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FTIR study of H-bonds cooperativity in complexes of 1,2-dihydroxybenzene with proton acceptors in aprotic solvents: Influence of the intramolecular hydrogen bond

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ABSTRACT

FTIR spectroscopic study of hydrogen bonding of 1,2-dihydroxybenzene (catechol) with proton acceptors has been carried out. The influence of intramolecular and intermolecular hydrogen bonds on the strengths of each other in complexes of 1,2-dihydroxybenzene with various proton acceptors has been analyzed. It was shown that intramolecular hydrogen bond is strengthened when 1,2-dihydroxybenzene interacts with bases (ethers, amines, nitriles, etc.) in inert solvents. The contribution of the cooperativity of intramolecular hydrogen bonds in the frequency of stretching vibrations of O–H groups linearly depends on the proton acceptor ability of the bases. The solvent effect on hydrogen bond cooperativity in 1,2-dihydroxybenzene-base complexes has been studied. The approach to determine the influence of cooperative effects on the formation of intermolecular complexes with 1,2-dihydroxybenzene is proposed. It was shown that the strength of intramolecular hydrogen bonds in the strength of interactions increases by 30–70%, and the strength of intermolecular hydrogen bond by 7–22%.

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1. Introduction

Hydrogen bonds (HB) have a significant influence on various physical, chemical and biological processes in condensed matter [1–3]. One of the main properties of hydrogen bonds is cooperativity, which refers to the strengthening of the hydrogen bond in multi-particle complex as compared with the hydrogen bond in complex of 1:1 stoichiometry [4,5]. Cooperative effects play a key role in supramolecular chemistry and biochemistry, and are the reason of association of polar groups in solution, as well as of the processes of molecular recognition [3,6–9].

To date, studies of cooperativity in systems with intermolecular hydrogen bonds, making use of theoretical and experimental methods have been carried out [10-19]. Approaches for assessing the cooperativity factors and the energy of cooperative hydrogen bonding have been developed [5,20-23]. Particularly, multi-particle complexes of monohydric aliphatic alcohols have been thoroughly studied [5,22-31].

Increasing the number of hydroxyl groups in the alcohol molecule creates the possibility of appearance of H-bonded complexes in solution, in which, in addition to the intermolecular interactions, intramolecular hydrogen bonds are formed. Determination of quantitative parameters of cooperative effects in systems with intramolecular hydrogen bonds is an important task, since such bonds affect the properties of various molecules (e.g., polyols, carbohydrates, and polyphenols) in the condensed state [32–35]. In addition, intra-HB cooperativity affects the conformational state of supramolecular receptors such as calixarenes and resorcinarenes [36–38].

Intramolecular hydrogen bonds affect the ability of substances to intermolecular binding. In the work of Kuhn [39] the red frequency shift of the stretching vibration band of the intramolecular H-bonded O-H group of aliphatic diols in an inert solvent was recorded. This shift was caused by the addition of diethyl ether, which forms a hydrogen bond with the second hydroxyl group of diol molecules. A similar change in the strength of hydrogen bonds was found by Spencer et al. [40,41] in the study of complexes of catechol and pyrogallol with various bases in carbon tetrachloride. Using the infrared spectral data obtained at different temperatures, Spencer et al. [40,41] found that the equilibrium constants and enthalpies of hydrogen bonds in these systems are significantly greater than in the complexes of phenol. For example, in complex of tetrahydrofuran with catechol the equilibrium constant and enthalpy is equal to K = 27.7 and $\Delta_{HB}H = -8.6$ kcal \times mol⁻¹, while in the complex with phenol they are K=13.5 and $\Delta_{HB}H=-4.9$ kcal \times mol⁻¹.

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Intermolecular hydrogen bonds also significantly affect the strength of intramolecular hydrogen bonds. The result of these influences is the change in reactivity and antioxidant properties of O–H groups in polyhydroxybenzenes [42]. It was found by Foti et al. [43,44] that the intramolecular hydrogen bond in the complexes of 1,2-dihydroxybenzene with proton acceptors is strengthened, whereas in the case of 2-methoxyphenol such effect was not observed.

In this paper the study of non-covalent interactions in complexes of 1,2-dihydroxybenzene with proton acceptors is carried out. This molecule has two hydroxyl groups in *ortho*-position, forming an intramolecular hydrogen bond. It allows a quantitative study of the mutual influence of intra- and intermolecular hydrogen bonds on each other. Based on the infrared spectroscopy, an attempt to estimate the cooperativity of hydrogen bonds in the complexes of 1,2-dihydroxybenzene with proton acceptors is undertaken. The data obtained allow to analyze the relationship between the values of cooperative effect and properties of interacting molecules. In addition, the solvent effect on the formation of complexes with cooperative hydrogen bonds is studied.

