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СОЛЬВАТАЦИОННЫЕ ВКЛАДЫ ФУНКЦИОНАЛЬНЫХ ГРУПП МОЛЕКУЛЫ ПИРИДИНА В ЭНТАЛЬПИИ ПЕРЕНОСА АМИНА ИЗ МЕТАНОЛА В АЦЕТОНИТРИЛ, ДИМЕТИЛСУЛЬФОКСИД И ДИМЕТИЛФОРМАМИД

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Методом квантовой химии с использованием теории функционала электронной плотности (DFT) в варианте B3LYP с применением базисного набора 6-31G, дополненного поляризационными функциями, и в рамках модели самосогласованного реактивного поля (PCM) проведены расчеты энергетики и структуры молекулы пиридина (Py) в свободном состоянии, метаноле (MeOH), ацетонитриле (AN), диметилсульфоксиде (DMSO) и диметилформамиде (DMF). Установлено, что переход молекулы пиридина из свободного состояния в среду MeOH, AN, DMF и DMSO приводит: к увеличению длин связей только между атомами азота и углерода амина; к значительным изменениям величин зарядов на атомах углерода, связанных с реакционным центром (рост положительных зарядов изменяется в ряду: DMF = DMSO < MeOH = AN); к росту положительного заряда на атомах водорода, который изменяется в ряду: MeOH = AN < DMF = DMSO. Проведен сравнительный анализ энтальпий переноса пиридина из MeOH в AN, DMF и DMSO ($\Delta_{tr}H^0(Py)_{MeOH\rightarrow solv}$), полученных из калориметрических измерений и учитывающих как универсальные, так и специфические типы взаимодействий, с величинами $\Delta_{tr}H^0(Py)_{MeOH\rightarrow solv}$, полученными из квантово-химических расчетов, которые учитывают только универсальную составляющую пересольватации. Установлено, что основной вклад в изменение сольватного состояния пиридина при смене состава растворителя MeOH→DMF и MeOH→AN дает пересольватация атома азота. В случае переноса Py из MeOH в DMSO вклады от пересольватации атома азота и углеводородного радикала в общую энергетику пересольватации молекулы примерно одинаковы.

Ключевые слова: сольватация, пиридин, метанол, ацетонитрил, диметилсульфоксид, диметилформамид

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SOLVATION CONTRIBUTIONS OF PYRIDINE FUNCTIONAL GROUPS IN TRANSFER ENTHALPY OF AMINE FROM METHANOL TO ACETONITRILE, DIMETHYL SULFOXIDE AND DIMETHYLFORMAMIDE

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Quantum-chemical calculations of the energy and structure of pyridine molecule (Py) in the free state, methanol (MeOH), acetonitrile (AN), dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) have been performed using the density functional theory (DFT) at the B3LYP with the 6-31G basic set supplemented by polarization and diffuse functions and within the model of the self-consistent reactive field (PCM). It was found that the transfer of the pyridine molecule from the free state to the MeOH, AN, DMF and DMSO media leads to: an increase in bond distances only between nitrogen and carbon atoms of amine; significant changes in the charges on the carbon atoms associated with the reaction center (the growth of positive charges varies in the series: DMF = DMSO < MeOH = AN); an increase in the positive charge on hydrogen atoms, which varies in the series: MeOH = AN < DMF = DMSO. A comparative analysis of the results from quantum chemical calculations was carried out with data on transfer enthalpies of amine from MeOH to AN, DMF and DMSO ($\Delta_{tr}H^0(Py)_{MeOH \rightarrow solv}$) which were obtained by calorimetric method. It was found that the resolvation of the nitrogen atom gives the major contribution to the change in the solvate state of pyridine when the composition of the solvent MeOH → DMF and MeOH → AN changes. In case of transfer of Py from MeOH to DMSO, contributions from the resolvation of the nitrogen atom and the hydrocarbon radical to the overall energy of the resolvation of molecule are approximately the same.

Key words: solvation, pyridine, methanol, acetonitrile, dimethyl sulfoxide, dimethylformamide

INTRODUCTION

Pyridine (Py) is a heterocyclic tertiary amine, capable of forming strong complexes with metal ions, so it is a relevant object of scientific research in the field of coordination compounds chemistry [1-3].

