



“Additive” cooperativity of hydrogen bonds in complexes of catechol with proton acceptors in the gas phase: FTIR spectroscopy and quantum chemical calculations

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ABSTRACT

Experimental study of hydrogen bond cooperativity in hetero-complexes in the gas phase was carried out by IR-spectroscopy method. Stretching vibration frequencies of O–H groups in phenol and catechol molecules as well as of their complexes with nitriles and ethers were determined in the gas phase using a specially designed cell. O–H groups experimental frequency shifts in the complexes of catechol induced by the formation of intermolecular hydrogen bonds are significantly higher than in the complexes of phenol due to the hydrogen bond cooperativity. It was shown that the cooperativity factors of hydrogen bonds in the complexes of catechol with nitriles and ethers in the gas phase are approximately the same. Quantum chemical calculations of the studied systems have been performed using density functional theory (DFT) methods. It was shown, that theoretically obtained cooperativity factors of hydrogen bonds in the complexes of catechol with proton acceptors are in good agreement with experimental values. Cooperative effects lead to a strengthening of intermolecular hydrogen bonds in the complexes of catechol on about 30%, despite the significant difference in the proton acceptor ability of the bases. The analysis within quantum theory of atoms in molecules was carried out for the explanation of this fact.

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1. Introduction

Among all types of non-covalent interactions, formed in organic molecules, hydrogen bonds have the greatest impact on their properties and reactivity [1–3]. Cooperativity is an important property of hydrogen bonds. The cooperativity means strengthening or weakening of the hydrogen bonds in the complexes with the adjacent hydrogen bonds in comparison with the binary complexes with a single one [2,4–6]. Cooperativity of hydrogen bonds determines the structure and properties of self-associated solvents (water, alcohols, amides, etc.) [7–10]. In addition, cooperative effect of H-bonding leads to additional stabilization of supramolecular architectures [11,12], proteins and nucleic acids [13,14]. One of the most suitable methods to study the cooperativity of hydrogen bonds is IR spectroscopy. This method was used for the investigation of cooperative effects in multi-particle complexes formed in solution [15] and in the inert gas matrices [16]. Study of the cooperative effects in condensed matter is complicated by the presence of various types of non-covalent interactions and the solvent effects [17]. Therefore, investigation of hydrogen bonds cooperativity in the gas phase is of great interest. These studies can give the opportunity to quantify “neat” cooperative effect and to understand the

nature of H-bond cooperativity phenomenon. Experimentally the cooperative hydrogen bonds in the gas phase were studied only in clusters of aliphatic alcohols and water. The main results of these investigations were reviewed in [18]. The authors [18,19] using IR-spectroscopy method showed that the strength of hydrogen bonds in clusters of alcohols and water is much greater than in dimers. Experimental studies of the hydrogen bond cooperativity in complexes consisting of different molecules were not carried out in the gas phase. In the last decade, the cooperativity of hydrogen bonds in the gas phase was mostly studied using various quantum chemical approaches. Theoretical calculations provide an opportunity to study systems with cooperative hydrogen bonds, consisting of different number of molecules, which are very difficult to study experimentally. Hydrogen bond cooperativity in clusters of amides [6,20], some biological molecules [21] and in systems with multiple unusual weak hydrogen bonds [22] was studied using different quantum-chemical methods. Authors [23] also used quantum theory of atoms in molecules (QTAIM) approaches for analysis of this phenomenon. In works [24,25] calculations of intramolecular hydrogen bond cooperativity were carried out. Despite significant progress in the use of theoretical calculations, experimental studies of hydrogen bond cooperativity in the gas phase are rather poorly distributed.

In this work, we have carried out the experimental study of hydrogen bond cooperativity in the gas phase using the infrared spectroscopy method. It is quite difficult task to determine spectral

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parameters of ternary hetero-complexes with adjacent hydrogen bonds in the gas phase. Therefore, we examined the complexes consisting of two molecules, one of which forms an intramolecular hydrogen bond. Complexes of catechol with different proton acceptors were used as objects of investigation. Catechol is a polyhydroxy organic compound, which is widely used in industry. It is able to form adjacent hydrogen bonds with proton acceptors that can significantly affect its reactivity and antioxidant capacity [26–28]. Earlier complexes of catechol with proton acceptors were investigated in the liquid state [26,27,29]. In this paper we study them in the gas phase and analyze the effect of proton acceptors on the value of cooperative effect. Theoretical calculations were carried out for the validation of the new experimental results. Geometrical, spectroscopic and energetic parameters of studied complexes were calculated using the DFT methods. The nature of cooperative effect was discussed using QTAIM analysis.

2. Experimental

Samples of phenol and catechol were purchased from Aldrich with a mass-fraction purity of about 0.99. Before experiments they were additionally purified. Catechol was recrystallized in benzene. Additionally it was purified by repeated fractional sublimation under reduced pressure. Analytical grade phenol has water as its main impurity. Therefore, phenol was dried by distillation from a benzene solution to remove the water-benzene azeotrope and the excess benzene, followed by distillation of the phenol at reduced pressure. All purification procedures were performed 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 substances was checked by IR spectroscopy.

Nitriles and ethers used in IR measurements were analytical grade (Aldrich, 99%). They were dried and distilled before use by standard methods [30]. Nitriles were shaken with Linde 4A molecular sieves. Subsequently they were stirred with calcium hydride until no further hydrogen is evolved. The nitriles were then fractionally distilled over P_2O_5 to remove most of the remaining water. Traces of P_2O_5 were removed by distilling from anhydrous potassium carbonate. Ethers were refluxed with and distilled from $LiAlH_4$ to remove water, peroxides and other impurities. After they were additionally dried and fractionally distilled from sodium. Residual water content in nitriles and ethers was checked by Karl Fischer titration and IR spectroscopic measurements. It does not exceed 5×10^{-3} volume percent for the studied chemicals.

