S	$\Delta_{HB}H^{CH_2Cl_2/S}$, kJ/mol
1	*N*-Methylimidazole	–8.7	13	*N*-Methylimidazole	–3.1
2	2-Methylpyridine	–10.7	14	Piperidine	–4.3
3	3-Methylpyridine	–11.2	15	Pyrrolidine	–4.5
4	4-Methylpyridine	–11.0	16	3-Methylpyridine	–3.4
5	Pyrrolidine	–11.2	17	3-Methylpyridine	–3.3
6	Piperidine	–10.7	18	4-Methylpyridine	–3.2
7	Pyridine	–9.0	19	*N*-Methylpyrrole	–2.9
8	*N*-Methylpyrrole	–6.0	20	Pyridine	–2.9
9	*N*,*N*-Dimethylaniline	–5.2	21	*N*,*N*-Dimethylaniline	–2.1
10	*N*-Methylaniline	–3.8	22	*N*-Methylaniline	–1.5
11	Aniline	–2.4, [34]	23	Aniline	–0.2
12	Pyrrole	0.7	24	Pyrrole	2.8

N-methylimidazole dissolves in chloroform and dichloromethane. The hydrogen bond enthalpies of aniline, *N*-methylaniline, and pyrrole also deviate from line $y = x$. Along with proton-acceptor abilities, these compounds have proton-donor properties and are capable to self-association [8, 9]. They present a mixture of associative species of different compositions and structures which are in equilibrium among themselves [8, 9]. During the dissolution of chloroform and dichloromethane in a medium of *N*-methylaniline and pyrrole, there is competition between the acidic protons of the C–H groups of proton donors and the N–H groups of amine for the acceptor centers of the latter; this breaks the associative equilibrium and leads to reorganization of the solvent [22–24, 28–38] ($\Delta_{reorg}H^{RNH}$), i.e., the breaking of solvent–solvent hydrogen bonds. The enthalpy of this process (e.g., for chloroform) can be written summarily as

$$\Delta_{HB}H^{CHCl_3/S} = \Delta_{HB}H^{Cl_3CH\cdots N(H)R} + \Delta_{reorg}H^{RNH}. \quad (5)$$

In agreement with Eq. (5), the summary enthalpy hydrogen bonding process of C–H group of proton donors in aniline, *N*-methylaniline, and pyrrole can be not only negative but positive as well, if the strength of the C–H···N hydrogen bonds is weaker than that of the N–H···N hydrogen bonds. The enthalpy of reorganization in Eq. (5) is equal to that of the self-association of a solvent with reversed sign.



Comparison of the hydrogen bond enthalpies of chloroform and dichloromethane in a medium of nitrogen-containing compounds ($\Delta_{HB}H^{RCH/RN}$) and the hydrogen bond enthalpies of nitrogen-containing compounds in a medium of chloroform and dichloromethane ($\Delta_{HB}H^{RN/RCH}$): (I) pyridines, piperidine, pyrrolidine, *N*-methylpyrrole, *N*,*N*-dimethylaniline; (II) *N*-methylimidazole; (III) aniline, *N*-methylaniline, and pyrrole, kJ/mol (the points correspond to the numbers in Table 4).

CONCLUSIONS

We determined the enthalpies of hydrogen bonds of nitrogen-containing cyclic and aromatic compounds with chloroform and dichloromethane. It was shown that for *N*,*N*-dimethylaniline, *N*-methyl aniline, pyridine, 2-, 3-, 4-methylpyridine, *N*-methylpyrrole, pyrrolidine, and piperidine (all of which have only one acceptor center), the strength of hydrogen bonds with C–H proton donors (and thus their proton acceptor abilities) does not depend on whether they are solutes or solvents: in both cases, complexes of 1 : 1 ratio are formed in the solution. The number of nitrogen atoms and the possibility of solvent to self-association are the main reasons of the difference between hydrogen bond

enthalpies. At the same time, neither the size of a cycle (piperidine, pyrrolidine) nor its aromaticity (piperidine, pyridines) affects the proton-acceptor abilities of the investigated molecules.

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