Solvation processes of both reagents and products accompany complex formation reactions, which proceed in solutions. Therefore, understanding of the factors that determine the stability of the formed complexes and the energy of reactions of their formation is impossible without studying the influence of the solvent on the solvation of the reacting and forming particles. In turn, changes in solvation state of molecules depend on changes in the solvation state of their individual atoms, functional groups and reaction centers. On these reasons, the calculation of the bond lengths (r_e) between atoms in the Py molecule, of the charge values on the atoms (q) in the amine molecule in a gas phase, in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) media, as well as the enthalpies of Py

solvation ($\Delta_{solv}H^0_{calc}$(Py)) in methanol (MeOH), acetonitrile (AN), DMSO and DMF were made. The values of re and q of Py in MeOH and AN were taken from the literature [4].

Using the literature data on the enthalpy of Py dissolving in MeOH [5], AN [5], DMSO [6] and DMF [6], obtained by calorimetric method, the energy contributions from the universal and specific interactions between the Py molecules and the solvent molecules to the common energy of amine resolution were estimated.

DETAILS OF QUANTUM-CHEMICAL CALCULATIONS

Quantum-chemical calculations were performed using the GAUSSIAN 03 software package [7]. The calculations were performed using density functional theory (DFT) at the B3LYP [8-10]. In all calculations, bases 6-31G [11, 12] supplemented by polarization and diffuse functions [13] were used. Visualization of completed structures was performed in ChemCraft program [14]. The study of Py structure in solvated state, as well as the determination of amine solvation enthalpies in MeOH, AN, DMSO and DMF, was performed within the polarizable continuum model (PCM) [15].

RESULTS AND DISCUSSION

The geometric parameters of the pyridine molecule in the gas phase and in the solvent medium, as well as Mulliken charges on atoms in the free and solvated states obtained as a result of optimization are given in Tables 1-2. The structure of the amine molecule is shown in Fig.
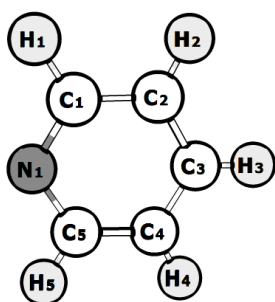

Fig. Structure of the pyridine molecule
Рис. Структурная формула молекулы пиридина

As follows from Table 1, the transition of the pyridine molecule from the gas phase to MeOH, AN, DMSO and DMF leads to the increasing of bond lengths only between nitrogen and carbon atoms. The bond distances between other atoms in the molecule of solvated Py and in the amine molecule in the gas phase do not differ significantly from each other.

Table 1
Values of the bond distances in the pyridine molecule
Таблица 1. **Величины межъядерных расстояний в молекуле пиридина**

Designation of the bond distance	re, Å				
	in the gas phase	in MeOH [4]	in AN [4]	in DMSO	in DMF
C1-H1	1.089	1.089	1.089	1.089	1.089
C2-H2	1.086	1.085	1.085	1.085	1.085
C3-H3	1.087	1.086	1.086	1.086	1.086
C4-H4	1.086	1.085	1.085	1.085	1.085
C5-H5	1.089	1.088	1.089	1.089	1.089
N1-C1	1.339	1.343	1.342	1.342	1.342
C1-C2	1.396	1.396	1.395	1.395	1.395
C2-C3	1.395	1.395	1.395	1.395	1.395
C3-C4	1.395	1.395	1.395	1.395	1.395
C4-C5	1.396	1.396	1.395	1.395	1.395
C5-N1	1.339	1.343	1.342	1.342	1.342

Analysis of the charges on atoms in the Py molecule in the gas phase, in MeOH, AN, DMSO and DMF shows (Table 2) that the maximum negative charge is concentrated on the nitrogen atom of the amine molecule.

Table 2
Values of the Mulliken charges on the atoms in the pyridine molecule
Таблица 2. **Величины зарядов по Малликену на атомах в молекуле пиридина**

The designation of a charge on an atom	q, ē				
	in the gas phase	in MeOH [4]	in AN [4]	in DMSO	in DMF
N1	-0.358	-0.430	-0.430	-0.485	-0.484
C1	0.058	0.094	0.094	0.074	0.074
C2	-0.089	-0.093	-0.093	-0.112	-0.112
C3	-0.057	-0.058	-0.058	-0.070	-0.074
C4	-0.089	-0.093	-0.093	-0.112	-0.112
C5	0.058	0.094	0.094	0.074	0.075
H1	0.100	0.100	0.100	0.124	0.124
H2	0.090	0.093	0.093	0.126	0.125
H3	0.098	0.100	0.100	0.134	0.134
H4	0.090	0.093	0.093	0.126	0.125
H5	0.100	0.100	0.100	0.124	0.124

The influence of solvents on the electronegativity of the pyridine reaction center increases in the series: MeOH = AN < DMF = DMSO. This correlates with the change in the donor properties of these solvents (DN_{MeOH} = 19.0 ≈ DN_{AN} = 14.1 < DN_{DMF} = 26.6 ≈ DN_{DMSO} = 29.8 [16]).