The infrared spectra were received using the FTIR Bruker Vector-22 spectrometer ($400\text{--}4000\text{ cm}^{-1}$) equipped with a global source, a KBr beamsplitter and MCT (mercury cadmium telluride) detector. The interferograms were recorded with a resolution of 2 cm^{-1} and Fourier transformed using a Blackman-Harris apodization function. The number of scans used in a particular experiment was 64.

The gas phase experiments were performed exploiting hand made glass cell, similar enough to use by Lin and Fishman [31]. The sample path length for all experiments was 10 cm. The cell windows were 32 mm diameter CaF_2 disks. Spectra were obtained under inert N_2 atmosphere. Temperature was measured by the thermocouple and was kept constant using the power supply with adjustable voltage to ensure a standard deviation smaller than 1 K.

Experiments in vapor phase included the measurements of the IR-spectra of pure phenols, proton acceptors and their mixtures, respectively, at the same temperature. Weight of sample of studied substances, placed in a cuvette for measurement, was always the same and equal to 50 mg. The interactive spectral subtraction was performed for the determination of H-bonded O–H group vibration frequencies in complexes $ROH \cdots B$. The spectra of pure base and phenol or catechol were subtracted from the spectra of their

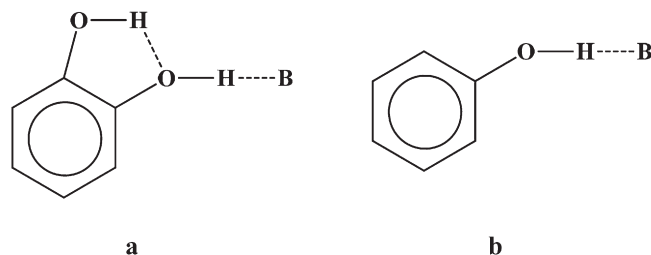


Fig. 1. Studied complexes of catechol (a) and phenol (b) with proton acceptors (B).

mixtures. The position of the absorption band (in cm^{-1}) was found as the abscissa of the experimental contour maximum. Thus, an experimental contour was wide, first-order derivatives were used for location the maximum.

3. Computational details

Quantum chemical calculations of catechol and phenol molecules, as well as of its complexes were carried out in Firefly package [32] using B3LYP hybrid DFT functional [33], which combines Becke's three-parameter functional [34] with the non-local correlation provided by the correlation functional of Lee et al. [35] and VWN formula 1 [36] RPA correlation (as in Gaussian and NWChem but GAMESS packages). It is well-known fact that the DFT methods require a moderate expense of time and provide good results for normal stretching vibration frequencies of molecules [37]. Pople's basis set 6-311++G(d,p) of triple-zeta quality for valence shell with diffuse and polarization functions on all atoms was used for calculation. High quadratures with 155 radial points and 590 Lebedev angular grid points were used. Tight SCF criteria was applied to get accurate vibration frequencies. It was found in our tests (see Table S1 of supporting materials) that the results obtained with chosen basis set do not differ significantly from those obtained by using extremely precise calculation with basis set 6-311++G(3df,3dp) and "army-grade" quadratures (200 radial points and 2090 Lebedev angular grid points). Basis set 6-311++G(d,p) provides very small BSSE error (less than 0.5 kcal/mol). The structure of all the molecules and complexes was obtained by complete optimization of geometry. The optimized structures belong to the minimum of potential energy surface, which was verified by calculating the second derivatives matrix (Hessian), all of whose members had a positive value. The magnitude of the superposition error slightly changes in going from one complex to another (less than 0.1 kcal/mol in most cases). Thermodynamic functions were calculated with the inclusion of BSSE correction (see Table S1).

The calculations of topological characteristics of the electron distribution in molecules as well as integrated atomic characteristics within quantum theory of atoms in molecules (QTAIM) [38] approaches were carried out on AIMAll Professional package [39]. All discussed QTAIM-properties are in atomic units (the list of atomic units and transition coefficients are in Table S2 of supporting material).

4. Results and discussion

4.1. IR-spectroscopy

We have studied cooperative hydrogen bonding of catechol with proton acceptors in gas phase using IR-spectroscopy method. Catechol forms complexes with the adjacent hydrogen bonds with an equimolar amount of base (B) (Fig. 1). In such complexes the inter- and intramolecular hydrogen bonds influence on the strength of each other (cooperative effect) as was shown in [25–27,29].

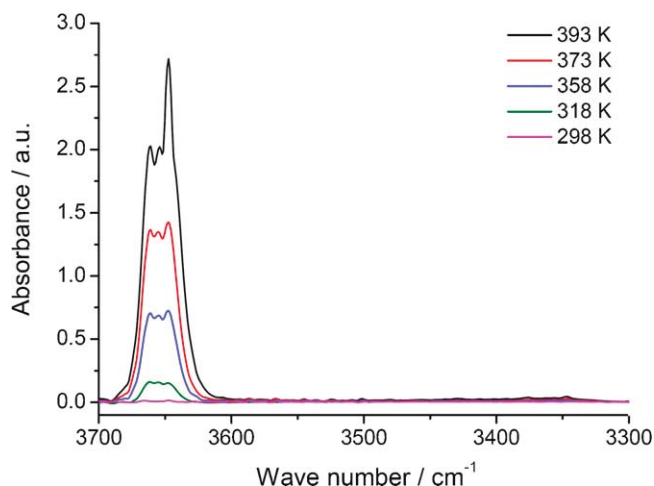


Fig. 2. IR spectra of phenol in the gas phase at different temperatures (O–H stretching vibration region).