2. Experimental

Samples of substituted phenols were purchased from Acros Organics. Before experiments they were additionally purified [45]. 1,2-Dihydroxybenzene was recrystallized in benzene, 1,4dihydroxybenzene in acetone, 2-methoxyphenol was distilled under reduced pressure. All purification procedures were made in a nitrogen atmosphere. The degree of purity was controlled by gas chromatography. The lack of oxidation of the studied phenols in the presence of organic solvents was checked by IR spectroscopy.

Solvents used in IR measurements were analytical grade (Aldrich, 99%). They were dried and distilled before use by standard methods [45]. Residual water content in them was checked by Karl Fischer titration and IR spectroscopic measurements. It does not exceed 5×10^{-3} volume percent for the studied chemicals.

Infrared spectra were recorded on FTIR Bruker Vector 22 spectrometer. Interferrograms were collected at a resolution of 1 cm⁻¹. The number of scans accumulated was 64. CaF₂ cells were used with different spacers to achieve the best signal/noise ratio. Concentrations of substituted phenols varied from 5 mM to 20 mM, whereas concentration of bases in inert solvents was 200–500 mM. All measurements were made in the thermo controlled cuvette at 298 K. Processing of the measured IR spectra was carried out using the software package OPUS 6.0.

3. Results and discussion

Intramolecular H-bonded molecule of 1,2-dihydroxybenzene has a free proton of one O–H group able to interact with proton acceptors in solution. One of the most suitable methods for studying these interactions is infrared spectroscopy, since the absorption frequency of stretching vibrations are very sensitive to the formation of hydrogen bonds [46]. In this work the stretching vibration region of O–H groups of 1,2-dihydroxybenzene (3800–3000 cm⁻¹) was analyzed. The experimental frequency shift of the hydroxyl group in the solution relative to the absorption of free molecule in the gas phase can be represented as the sum of contributions arising from a manifestation of different types of intermolecular interactions (Eq. (1)) such as van der Waals interactions, hydrogen bond, and cooperative effect.

$$\Delta \nu_{\rm exp} = \Delta \nu_{\rm vdW} + \Delta \nu_{\rm HB} + \Delta \nu_{\rm coop} \tag{1}$$

When you transfer the alcohol or phenol molecules from the gas phase to any inert solvent or mixture of solvents, the band of O-H group is shifted to lower frequencies due to the van der Waals interactions (Δv_{vdW}). It should be noted that contribution of Δv_{udW} can be quite substantial and in some cases reaching more than 100 cm^{-1} [23]. If the solvent molecules possess proton acceptor ability, the additional frequency shift of O-H stretching vibration due to the formation of hydrogen bonds, is observed in the spectra. The frequency shift of the hydroxyl group due to the formation of single hydrogen bond in 1:1 complexes, such as alcohol-base (ROH...B) in the gas phase and in condensed state is denoted as Δv_{HB} . In more complicated complexes, with two or more simultaneous hydrogen bonds such as the ternary complex ROH…O(R)H…B, the strength of O–H…B hydrogen bond changes. This happens because the molecules at the expense of adjacent hydrogen bonds affect the donor and acceptor properties of each other. Consequently, the value of frequency shift of H-bonded O-H group in the ternary complex is different from $\Delta v_{\rm HB}$ in a complex with single hydrogen bond. The difference is due to cooperativity of hydrogen bonds (Δv_{coop}). In fact, both quantities (Δv_{HB} and Δv_{coop}) characterize the process of formation of hydrogen bonds. One (Δv_{HB}) characterizes the strength of complexes with single hydrogen bonds, another (Δv_{coop}) shows the change in the strength of the same H-bond, in the multi-particle complex with two or more adjacent hydrogen bonds.

These contributions ($\Delta \nu_{\text{HB}}$ and $\Delta \nu_{\text{coop}}$) in Eq. (1) are of special interest, since hydrogen bond formation defines the reactivity of molecules in solution. In order to evaluate and analyze them, the value of $\Delta \nu_{\text{vdW}}$ need to be known. Currently, there are a large number of parameters of solvent used to study the effect of media on the properties of solute [47]. The most widely used parameter for describing the van der Waals interactions is the parameter of polarity–polarizability of Kamlet–Abboud–Taft π^* -constant [47,48]. It derives from solvatochromic effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions [47,48].

3.1. Cooperativity of intramolecular hydrogen bonds in complexes of 1,2-dihydroxybenzene with proton acceptors

The infrared spectra of the three substituted phenols (Fig. 1) in carbon tetrachloride were measured. In the absorption region of the hydroxyl group of 1,2-dihydroxybenzene (structure **1**, Fig. 1) two bands (3615 cm^{-1} and 3569 cm^{-1}) are observed (Fig. 2). One band (3615 cm^{-1}) refers to the free O–H group, the second (3569 cm^{-1}) is a band of the O–H group, which forms an intramolecular hydrogen bond. 2-Methoxyphenol (structure **2**, Fig. 1) absorbs at 3558 cm^{-1} (Fig. 2), which corresponds to the intramolecularly H-bonded O–H group. 1,4-Dihydroxybenzene (structure **3**, Fig. 1) has only one band in the area of 3617 cm^{-1} , which corresponds to the absorption of two free O–H groups.