Charges on carbon atoms directly combined with the reaction center of pyridine are positive,

charges on other carbon atoms are negative. The transition of the amine molecule from a free state to the solvent medium results in significant changes in the charge values at the carbon C1 and C5 atoms, and the growth of positive charges changes in the series: DMF = DMSO < MeOH = AN. The transition of the amine molecule from the gas phase to the DMSO and DMF media leads to an increase of the negative charge on the carbon atoms which are not combined with the reaction center. The charges on these carbon atoms in the gas phase, methanol and acetonitrile are approximately the same.

Charges on hydrogen atoms of solvated pyridine are more positive than those in the gas phase and change in the series: MeOH = AN < DMF = DMSO.

Earlier we determined by a calorimetric method the enthalpies of dissolution of pyridine in mixtures of methanol with acetonitrile [5], dimethylsulfoxide [6] and N,N-dimethylformamide [6]. On their bases the enthalpies of the amine transfer from MeOH to the MeOH-AN, MeOH-DMSO and MeOH-DMF mixed solvents were calculated. It was found that an increase in the concentration of aprotic solvents in the binary mixture provides the decreasing of exothermicity of Py solvation.

Changes in the solvation energy of dissolved substances are known to depend on the changes in the solvation state of individual atoms or functional groups in their molecules when the composition of the solvent is changed. One can distinguish the following contributions to the energy of the resolvation of pyridine: contribution from the resolvation of the nitrogen atom of the amino group and the contribution from the resolvation of the hydrocarbon radical (benzene ring), and solvation of the reaction center in the Py molecule by the molecules of the mixed solvent should be performed, mainly, by the donor-acceptor mechanism, and the solvation of the hydrocarbon radical occurs largely due to Van der Waals forces.

In order to estimate the energy contribution to the common energy of the resolution of amine from universal and specific interactions between pyridine molecules and solvent molecules, there were compared the values of the enthalpies of the Py transfer from methanol to acetonitrile, dimethyl sulfoxide and dimethylformamide, obtained from calorimetric measurements and considering both universal and specific types of interactions, and the values of $\Delta_{tr}H^0(Py)$ obtained from quantum chemical calculations using the model of the self-consistent reactive field (PCM) [15]. The values of $\Delta_{tr}H^0_{exp}(Py)_{MeOH \to solv}$ and $\Delta_{tr}H^0_{calc}(Py)_{MeOH \to solv}$ are presented in Table 3 along with the values of $\Delta_{solv}H^0_{exp}(Py)$ и $\Delta_{solv}H^0_{calc}(Py)$.

It can be noted that the calculated and experimental values of the enthalpy of amine solvation are fairly close, although the transfer enthalpies $\Delta_{tr}H^0_{exp}(Py)_{MeOH \to solv}$ and $\Delta_{tr}H^0_{calc}(Py)_{MeOH \to solv}$ differ, which may be due to the use of a self-consistent reactive field model in calculations that takes into account only the universal component of resolution [15].

As was noted earlier, the transfer of pyridine from the amphoteric solvent to the basic leads to a decrease in the exothermicity of the amine solvation, which can be mainly due to a decrease in the energy of the donor-acceptor interactions between the hydrogen atoms of the solvent molecules with the unshared electron pairs of the amine nitrogen atom due to the decrease in the acid properties of the solvents ($AN_{MeOH} = 41.3$, $AN_{AN} = 18.9$, $AN_{DMF} = 16.0$, $AN_{DMSO} = 19.3$ [16]) [5,6].