Formation of hydrogen bonds is accompanied by a shift of the O–H group stretching vibration band, increasing the length of the covalent O–H bond and decreasing the distance between the hydrogen bonded atoms. All these parameters characterize the strength of hydrogen bond in the gas phase.

The measure of the cooperative effect is a cooperativity factor of hydrogen bonds [40], which is calculated as the ratio of X–H (X=O or N) stretching vibration frequency shift in the complexes with the adjacent hydrogen bonds ($\Delta\nu_{\text{HB}}^{\text{O-H}\cdots\text{O-H}\cdots\text{B}}$) to the X–H stretching vibration frequency shift in a complex with a single hydrogen bond ($\Delta\nu_{\text{HB}}^{\text{O-H}\cdots\text{B}}$) (double complex or one molecule):

$$A_b = \frac{\Delta\nu_{\text{HB}}^{\text{O-H}\cdots\text{O-H}\cdots\text{B}}}{\Delta\nu_{\text{HB}}^{\text{O-H}\cdots\text{B}}} \quad (1)$$

The frequency shift in a complex with cooperative hydrogen bonds ($\Delta\nu_{\text{HB}}^{\text{O-H}\cdots\text{O-H}\cdots\text{B}}$) can be determined from the IR spectra of catechol with equimolar quantity of bases in the gas phase (structure a in Fig. 1). Value of $\Delta\nu_{\text{HB}}^{\text{O-H}\cdots\text{B}}$ can be obtained from the infrared spectra of the complexes of phenol (structure b in Fig. 1). Phenol molecule contains only one hydroxyl group, so it is not capable to intramolecular hydrogen bonding by definition. In addition, phenol has a similar H-donor ability to hydrogen bonding as the *meta*- and *para*-isomers of dihydroxybenzenes and methoxyphenols.

Stretching vibrations band related to the H-bonded O–H groups in the complexes of catechol and phenol with strong bases is shifted to the region of C–H vibrations. Consequently, it is not possible to determine its frequency experimentally. Therefore, the bases of moderate strength were studied.

IR-spectra of pure phenol and catechol in the gas phase at different temperatures were measured (Figs. 2 and 3). Phenol has one band in the O–H stretching vibrations region, which refers to the absorption of the “free” hydroxyl group (3654 cm^{-1}) (Fig. 2). In the IR spectra of catechol two bands of O–H stretching vibrations (3665 cm^{-1} and 3605 cm^{-1}) are observed. One band (3665 cm^{-1}) refers to the “free” O–H group, the second (3605 cm^{-1}) is a band of the O–H group, which forms an intramolecular hydrogen bond (Fig. 3). It is evident that the intensity of the O–H stretching vibration bands is increased with temperature rise due to increase of the number of molecules, referred from the condensed state into a gas. At the same time the peak position of bands (the absorption frequency) does not change with temperature (Figs. 2 and 3). Also, the IR spectra of pure bases (acetonitrile, propionitrile, 1,4-dioxane, tetrahydrofuran and di-*n*-butyl ether) were measured at different

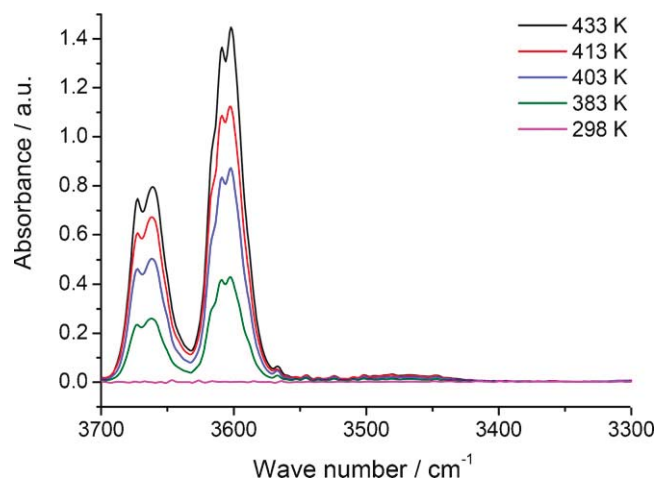


Fig. 3. IR spectra of catechol in the gas phase at different temperatures (O–H stretching vibration region).

temperatures. Proton acceptor molecules do not have intensive bands in the absorption region of O–H stretching vibrations.

IR spectra of the mixtures of catechol and phenol with equimolar quantity of nitriles and ethers in the gas phase were measured at several temperatures. The IR spectra of mixtures of phenol and catechol with tetrahydrofuran in the gas phase are shown in Figs. 4 and 5 as an example. It is clearly seen that the addition of base to catechol and phenol cause the appearance of new absorption bands in the O–H stretching vibrations region at lower frequencies. It is due to the formation of complexes with intermolecular hydrogen bonds. Catechol can form complexes with proton acceptors of 1:1 (with an intramolecular hydrogen bond) and 1:2 (without intramolecular hydrogen bond) structures. Since the absorption band of free O–H groups of catechol is intense enough after the entering the proton acceptor, in these conditions complexes with one molecule of the base are mainly formed (structure a in Fig. 1). Absorption frequencies of intermolecularly H-bonded O–H groups in studied systems were determined from the experimentally obtained spectra (Table 1).