When adding proton acceptor (200-500 mM) in solution of substituted phenol in carbon tetrachloride, intermolecular hydrogen bonds are formed. As a result, new band in the infrared spectra appears. In all studied systems the concentration of proton acceptor was several times greater than the concentration of substituted phenols. The IR spectra of 2-methoxyphenol with proton acceptors in carbon tetrachloride (Fig. 3) show a decrease in the intensity of the band related to intramolecularly H-bonded O-H group. The magnitude of decrease in the intensity is different depending on the base. At the same time in the spectra (Fig. 3) new bands related to hydroxyl groups of the intermolecular complex with proton acceptors at much lower frequencies appear. It should be noted that the position (frequency) of intramolecularly H-bonded O-H group of 2-methoxyphenol remains practically unchanged after the addition of bases. 1,4-Dihydroxybenzene also forms hydrogen bonds with bases, as evidenced by the appearance of bands at lower frequencies, corresponding to the stretching vibrations of O-H groups of the complex (Fig. 4). The formation of intermolecular hydrogen



Fig. 1. Structure of studied substituted phenols.



Fig. 2. IR spectra of 1,2-dihydroxybenzene (1), 1,4-dihydroxybenzene (2) and 2-methoxyphenol (3) in carbon tetrachloride (OH-stretching vibration region).

bonds causes a decrease in the intensity of the free O–H groups (Fig. 4).

The IR spectra in Figs. 3 and 4 show that in carbon tetrachloride 1,4-dihydroxybenzene forms with bases much more complexes than 2-methoxyphenol. The reason is that, before the intermolec-



Fig. 3. IR spectra of 2-methoxyphenol (20 mM) (1) and its complexes with propionitrile (400 mM) (2), tetrahydrofuran (400 mM) (3) and triethylamine (400 mM) (4) in carbon tetrachloride (O–H stretching vibration region).



Fig. 4. IR spectra of 1,4-dihydroxybenzene (dash line) and its complex with diethyl ether (400 mM) (solid line) in carbon tetrachloride (O–H stretching vibration region).

ular hydrogen bond between the base and 2-methoxyphenol is formed, the intramolecular hydrogen bond must be broken. Hence if the molecule of substituted phenol has two hydroxyl groups in *ortho*-position, one of which is intramolecularly H-bonded, the base forms mainly the intermolecular hydrogen bond with the free O-H group. This fact is confirmed experimentally, as follows from the IR spectra of 1,2-dihydroxybenzene with bases in carbon tetrachloride (Fig. 5).



Fig. 5. IR spectra of 1,2-dihydroxybenzene (dash line) and its complex with propionitrile (400 mM) (solid line) in carbon tetrachloride (O–H stretching vibration region).



Fig. 6. IR spectra of complexes of 1,2-dihydroxybenzene (DHB)(10 mM) with proton acceptors (200–500 mM) in carbon tetrachloride (1 – DHB, 2 – DHB + acetonitrile, 3 – DHB + tetrahydrofuran, 4 – DHB + propionitrile, 5 – DHB + N,N-dimethylformamide, 6 – DHB + triethylamine).

After adding the base, band intensity of free O–H group of 1,2dihydroxybenzene falls several times greater than the intensity of the intramolecularly H-bonded O–H group (Fig. 5). At the lower frequency band of intermolecularly H-bonded O–H group appears (Fig. 5). Increasing concentration of the base leads to a complete disappearance of the band of free O–H group in the spectra. An interesting fact was discovered in the IR absorption spectra of 1,2-dihydroxybenzene with propionitrile in carbon tetrachloride. Under the action of the base, the frequency corresponding to the intramolecularly H-bonded O–H group of 1,2-dihydroxybenzene is shifted towards the region of lower frequencies. A similar pattern is observed in the spectra of 1,2-dihydroxybenzene in carbon tetrachloride by adding various bases (Fig. 6).

The absence of band of the free O–H group (3615 cm^{-1}) in the spectra indicates a full complexation of 1,2-dihydroxybenzene with the base. Therefore, it can be assumed that the solution mainly contains complexes of the next structure (Fig. 7).

Under the influence of H-bond formation with the bases intramolecular hydrogen bond in 1,2-dihydroxybenzene becomes stronger. This is a manifestation of the cooperative effect of hydrogen bonds. Earlier, Foti et al. [43,44] found that the absorption frequency of intramolecularly H-bonded O–H groups of 1,2-dihydroxybenzene in an inert solvent shifts to the lower frequencies due to interaction with the bases. Values of these shifts were proportional to the basicity scale β of Kamlet–Abboud–Taft [43,44]. In accordance with the results of Refs. [42,43], solvents significantly influence on the reactivity of 1,2-dihydroxybenzenes. In the present work, unusual behavior of intramolecularly H-bonded



Fig. 7. Structure of complex between 1,2-dihydroxybenzene and base (B) with cooperative hydrogen bonds.