Table 3

The enthalpies of pyridine solvation ($\Delta_{tr}H^0_{exp}(Py)$, $\Delta_{tr}H^0_{calc}(Py)$) in methanol, acetonitrile, N,N-dimethylformamide and dimethyl sulfoxide and the transfer enthalpies of amine from MeOH to AN, DMF and DMSO

($\Delta_{tr}H^0_{exp}(Py)_{(MeOH \to solv)}$, $\Delta_{tr}H^0_{calc}(Py)_{(MeOH \to solv)}$)

Таблица 3. **Энтальпии сольватации пиридина ($\Delta_{solv}H^0_{эксп}(Py)$, $\Delta_{solv}H^0_{расч}(Py)$) в метаноле, ацетонитриле, диметилформамиде и диметилсульфоксиде и энтальпии переноса аминов из MeOH в AN, DMF и DMSO**

($\Delta_{tr}H^0_{эксп}(Py)_{(MeOH \to solv)}$, $\Delta_{tr}H^0_{расч}(Py)_{(MeOH \to solv)}$)

Solvent	$\Delta_{solv}H^0_{exp}(Py)$*, kJ/mol	$\Delta_{solv}H^0_{calc}(Py)$, kJ/mol	$\Delta_{tr}H^0_{exp}(Py)_{(MeOH \to solv)}$**, kJ/mol	$\Delta_{tr}H^0_{calc}(Py)_{(MeOH \to solv)}$**, kJ/mol
MeOH	-44.08	-35.55	-	-
AN	-38.14	-39.23	5.94	-3.68
DMF	-40.61	-35.97	3.47	-0.42
DMSO	-39.11	-32.43	4.97	3.12

Notes: * calculated by the formula: $\Delta_{solv}H^0_{exp} = \Delta_{sol}H^0 - \Delta_{vap}H^0$, where $\Delta_{sol}H^0$ – enthalpies of Py dissolution in the solvents ([3,4]); $\Delta_{vap}H^0$ – enthalpy of vaporization of pyridine (40.21 kJ/mol, [17]).

** calculated by the formula: $\Delta_{tr}H^0(Py)_{MeOH \to solv} = \Delta_{solv}H^0(Py)_{AN,DMF,DMSO} - \Delta_{solv}H^0(Py)_{MeOH}$

Примечания: * рассчитаны по формуле: $\Delta_{solv}H^0_{эксп} = \Delta_{sol}H^0 - \Delta_{vap}H^0$, где $\Delta_{sol}H^0$ - энтальпии растворения Py в изучаемых растворителях ([3,4]); $\Delta_{vap}H^0$ – энтальпия испарения пиридина (40,21 кДж/моль, [17]).

** рассчитаны по формуле: $\Delta_{tr}H^0(Py)_{MeOH \to solv} = \Delta_{solv}H^0(Py)_{AN,DMF,DMSO} - \Delta_{solv}H^0(Py)_{MeOH}$

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Methanol, acetonitrile, dimethylformamide and dimethylsulfoxide belong to the group of mid-polar solvents ($\varepsilon_{(MeOH)}$ = 32.6, $\varepsilon_{(AN)}$ = 37.5, $\varepsilon_{(DMF)}$ = 36.7, $\varepsilon_{(DMSO)}$ = 46.6 [18]). It was suggested in [5,6] that changes in the solvate state of the hydrocarbon radical in the Py molecule upon changing the composition of the solvent MeOH → AN, DMSO, DMF will not have a significant effect on the change in the overall solvation energy of the molecule. The calculation of $\Delta_{tr}H^0_{exp}$(Py) showed that this assumption is valid only in the case of transfer of pyridine from MeOH to DMF (Table 3). Replacement of MeOH by AN leads to a significant increase in the solvation of the hydrocarbon radical, and the change of the solvent MeOH → DMSO – to its desolvation (Table 3).

Analysis of the solvation contributions of the functional groups of the pyridine molecule in the enthalpy of amine transfer from methanol to acetonitrile, dimethyl sulfoxide and dimethylformamide carried out with allowance for quantum-chemical modeling, showed that the main contribution to the change in the solvate state of pyridine during its transfer from MeOH to DMF is provided by the resolvation of the nitrogen atom. The change in the energy of solvation of pyridine with the replacement of MeOH by AN and DMSO is due to both a change in the solvate state of its reaction center and the hydrocarbon radical. Moreover, in the case of the transfer of pyridine to acetonitrile, the resolvation of the reaction center is dominant (Table 3), and in the case of transfer of pyridine from MeOH to DMSO, the contributions from the resolvation of the nitrogen atom and the hydrocarbon radical to the total energy of the resolvation of the molecule are approximately the same (Table 3).

Thus, a comparative analysis of the values of $\Delta_{tr}H^0$(Py), obtained by calorimetric method and by quantum-chemical modeling, showed that quantum chemical calculations can be useful for detailing intermolecular interactions in solutions.

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