Table 1 contains the absorption frequency shifts of H-bonded O–H groups in complexes of phenol and catechol with bases relative to the “free” O–H stretching vibrations in the gas phase. The data obtained (Table 1) show that the absorption frequency shift of the intermolecularly H-bonded O–H groups of catechol with base

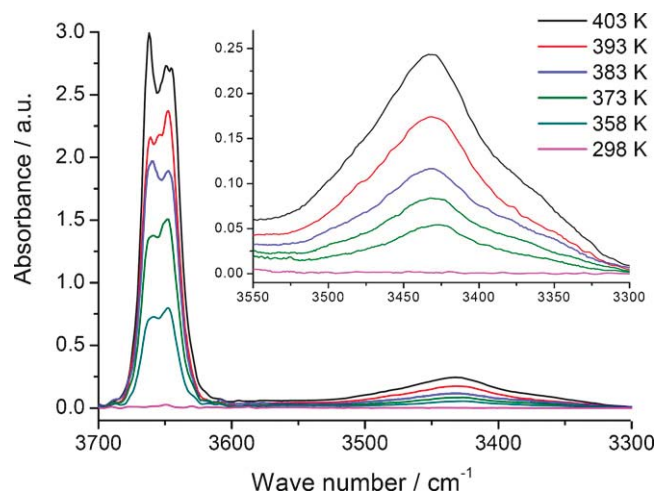


Fig. 4. IR spectra of phenol with tetrahydrofuran in the gas phase at different temperatures (O–H stretching vibration region).

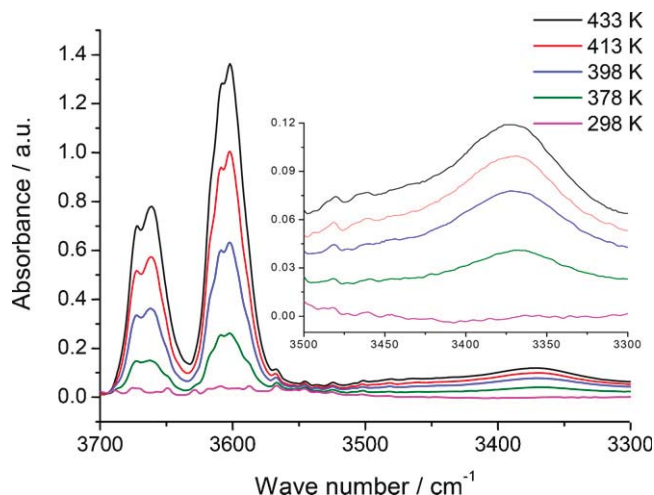


Fig. 5. IR spectra of catechol with tetrahydrofuran in the gas phase at different temperatures (O–H stretching vibration region).

is much larger than the absorption frequency shift of H-bonded O–H groups in complexes of phenol. Consequently, the intermolecular hydrogen bonds in the complexes of catechol with nitriles and ethers are strengthened in comparison with the complexes of phenol due to the cooperative effect of intramolecular hydrogen bond. Obtained by Eq. (1) cooperativity factors (A_b^{exp}) of intermolecular hydrogen bonds in complexes of catechol with five bases are practically equal 1.32 ± 0.01 (Table 1).

In work of Kleeberg and Luck [5] the method for determining the cooperativity factors was proposed. This method was based on the graphic comparison between the absorption frequency shifts of the H-bonded O–H bands in the complexes with cooperative hydrogen bonds and the absorption frequencies shifts of the H-bonded O–H bands in the complexes with single hydrogen bond. The cooperativity factor according to method [5] is equal to the slope of the linear relationship describing the experimental points. Comparison of the absorption frequency shifts of intermolecularly H-bonded O–H groups of complexes of catechol and phenol with proton acceptors is shown in Fig. 6. The obtained linear relationship is described by Eq. (2).

$$\Delta\nu_{\text{Catechol}}^{\text{O-H}\cdots\text{B}} = 1.31 \times \Delta\nu_{\text{Phenol}}^{\text{O-H}\cdots\text{B}} \quad (R^2 = 0.9988, \quad \text{SD} = 1 \text{ cm}^{-1}) \quad (2)$$

This result shows that for the systems studied the cooperativity factor does not depend on the choice of proton acceptor. Cooperative effect leads to the strengthening of the intermolecular hydrogen bonds in the complexes of catechol on 31–32% due to intramolecular hydrogen bonding. In accordance with the definitions given in work [6] in complexes of catechol with bases “additive” cooperativity takes place. It can be taken into account using one factor for different interacting molecules.

Table 1

IR stretching vibration frequencies (cm^{-1}) of H-bonded O–H groups of phenol and catechol in complexes with nitriles and ethers in the gas phase, hydrogen bond cooperativity factors.

Bases	$\nu_{\text{Phenol}}^{\text{O-H}\cdots\text{B}}$	$\nu_{\text{Catechol}}^{\text{O-H}\cdots\text{B}}$	$\Delta\nu_{\text{Phenol}}^{\text{O-H}\cdots\text{B}}$	$\Delta\nu_{\text{Catechol}}^{\text{O-H}\cdots\text{B}}$	A_b^{exp}
<i>Nitriles</i>					
Acetonitrile	3541	3513	113	152	1.34
Propionitrile	3537	3509	117	156	1.33
<i>Ethers</i>					
Di- <i>n</i> -butyl ether	3401	3336	253	329	1.30
Tetrahydrofuran	3432	3374	222	291	1.31
1,4-Dioxane	3458	3409	196	256	1.31

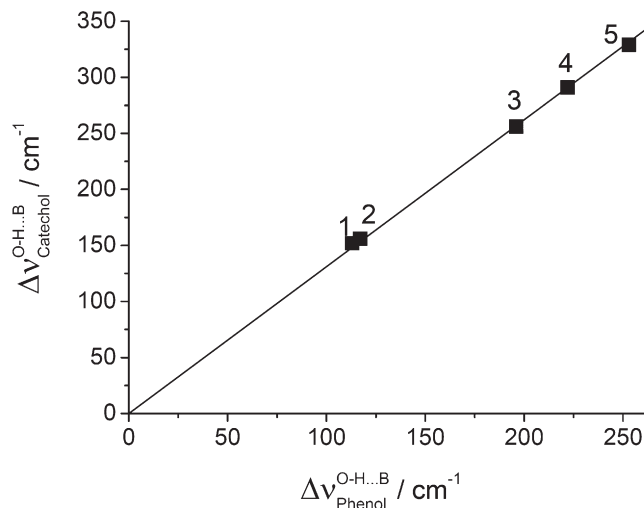


Fig. 6. The relationship between experimental frequency shifts of H-bonded O–H group of phenol and frequency shifts of H-bonded O–H group of catechol in the gas phase in complexes with: (1) acetonitrile, (2) propionitrile, (3) 1,4-dioxane, (4) tetrahydrofuran, (5) di-*n*-butyl ether.