Table 1

Frequencies of the intramolecularly H-bonded O–H group of 1,2-dihydroxybenzene in complexes with proton acceptors (B) in carbon tetrachloride and frequency shifts due to cooperativity effect $(\Delta \nu_{coop}^{\text{intra}})$ (cm⁻¹), enthalpies of hydrogen bond formation of methanol with proton acceptors (B) $(\Delta_{\text{HB}}\text{H}^{\text{ROH} - \text{B}})$ (kJ mol⁻¹).

N	Proton acceptor (B)	$v_{\rm coop}^{\rm intra}$	$\Delta v_{ m coop}^{ m intra}$	$\Delta_{HB} H^{ROH\cdots Ba}$
1	Nitromethane	3563	6	-2.6
2	1,4-Dioxane	3560	9	-8.3
3	Ethyl acetate	3560	9	-8.6
4	Acetonitrile	3557	12	-6.4
5	Acetone	3557	12	-10.0
6	Propionitrile	3556	13	-8.1
7	Tetrahydrofuran	3556	13	-12.8
8	Diethyl ether	3555	14	-13.6
9	N,N-dimethylformamide	3551	18	-13.8
10	Dimethyl sulphoxide	3548	21	-13.3
11	Pyridine	3547	22	-15.9
12	3-Methylpyridine	3545	24	-18.0
13	Tri-n-butylamine	3540	29	-22.1
14	Triethylamine	3539	30	-24.1

^a Values of hydrogen bond enthalpy were taken from Ref. [49].

O–H group in the complexes of 1,2-dihydroxybenzene with proton acceptors was analyzed.

Frequency shifts of the intramolecularly H-bonded O–H group induced by cooperative effect ($\Delta \nu_{\text{coop}}^{\text{intra}}$) were calculated by Eq. (2).

$$\Delta \nu_{\rm coop}^{\rm intra} = \nu^{\rm intra}({\rm CCl}_4) - \nu_{\rm B}^{\rm intra}({\rm CCl}_4) \tag{2}$$

where $\nu^{intra}(CCl_4)$ is the frequency of the intramolecularly H-bonded O-H group of 1,2-dihydroxybenzene in carbon tetrachloride; $\nu_B^{intra}(CCl_4)$ is the frequency of the intramolecularly H-bonded O-H group of 1,2-dihydroxybenzene after adding of the base (B) in carbon tetrachloride.

The values obtained are shown in Table 1. In all cases, the red frequency shift of the intramolecularly H-bonded O–H group of the complex 1,2-dihydroxybenzene–base is observed. Consequently, the strengthening of the intramolecular hydrogen bonds takes place. The values of $\Delta \nu_{\rm coop}^{\rm intra}$ vary significantly from one base to another. They were compared with the enthalpy of hydrogen bond [49], taken as the measure of the proton acceptor ability of the base (Table 1). It was shown that between frequency shift and values of $\Delta_{\rm HB} H^{\rm ROH \cdots B}$, there is a direct relation.

Fig. 8 shows a linear relationship between the obtained values of $\Delta v_{\text{coop}}^{\text{intra}}$ and the thermodynamic scale of the proton acceptor ability



Fig. 8. The relationship between frequency shifts of the intramolecularly Hbonded O–H group of 1,2-dihydroxybenzene, induced by cooperative effect, with $\Delta_{\text{HB}}\text{H}^{\text{ROH}\dots\text{B}}$ (numbers of points correspond to the Table 1).

Table 2

Frequencies of the free and the intramolecularly H-bonded O–H group of 1,2dihydroxybenzene in *n*-hexane, carbon tetrachloride and benzene, frequency shifts of intramolecular hydrogen bond in these solvents (Δv_{intra}), values of polarity–polarizability parameter π^* of solvents.

Solvent (S)	$v_{intra} \left(cm^{-1} \right)$	$v_{\rm free} ({\rm cm}^{-1})$	$\Delta v_{intra} (cm^{-1})$	π^{*a}
n-Hexane	3579	3628	49	-0.11
Carbon tetrachloride	3569	3615	46	0.21
Benzene	3555	3598 ^b	43	0.55

^a Values of π^* were taken from Ref. [47].

^b This value was calculated by Eq. (7).

of bases ($\Delta_{\text{HB}}\text{H}^{\text{ROH}\dots\text{B}}$). This dependence is described by Eq. (3): $\Delta\nu_{\text{rcon}}^{\text{intra}} = 1.29 \times \Delta_{\text{HB}}\text{H}^{\text{ROH}\dots\text{B}}$ (R = 0.948, SD = 2.5 cm⁻¹) (3)

Early Foti et al. [42,43] have found a complex relationship between the values of basicity β and an additional frequency shift of the intramolecularly H-bonded O–H group of 1,2dihydroxybenzene induced by interaction with the base. They have explained this dependence by the difference in the nature of hydrogen bonds for the N- and O-bases. Furthermore, in our view, the parameter β includes not only the contribution of hydrogen bonds, but also partially the van der Waals interaction term. From this perspective, the use of the enthalpy of complexation of methanol with the bases as a measure of the proton acceptor ability seems more justified, since this quantity determines the energy (strength) of hydrogen bonds. Consequently, the contribution of the cooperative effect of intermolecular hydrogen bonding on the strength of intramolecular hydrogen bond is proportional to the proton acceptor ability of bases (B).

The binding of molecules in solution is sensitive to solvation effects. Solvents also affect systems with cooperative hydrogen bonds, which was confirmed in the Ref. [50]. The cooperative effect in the 1,2-dihydroxybenzene complexes with proton acceptors in a series of inert solvents was analyzed. As inert solvents *n*-hexane, carbon tetrachloride and benzene were chosen because of their inability to form strong hydrogen bonds with 1,2dihydroxybenzene. First, the frequencies of the intramolecularly H-bonded O-H group of 1,2-dihydroxybenzene in these solvents were determined. They are given in Table 2. The frequency shifts due to the formation of intramolecular hydrogen bond are calculated relative to the frequency of the free O-H groups in the studied solvents (v_{free}). For hexane and carbon tetrachloride, the values of v_{free} were measured experimentally (Table 2). In the case of benzene the experimental absorption frequency of non-bonded intramolecularly O-H group contains the contribution of hydrogen bonds with solvent. Therefore, the frequency of the free O-H group of 1,2-dihydroxybenzene in benzene was calculated according to Eq. (7). This equation as will be shown below, takes into account only non-specific interaction with the solvent.

Frequency shift of intramolecularly H-bonded O–H group of 1,2-dihydroxybenzene relative to the frequency of free O–H group changes during the transfer from one solvent to another. In the series of *n*-hexane–carbon tetrachloride–benzene, the ability of solvents to the van der Waals interactions increases, as evidenced by the values of the parameter π^* (Table 2), in turn, the value of $\Delta \nu_{intra}$ in this area is slightly decreased.

The frequencies of the intramolecularly H-bonded O–H group of 1,2-dihydroxybenzene in *n*-hexane and benzene after adding of proton acceptors (Table 3) were determined. These values are always smaller (red-shifting) than the frequencies obtained in the studied solvents without bases. This result indicates the manifestation of the cooperative effect. The frequency of stretching vibrations of O–H groups depends strongly on the solvent (Table 3). Transfer of complexes of 1,2-dihydroxybenzene with bases from hexane to benzene causes less change in the frequency of intramolecu-

Table 3

Frequencies (cm⁻¹) of the intramolecularly H-bonded O-H group of 1,2dihydroxybenzene in complexes with proton acceptors in *n*-hexane and benzene, difference between these values obtained in two solvents $x(\Delta \nu \zeta_{HTA}^{cH_1} - \zeta_{GH_6})$ (cm⁻¹).

Base (B)	$v_{intra}^{n-C_6H_{14}}$	$v_{intra}^{C_6H_6}$	$\Delta \nu_{intra}^{C_{6}H_{14} \rightarrow C_{6}H_{6}}$
-	3579	3555	24
1,4-Dioxane	3565	3549	16
Acetonitrile	3563	3545	18
Diethyl ether	3563	3547	16
N,N-dimethylformamide	3556	3543	13
Propionitrile	3563	3546	17
Pyridine	3552	3537	15
Triethylamine	3545	3528	17
Tetrahydrofuran	3562	3547	15

larly H-bonded O–H group than the transfer of the free molecule of 1,2-dihydroxybenzene.

In the literature [5,23,50], cooperativity factors is used as a measure of the cooperative effect. The cooperativity factor is often calculated as the ratio of the frequency shift of the hydrogen bond in the multi-particle complex to the frequency shift of the double complex. In this work, the cooperativity factor is calculated as the ratio of the frequency shift of the intramolecularly H-bonded O–H group in the complex of 1,2-dihydroxybenzene with base ($\nu_{O-H...O-H...B}$) in an inert solvent to the frequency shift of the intramolecularly H-bonded O–H groups in pure inert solvent ($\nu_{O-H...O-H.}$) (Eq. (4)).

$$A_{\text{intra}} = \frac{\nu_{\text{free}}^{\text{OH}} - \nu_{\mathbf{0}-\mathbf{H}\cdots\mathbf{0}-\mathbf{H}\cdots\mathbf{B}}}{\nu_{\text{free}}^{\text{OH}} - \nu_{\mathbf{0}-\mathbf{H}\cdots\mathbf{0}-\mathbf{H}}}$$
(4)

where v_{free}^{OH} is the frequency of free O–H group of 1,2-dihydroxybenzene in the studied solvents.