4.2. Quantum chemical calculations

The result that cooperativity factor does not depend on H-acceptor strength is unconventional and rather surprising. Quantum chemical calculations were used to test the experimental results and explain their nature. Quantum chemistry allows us to study the hydrogen bonding of catechol with any bases, regardless of their proton acceptor ability.

4.2.1. Structure, geometrical parameters and frequencies

The theoretical investigation of complexes of catechol and phenol with acetonitrile, propionitrile, diethyl ether and tetrahydrofuran as proton acceptors of medium strength was carried out. Calculations of complexes of di-*n*-butyl ether are rather time-consuming, so diethyl ether was used as proton acceptor instead. Highly basic proton acceptors (pyridine and trimethylamine) were also included to the list of H-acceptors. In Fig. 7 optimized structures of the complexes studied are presented. Geometrical parameters and O–H frequencies of the complexes, calculated at the B3LYP/6-311++G(d,p) level, are presented in Table 2.

First of all, it was found that for complex of catechol with acetonitrile (used as example), where both O–H groups are turned away from each other (*trans*-form), the O–H stretching vibration frequency shift (167 cm^{-1}) and hydrogen bond energy (-5.28 kcal/mol) are almost the same as in phenol-acetonitrile complex (167 cm^{-1} and -5.36 kcal/mol). Thus, the strengthening of hydrogen bonds (cooperative effect) in the complex of “*trans*-configuration” of catechol is absent in comparison with phenol complexes. The existence of intramolecular O–H \cdots O hydrogen bond within catechol fragment is the only one factor leading to the existence of cooperativity (electron distribution factors have negligible effect). This result additionally supports the used way of calculation of cooperativity and the reliability of Eq. (1).

Stretching vibration bands of H-bonded O–H groups in complexes of catechol are shifted to lower frequencies compared with the complexes of phenol (Table 2). This fact indicates greater strength of intermolecular bonds in the complexes with two adjacent hydrogen bonds, which is due to cooperativity. Calculated frequencies of O–H stretching vibrations overestimate the experimental values on about 3.0–3.5%. This result is consistent with previous works [37,41]. The calculated stretching vibrations frequency shifts of H-bonded O–H groups in complexes of catechol