According to Eq. (4) cooperativity factors of intramolecular hydrogen bonds in the three solvents were calculated (Table 4). During analysis of the data obtained two important facts can be noticed. First, the cooperativity factor increases with the proton acceptor ability of base. Second, the cooperativity factor decreases by transferring the complexes from *n*-hexane to carbon tetrachloride and from carbon tetrachloride to benzene.

3.2. Cooperativity of intermolecular hydrogen bonds in complexes of 1,2-dihydroxybenzene with proton acceptors

In this study, we have found that the intramolecular hydrogen bond in 1,2-dihydroxybenzene is strengthened during the formation of intermolecular hydrogen bond with the base. The question arises: how does the intramolecular hydrogen bond affect the strength of intermolecular hydrogen bonding in complexes of 1,2dihydroxybenzene with proton acceptors.

1,2-Dihydroxybenzene has a high proton donor ability. Stretching vibrations band related to H-bonded O–H groups in complexes of 1,2-dihydroxybenzene with strong bases (amines) is shifted to the region of absorption of C–H vibrations. Consequently, it is

Table 4

Cooperativity factors of the intramolecular hydrogen bonds in the complexes of 1,2-dihydroxybenzene with different bases (B) in n-hexane, carbon tetrachloride and benzene.

Base (B)	A ^{n-hexane} intra	$A_{intra}^{CCl_4}$	$A_{intra}^{C_6H_6}$
1,4-Dioxane	1.31	1.20	1.14
Acetonitrile	1.35	1.26	1.23
Diethyl ether	1.35	1.26	1.19
N,N-dimethylformamide	1.49	1.39	1.28
Propionitrile	1.35	1.30	1.21
Pyridine	1.57	1.48	1.42
Tetrahydrofuran	1.37	1.26	1.19
Triethylamine	1.71	1.65	1.63



Fig. 9. O–H stretching vibration region of IR spectra of 1,2-dihydroxybenzene in binary mixture of carbon tetrachloride with diethyl ether (content of the base in a mixture is presented in figure).

not possible to determine its frequency. Therefore, complexes of 1,2-dihydroxybenzene with the bases of moderate strength were studied.

Figs. 9 and 10 show the infrared spectra of O–H stretching vibrations of 1,2-dihydroxybenzene in the two binary mixtures: diethyl ether–carbon tetrachloride and 1,4-dioxane–1,2-dichloroethane. The components of binary mixtures are selected so that only one of solvents is able to form strong hydrogen bonds with 1,2dihydroxybenzene, but they both have almost equal ability to establish van der Waals (non-specific) interactions. The last statement follows from the similarity of values of the parameters of van der Waals interactions π^* and S_{VW} [29,49,50] for the components of a binary mixture.

In the spectra of 1,2-dihydroxybenzene in pure diethyl ether and 1,4-dioxane (Figs. 9 and 10), the absorption band due to intramolecularly H-bonded O–H group almost completely disappears. These data indicate a breaking of the intramolecular hydrogen bond due to interaction with the base. In accordance with the measured IR spectra in the medium of the base, 1,2-dihydroxybenzene forms complexes with two molecules of the proton acceptor (Fig. 11). In these complexes (Fig. 11) there are no cooperative effects, since



Fig. 10. O–H stretching vibration region of IR spectra of 1,2-dihydroxybenzene in binary mixture of 1,2-dichloroethane with 1,4-dioxane (content of the base in a mixture is presented in figure).



Fig. 11. Structure of complexes of 1,2-dihydroxybenzene formed in neat bases.

there is no adjacent hydrogen bonds, as in the complexes of 1,2dihydroxybenzene with one molecule of base formed in an inert solvent (Fig. 7).

In both cases in Figs. 9 and 10, the same pattern is observed. Increasing the concentration of bases (diethyl ether or 1,4-dioxane) induces a shift of the stretching vibration band of hydroxyl groups of the intermolecular complex in the direction of higher frequencies (blue-shifting). Such result suggests that the strength of intermolecular hydrogen bond of 1,2-dihydroxybenzene with a proton acceptor in pure base is lower than in an inert solvent. Changing the strength of hydrogen bonds can be explained either by the sterical hindrance in the complexes of 1:2 (Fig. 11) or by the influence of cooperative effect in the complexes of 1:1 (Fig. 7). IR spectral measurements show that the frequency in the complexes of 1,4-dihydroxybenzene with diethyl ether in a binary mixture of carbon tetrachloride-diethyl ether varies very little (from 3357 cm⁻¹ in carbon tetrachloride to 3365 cm⁻¹ in neat diethyl ether), despite the change in the composition of the complex with increasing concentration of the base. The frequency of the complex of diethyl ether with various substituted phenols obtained in a base medium decreases in the following 1,4-dihydroxybenzene $(3365 \text{ cm}^{-1}) > 2$ -methoxyphenol order (3332 cm⁻¹)>1,2-dihydroxybenzene $(3354 \, \text{cm}^{-1})$ > phenol $(3307 \, \text{cm}^{-1})$. These data show that the hydrogen bonds of 1,2-dihydroxybenzene with two molecules are not spatially difficult. On the contrary, the introduction of the second O-H group in the ortho-position of phenol molecule increases its proton donor ability. Consequently, the greatest strength of hydrogen bonds in complexes of 1,2-dihydroxybenzene with one molecule of the base formed in inert solvents (Fig. 7) is induced by the cooperative effect of intramolecular hydrogen bond. The question arises: how to estimate the value of the H-bond cooperativity in such complexes. It is possible to calculate the difference between the frequencies of H-bonded O-H groups of 1,2-dihydroxybenzene obtained in the pure base and in solution of base in an inert solvent. However, depending on what is selected as the inert solvent (S) (*n*-hexane, carbon tetrachloride, benzene, 1,2-dichloroethane) contribution of the cooperative effect (Δv_{coop}^{inter}) will change its value. The absorption frequencies of H-bonded O-H groups of 1,2-dihydroxybenzene in complexes with ethers and nitriles in a series of solvents (Table 5) confirm this statement.

Table 5

Stretching vibration frequencies (cm^{-1}) of O–H groups of 1,2-dihydroxybenzene H-bonded with the proton acceptors in a series of solvents and in pure bases.

Base (B)	$\nu_{n-C_6H_{14}}^{O-H\cdots B}$	$\nu^{O-H\cdots B}_{CCl_4}$	$\nu^{O-H\cdots B}_{C_6H_6}$	$\nu^{0-H\cdots B}_{1,2-C_2H_4Cl_2}$	$v_{neat}^{O-H\cdots B}$
1,4-Dioxane	3338	3313	3290	3276	3321
Acetonitrile	3426	3400	3380	3364	3381
Diethyl ether	3286	3258	3232	3210	3307
Propionitrile	3418	3390	3375	3358	3385
Tetrahydrofuran	3284	3252	3219	3196	3286



Fig. 12. Correlation between stretching vibration frequencies of H-bonded O–H group of 1,2-dihydroxybenzene with tetrahydrofuran in aprotic solvents and values of π^* -constant.

One should take into account the difference in the non-specific interactions in order to properly evaluate the contribution of the cooperative effect. The decision of this problem is to use the scales of solvents, such as π^* -constant. Comparison of frequencies of O–H groups of 1,2-dihydroxybenzene H-bonded with the bases (B) in solvents (S), which are not capable to strong specific interactions, with the values of the π^* -parameter of these solvents gives a linear dependence of high quality (Eq. (5)).

$$\nu_{\rm S}^{\dots \rm O-H\dots \rm B} = a + b \times \pi^* \tag{5}$$

Fig. 12 presents an example of such dependence for complexes of 1,2-dihydroxybenzene with tetrahydrofuran.

Table 6 contains the parameters of correlations described by Eq. (5). It is clearly seen that the slope varies depending on the base, and characterizes the sensitivity of the O–H group of the complex to the influence of the solvent.

From the linear correlations described by Eq. (5), the values of $\nu_{neat}^{O-H\dots B}$ obtained in pure base fall out (Fig. 12). The contribution of cooperativity of intermolecular hydrogen bond in the O-H stretching vibration frequencies is equal to the value of this deviation. The values of the frequency shift due to the cooperative effect of intramolecular hydrogen bonding on the intermolecular hydrogen bonds ($\Delta \nu_{coop}^{inter}$) are shown in Table 8. It is evident that the increasing of proton acceptor ability of base increases the contribution of the cooperative effect. For calculation of cooperativity factors Eq. (6) was used.

$$A_{\text{inter}} = \frac{\nu_{\text{free}}^{\text{OH}}(B) - \nu_{\text{O}-H\cdots B}}{\nu_{\text{free}}^{\text{OH}}(B) - \nu_{\text{O}-H\cdots B}}$$
(6)

where $v_{free}^{OH}(B)$ is the frequency of free O–H group of 1,2dihydroxybenzene molecule in base (B) environment, $v_{O-H\cdots O-H\cdots B}$ is the frequency of H-bonded O–H group of 1,2-dihydroxybenzene in the complex with proton acceptor formed in an inert solvent

Table 6

Parameters of correlations $\nu_{S}^{-O-H\dots B} = a + b \times \pi^{*}$ for complexes of 1,2-dihydroxybenzene with different bases (B) (SD – standard deviation (cm⁻¹), R – correlation coefficient).