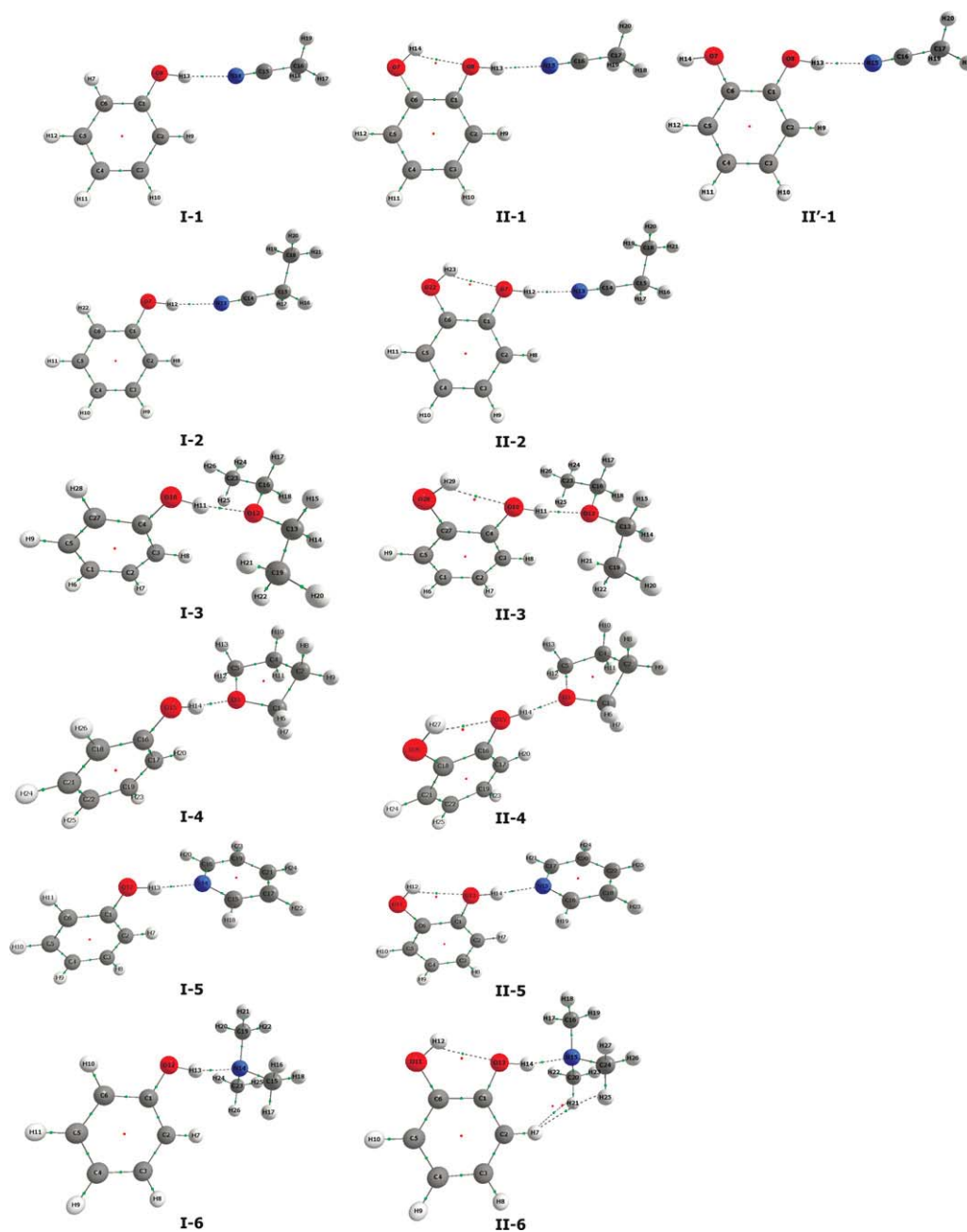


Fig. 7. Topological graphs of the complexes under study (bond critical points are showed green, ring critical points are red, H-bonds are showed by dotted lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and phenol with H-acceptors relative to the frequencies of the free O–H vibrations in the gas are given in Table 3. These values were plotted against the experimental data (Table 1) in Fig. 8.

It is evident, that between the experimental and theoretical values the linear relationship of rather high quality ($R^2 = 0.9945$, $SD = 5.7 \text{ cm}^{-1}$) is observed, which indicates the consistency of the data. Scaling factor estimated from the comparison of theoretical and experimental frequencies of H-bonded O–H groups (0.969) in studied complexes agrees well with the value, proposed by Anderson and Uvdal [41]. Cooperativity factors were determined by Eq. (1) using calculated O–H frequencies. Obtained values of A_b^{calc} (Table 3) show that the cooperative effect in complexes of catechol due to the influence of intramolecular hydrogen bond leads to the strengthening of the intermolecular hydrogen bond with bases on about 30% compared with the complexes of phenol. This

value is insensitive to H-acceptor strength and almost the same for such weak bases as nitriles, and such strong bases as pyridine and trimethylamine. An exception is the complex of catechol with tetrahydrofuran, for which the cooperativity factor is a little smaller (Table 3). Possible reason can be the neglect of dynamic effects in the complex formation. The frequency of the O–H vibrations in the complex of phenol with tetrahydrofuran, in which the oxygen atom of tetrahydrofuran is out of the plane of heavy atoms of molecule, is characterized by a 22 cm^{-1} higher frequency of vibrations of O–H group than the most stable conformation, used in further analysis, in which a carbon atom is out of the plane of the molecule. At the same time former conformation is only slightly (by about 0.3 kcal/mol) less stable. The cooperativity factors derived from the calculated values of the O–H stretching vibrations absorption frequencies (see Table 3) are in good agreement with experimental

Table 2

O—H bond length (Å), X...H distance (Å) and O—H stretching vibration frequency (cm^{-1}) in “free” molecules of phenol (I), catechol (II) and its *trans*-form (II') and hydrogen bonded complexes calculated at the B3LYP/6-311++G(d,p) level.

Base	Type ^a	$d(\text{O—H})$	$d(\text{O}\cdots\text{H})$	$\nu^{\text{O—H}}$	
I		0.9628		3834	
II		0.9645 ^b	2.1491	3850	
II'		0.9628		3834	
I-1	Acetonitrile	Inter	N...H 0.9717	1.9970	3667
II-		Intra	O...H 0.9670	2.1101	3772
1		Inter	N...H 0.9733	1.9474	3633
II-1'		Inter	N...H 0.9716	1.9951	3668
I-2	Propionitrile	Inter	N...H 0.9720	1.9899	3553
II-		Intra	O...H 0.9671	2.1087	3772
2		Inter	N...H 0.9737	1.9394	3501
I-3	Diethyl ether	Inter	O...H 0.9768	1.8439	3660
II-		Intra	O...H 0.9669	2.1123	3774
3		Inter	O...H 0.9793	1.8003	3623
I-4	Tetrahydrofuran	Inter	O...H 0.9786	1.7900	3518
II-		Intra	O...H 0.9670	2.1103	3772
4		Inter	O...H 0.9810	1.7522	3467
I-5	Pyridine	Inter	N...H 0.9850	1.8541	3379
II-		Intra	O...H 0.9675	2.0977	3764
5		Inter	N...H 0.9899	1.8010	3278
I-6	Trimethylamine	Inter	N...H 0.9914	1.8344	3250
II-		Intra	O...H 0.9674	2.0997	3765
6		Inter	N...H 0.9978	1.7810	3124

^a The values corresponding to intermolecular X...H—O H-bonds denoted as “inter” and the ones corresponding to intramolecular O...H—O H-bond denoted as “intra”.

^b The value corresponds to the “free” O—H group.

data (see Table 1). Thus our DFT calculations are fully supported by FTIR-spectroscopic results in gas phase.

We have also calculated energies of intermolecular hydrogen bonds in studied complexes (see Table S1). Cooperativity factor obtained from H-bond strength at 0 K is equal to 1.18 ± 0.02 . It also does not depend on proton acceptor ability of the bases.

4.2.2. Topological parameters. Nature of H-bond cooperativity

The question rises: why the cooperativity factor value does not depend on the nature of the base for catechol complexes (where one of the H-bond is intramolecular one) unlike the complexes [40] containing only intermolecular H-bonds? QTAIM analysis of electron density was carried out to answer the question. Properties of inter- and intramolecular hydrogen bonds critical points (BCP) are collected in Table 4. BCPs of intramolecular H-bond are always close to degeneracy: bond and ring critical points are located very close to each other (see Fig. 7) and large ellipticity in BCP ($\varepsilon(r)$ in Table 4) exceeding unity is always found. In catechol molecule BCP corresponding to intramolecular H-bond do not located. We used high-level calculations (the best were MP2/6-311++G(3df,3p)

Table 3

Calculated O—H stretching vibration frequency shifts in hydrogen bonded complexes of phenol and catechol with bases (cm^{-1}), cooperativity factors of hydrogen bonds.

Base (B)	$\Delta\nu_{\text{Phenol}}^{\text{O—H}\cdots\text{B}}(\text{calc})$	$\Delta\nu_{\text{Catechol}}^{\text{O—H}\cdots\text{B}}(\text{calc})$	$A_{\text{b}}^{\text{calc}}$
Acetonitrile	167	217	1.31
Acetonitrile (<i>trans</i>) ^a	167	167	1.00
Propionitrile	174	227	1.30
Diethyl ether	281	349	1.25
Tetrahydrofuran	316	383	1.21
Pyridine	444	561	1.26
Triethylamine	574	715	1.25

^a Complex where O—H groups in catechol molecule are in *trans*-form (turned away from each other).

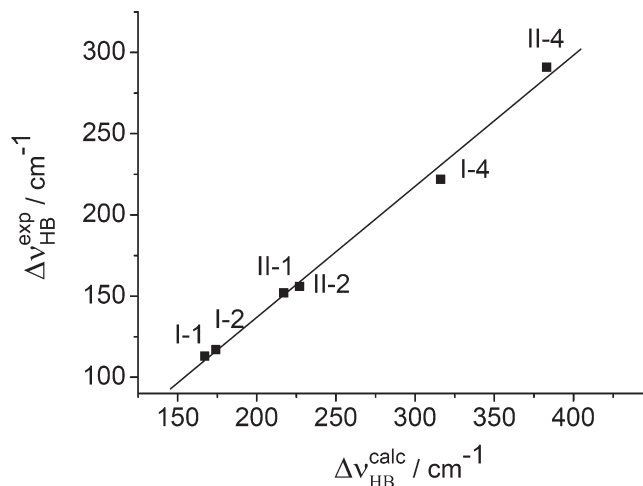


Fig. 8. Experimental vs. calculated stretching vibration frequency shifts of O—H groups in complexes of catechol and phenol with nitriles and ethers in the gas phase (the point numbers correspond to Table 2).

and MP4(SDTQ)/6-311++G(3d,3p)) but the intramolecular H-bond BCP nowhere appeared. Thus, intramolecular H-bond is topologically very unstable and appear/disappear readily if small changes in molecular geometry are induced that were also described by Mandado et al. [42]. Bond path length l^{BP} is quite large in complexes and larger than in free catechol molecule. Thus the electronic shell of oxygen and hydrogen cannot be polarized enough for BCP appearance.

The nature of inter- and intramolecular H-bonds differs very much. Intermolecular bond critical points properties change very much with increasing of base strength: $\rho(r)=0.023\text{--}0.047$, $\nabla^2\rho(r)=0.081\text{--}0.129$, $H(r)=-0.003\text{--}0.002$, $|V(r)|/G(r)=0.860\text{--}1.251$. Therefore the nature of interaction changes from pure closed-shell (here mostly electrostatic) to partially covalent. However, intramolecular hydrogen bonds properties are almost permanent ($\rho(r)=0.019\text{--}0.020$, $\nabla^2\rho(r)=0.090\text{--}0.091$, $H(r)=0.003$, $|V(r)|/G(r)=0.841\text{--}0.851$), no matter what bases were used. Intramolecular hydrogen bond is characterized by domination of kinetic energy over electron stabilization ($H(r)>0$, $|V(r)|/G(r)<1$), the electron density at BCP is lower and electronic energy density $H(r)$ is greater than the values observed for intermolecular hydrogen bonds (see Table 4). Delocalization index δ [43], which is equal to the number of electrons shared by atoms X...H, is about twice larger in intermolecular hydrogen bond than in an intramolecular H-bond counterpart. Thus intramolecular H-bonds are significantly more electrostatic in nature than intermolecular ones. According to the fact that intramolecular hydrogen bond critical point appears only in complexes we can conclude that intramolecular bond strengthens after complex formation. This was also supported by calculation of intramolecular H-bond strength by “*cis-trans* method”. The energy of intramolecular H-bonding is -5.43 kcal/mol in complex with acetonitrile and -4.27 kcal/mol in free catechol. The same conclusion was obtained by Koll et al. [25] in the studies of complexes of secondary Mannich bases with dioxane.

Charge transfer is important in the formation of hydrogen bonds. We tried to analyze how charge transfer in the complexes affects the atomic charges. At Fig. 9 the changes in QTAIM atomic charges of catechol and base molecules after complex formation are showed. We also show the data for water trimer and complex of pyridine with water dimer for comparison. Hydrogen atom in fragment O...H—O always loses its occupancy (positive charge rises) however atomic charge of oxygen atom of H-donor fragment changes backwards. For the complexes with adjacent intermolecular hydrogen

Table 4
Topological properties of X...H bond critical points (all values in a.u.).