Base	а	b	SD	R	π^*
1,4-Dioxane	-73.0	3329	1.0	0.999	0.49
Acetonitrile	-71.7	3417	2.4	0.997	0.71
Diethyl ether	-88.0	3277	3.1	0.997	0.24
Propionitrile	-67.7	3409	4.3	0.990	0.64
Tetrahydrofuran	-103.2	3273	2.3	0.999	0.55

Table 7

Absorption frequencies of free O–H groups of 1,2-dihydroxybenzene in inert solvents (cm⁻¹), values of π^* -constant of these solvents.

Solvent	n-Hexane	Cyclohexane	Carbon tetrachloride	Dichloromethane
$v_{\rm free}^{\rm OH}$	3628	3622	3615	3585
π^*	-0.11	0.00	0.21	0.82

Table 8

Frequencies of free O–H group ($\nu_{\text{free}}^{\text{OH}}(B)$) and cooperative intermolecularly Hbonded O–H group ($\nu_{\text{calc}}^{\text{OH}...O-H...B}$) of 1,2-dihydroxybenzene, experimentally measured frequency of intermolecularly H-bonded O–H group in complexes without intramolecular H-bonds ($\nu_{\text{exp}}^{\text{O-H}...B}$), contribution of the cooperative effect ($\Delta \nu_{\text{coop}}^{\text{inter}}$) and cooperativity factors of intermolecular hydrogen bond (A_{inter}).

Base	$v_{\text{free}}^{\text{OH}}(B)$	$v_{calc}^{OH\dots O-H\dots B}$	$v_{exp}^{0-\mathbf{H}\cdots\mathbf{B}}$	$\Delta \nu_{ m coop}^{ m inter}$	A _{inter}
1,4-Dioxane	3601	3293	3321	27	1.10
Acetonitrile	3593	3366	3381	15	1.07
Diethyl ether	3612	3256	3307	51	1.17
Propionitrile	3594	3366	3385	19	1.09
Tetrahydrofuran	3598	3216	3286	70	1.22

(Fig. 7) and $\nu_{O-H...B}$ is the frequency of H-bonded O–H group of 1,2dihydroxybenzene in the complex with proton acceptor formed in the base media (Fig. 11).

To get the correct amount of A_{inter} , it is necessary to know the frequency of absorption of free O–H groups of 1,2-dihydroxybenzene in the base environment, which, experimentally, is impossible to obtain. However, it can be calculated using the absorption frequency of free O–H groups of 1,2-dihydroxybenzene in solvents which are inactive to the proton of the hydroxyl group (Table 7). These values were determined in present work.

The measured data ($\nu_{\text{free}}^{\text{OH}}$) were compared with the values of π^* -parameter. Linear correlation described by Eq. (7) was obtained.

$$\nu_{\text{free}}^{\text{OH}} = 3623 - 45.9 \times \pi^* \quad (R = 0.998, \text{ SD} = 1.4 \text{ cm}^{-1})$$
 (7)

Based on Eq. (7) and values of the parameter π^* of the bases (B) the frequencies of the free O–H groups in proton acceptors were determined (Table 8). Using them, cooperativity factors (A_{inter}) were calculated by Eq. (6). The values of A_{inter} characterize the strengthening of intermolecular hydrogen bonds under the influence of intramolecular hydrogen bond. For example, the strengthening of intermolecular hydrogen bond in complex of 1,2-dihydroxybenzene with tetrahydrofuran is 23% relative to non-cooperative hydrogen bond. Cooperativity factors (A_{inter}) also linearly depend on proton acceptor ability of the bases.

4. Conclusion

The IR spectroscopic studies of cooperativity of intra- and inter-molecular hydrogen bonds in the complexes of 1,2dihydroxybenzene with different bases in various solvents were carried out. Methods for determination and analysis of quantitative parameters of the cooperative effects were proposed. Comparison of obtained data shows that the frequency shift due to the cooperative effect varies in wider range for the intermolecular hydrogen bonds, rather than for the intramolecular hydrogen bonds. In contrast, the cooperativity factors of the intramolecular hydrogen bond are of a higher magnitude than for the intermolecular hydrogen bond. This can be explained by the different strength of non-cooperative intra- and inter-molecular hydrogen bonds of 1,2-dihydroxybenzene. Analysis of the data shows that the cooperativity factors, both for intra- and inter-molecular hydrogen bonds is determined by the proton acceptor ability of the bases. The cooperative effect leads to the fact that the solvation of 1,2dihydroxybenzene in an inert solvent with a small amount of base (200-500 mM) had a more significant impact on its properties than the solvation in pure base. It should be noted that, when studying the binding of molecules of hydroxybenzenes, one must take into account van der Waals interaction with the solvent, since their contribution is also noticeable.

In general, one can conclude, that even when the proton acceptor interacts with such a simple molecule with intramolecular hydrogen bonds, such as the 1,2-dihydroxybenzene, great influence of cooperative effects on the frequency of absorption in the infrared spectra is observed. Thus, in supramolecular systems capable to forming more hydrogen bonds, one can expect even more significant manifestations of cooperativity, which may affect the properties and the reactivity of the interacting molecules.

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