	Type ^a		$\rho(r)$	$\nabla^2\rho(r)$	$\varepsilon(r)$	$H(r)$	δ^{AB}	$ V(r) /G(r)$
I-1	Inter	N...H	0.023	0.080	0.016	0.002	0.073	0.860
II-1	Intra	O...H	0.019	0.090	1.547	0.003	0.037	0.841
	Inter	N...H	0.026	0.087	0.017	0.002	0.079	0.906
II-1'	Inter	N...H	0.023	0.081	0.015	0.002	0.073	0.861
	Inter	N...H	0.023	0.081	0.016	0.002	0.074	0.866
II-2	Intra	O...H	0.019	0.090	1.484	0.003	0.037	0.841
	Inter	N...H	0.026	0.089	0.018	0.002	0.080	0.914
I-3	Inter	O...H	0.032	0.109	0.055	0.001	0.084	0.976
II-3	Intra	O...H	0.019	0.090	1.560	0.003	0.037	0.841
	Inter	O...H	0.035	0.117	0.056	0.000	0.090	1.011
I-4	Inter	O...H	0.036	0.122	0.056	0.000	0.089	1.009
II-4	Intra	O...H	0.019	0.090	1.520	0.003	0.038	0.842
	Inter	O...H	0.039	0.129	0.057	-0.001	0.097	1.042
I-5	Inter	N...H	0.037	0.096	0.027	-0.003	0.110	1.097
II-5	Intra	O...H	0.020	0.091	1.106	0.003	0.039	0.850
	Inter	N...H	0.042	0.100	0.026	-0.005	0.120	1.170
I-6	Inter	N...H	0.041	0.094	0.008	-0.005	0.120	1.174
II-6	Intra	O...H	0.020	0.091	1.142	0.003	0.039	0.851
	Inter	N...H	0.047	0.095	0.009	-0.008	0.131	1.251

^a The values corresponding to intermolecular X...H—O H-bonds denoted as “inter” and the ones corresponding to intramolecular O...H—O H-bond denoted as “intra”.

bonds (water trimer and pyridine-water dimer complex) the same effect is observed for “inner” H-bond (between water molecules) but it is at least three times greater in magnitude. Therefore when intermolecular H-bond with water dimer is formed, electron density transfers from H-acceptor molecule to both O—H groups, the “inner” H-bond becomes stronger and it influences the “outer” H-bond of water dimer with base. This is the reason for cooperativity dependence on the base strength. The more basic H-acceptor gives rise to greater charge transfer and the strengthening of “inner” H-bond. The more stable “inner” H-bond polarizes “outer” one and makes it stronger. However electronic occupancy of hydrogen and oxygen atoms of intramolecular H-bonds in catechol complexes is almost constant and there is no significant charge transfer from oxygen atom of “outer” O—H bond to “inner” O—H bond. Therefore the properties of H—O...H—O fragment in catechol depend on the basicity of H-acceptor as single O—H bond, and simultaneously the cooperativity value does not change.

Thus, one of the possible explanations for the independence of cooperativity factors from the proton acceptor ability of bases is that covalency (sharing of the electrons) of intramolecular H-bond

in catechol is very low in comparison with intermolecular ones because of sterical restrictions. The charge transfer in intramolecular H-bond does not take place in complexes of catechol and reorganization of electron distribution is practically absent. Therefore “inner” O—H bond, having presumably electrostatic nature, in catechol molecule does not participate in delocalization of electron density after complex formation.

5. Conclusion

First experimental study of hydrogen bond cooperativity in hetero-complexes in gas phase was carried out. IR-spectra of free molecules of phenol and catechol as well as their complexes with proton acceptors were measured in gas phase. Obtained experimental results show that intermolecular hydrogen bonds in complexes of catechol with nitriles and ethers are strengthened on 31–32% in comparison with phenol complexes. We have found that the cooperativity factor of intermolecular hydrogen bond in catechol complexes in gas phase has a constant value for all studied proton acceptors, despite the changing of intermolecular hydrogen bond frequency shifts from 152 cm⁻¹ (catechol-acetonitrile complex) to 329 cm⁻¹ (catechol-di-*n*-butyl ether complex).

Quantum chemical calculations of catechol and phenol complexes with moderate and strong bases were carried out on B3LYP/6-311++G(d,p) level. The calculated geometrical parameters and stretching vibrations frequencies show that the intermolecular hydrogen bonds in complexes of catechol are stronger than in the complexes of phenol due to cooperative effects. It was shown that the only reason for the intermolecular H-bond cooperativity in complexes of catechol in gas phase is the presence of intramolecular hydrogen bond. The cooperativity factors derived from the quantum chemical calculations data are in good agreement with experimental results. They have the same value for nitriles (weak bases) and for amines (strong bases).

Approaches of quantum theory of atoms in molecules were used for understanding of obtained experimental and theoretical results. It was shown that a constant value of cooperative effect in catechol complexes with bases of different strength apparently is due to weak charge transfer from base to intramolecular hydrogen bond and negligible reorganization of electron distribution in intramolecular H-bond after intermolecular bonding.

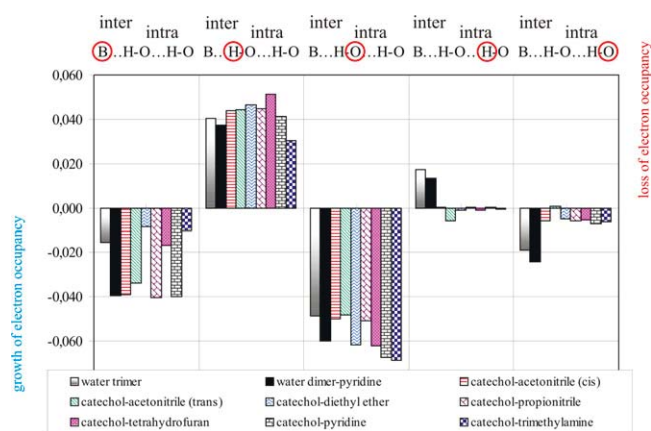


Fig. 9. Changes in atomic charges of fragment O—H...O—H...Base after complex formation. Inter- and intramolecular hydrogen bonds denoted as “inter” and “intra” respectively. The atom for which atomic charge calculated is picked out by red circle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2012.01.061.

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