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The effect of hydrogen bonding on the structure and infrared spectrum of 2-benzylphenol

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The effect of hydrogen bonding on the structure and vibrational spectra of 2-benzolphenol is investigated. Infrared (IR) spectra are measured in the region of $400-4000\,\mathrm{cm}^{-1}$ in a temperature range of $11-335\,\mathrm{K}$ in stable and metastable solid crystalline phases and in liquid. The B3LYP/6-31G(d) density functional theory method was used to build structural-dynamic models of the conformer of 2-benzolphenol molecule, which is the most stable in the stable crystal phase, and its H-complexes: a fragment of chain associate and a cyclic tetramer. Parameters of adiabatic potentials are calculated: the minimum energy, the optimal geometry, force constants, the dipole moment. Frequencies and waveforms of normal vibrations and their intensities in IR spectra are calculated. Based on the analysis of modeling and measurement results conclusions are made regarding the structure of 2-benzolphenol samples and an interpretation is given for its IR spectra.

Keywords: molecule, H-complex, molecular modeling, structure, IR spectrum.

Introduction

The 2-benzolphenol compound (C13H12O) belongs to the class of monohydric alcohols; it possesses unique properties, which make it a subject of theoretical and experimental studies for a long time [1–6]. A major problem in processing of nuclear waste and military waste is caesium separation. It has been found [1] that 2-benzolphenol injected into supramolecular assemblies makes them effective and highly selective extractants of Cs^+ that are used to detect caesium. According to X-ray diffraction analysis (XRDA) [1], hydroxyl group of the 2-benzolphenol molecule located on a tetragonal lattice is oriented to the symmetry axis of the forth order, so that cyclic tetramers are formed by four molecules equivalent in regards to the symmetry operation. 2-benzolphenol has polymorphism and glass phase [2–6]. Its structure and IR-spectra have been comprehensively (theory, experiment) investigated in [2]. The authors have demonstrated that in the solid crystalline phase the 2-benzylphenol molecule conformation corresponds to one of four potential energy minima predicted by ab initio quantum-mechanical calculations for an isolated molecule. It is found out that in the molten state and in diluted solutions of CCl$_4$ this conformer exists with two more spectrally distinguished conformers. It is established that the presence of several conformers is manifested in the corresponding number of bands in the region of $2840-2950\,\mathrm{cm}^{-1}$ of the IR spectrum, $v_s\mathrm{CH_2}$ and $v_{as}\mathrm{CH_2}$, related to stretching vibrations of C−H bonds. The

established fact has become an experimental proof of the sensitivity of frequency of above-mentioned vibrations to conformational changes. In [6] the crystalline polymorphism, the process of vitrification and the hydrogen bonding in 2-benzolphenole have been experimentally investigated by methods of differential scanning calorimetry and vibrational IR spectroscopy. Based on the analysis of IR spectra of the metastable phase in the region of $3100-3600\,\mathrm{cm}^{-1}$, the authors have made a conclusion, the long and short of which is that as opposed to the structure of 2-benzolphenol in a stable polymorphous modification composed of H-complexes in the form of cyclic tetramers, its structure in a metastable polymorphous modification can be represented by H-complexes in the form of chain associates.

Taking into account the interest in 2-benzolphenol from both fundamental science and applications, we continued its studies. These studies were focused on finding out the effect of the hydrogen bonding on the structure and IR spectrum of 2-benzolphenol. The studies were comprehensive and based on the methods of quantum chemistry and vibrational IR spectroscopy (experiment, theory). The structural-dynamic models of H-complexes of 2-benzolphenol had to be built for the first time : models of a cyclic tetramer and a fragment of chain associate, which had to be the basis for conclusions regarding the structure of samples and for the interpreting of the measured IR spectra.
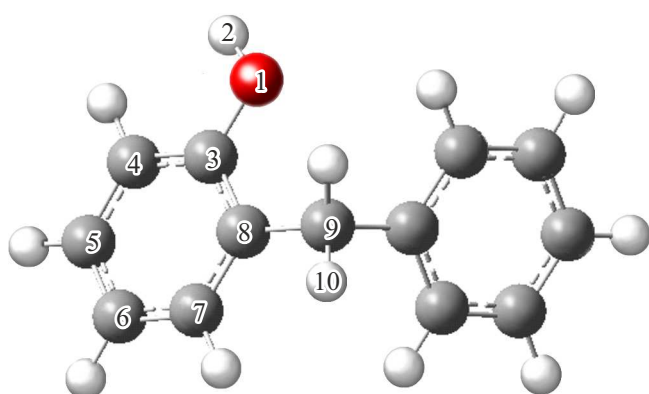
Figure 1. Structure of an isolated 2-benzolphenol molecule.

Experiment and modeling

Infrared spectra of 2-benzolphenol are measured in the region of $400-4000 \, \text{cm}^{-1}$ at temperatures of 11, 295 K in a stable crystalline phase, and at 295 K in a metastable crystalline phase, and at 335 K in liquid using a IFS-88 Fourier-spectrometer by Bruker with a resolution of $2 \, \text{cm}^{-1}$. The sample of the substance under study was secured in a OxfordND 1754 type cryostat that provided temperature varying from 12 to 350 K. The temperature controller of OxfordITC4 type provided a measurement error of 0.1 K. Software support for the experiment was provided using the OPUS package. Samples of 2-biphenylmethanol were placed between thoroughly polished plates of CsI crystals, which are transparent in the IR-range. The plates of CsI crystals were secured in a holder mounted on the cold finger in the cryostat.

The modeling used the B3LYP/6-31G(d) density functional theory (DFT) method [7,8], implemented in GAUSSIAN software packages [9]. The energy was minimized, the geometry was optimized, the mechanical (force constants) and electro-optical (dipole moment) parameters were calculated for an isolated molecule of 2-benzolphenol (I) and its H-complexes: a fragment of a chain associate (II) and a cyclic tetramer (III). Frequencies and waveforms of normal vibrations and their intensities in IR spectra of the molecule and its H-complexes were calculated in a harmonic approximation. For convenience of the analysis of measured and calculated IR spectra, the frequency scaling procedure was applied [10,11], which is widely used all over the world and allows overcoming the limitation of the harmonic approximation. The initial model of isolated molecule corresponded to a conformer that is implemented in accordance with [2,6] in a stable solid crystalline modification. Its structure is shown in Fig. 1. The following notations are introduced for convenience (Fig. 1 and Table 2): R is referred to the CH_2 methylene group, R1 and R2 are referred to phenyl rings, R3 is referred to the hydroxyl group. A variant of chain associate fragment is represented by three molecules united in a H-complex
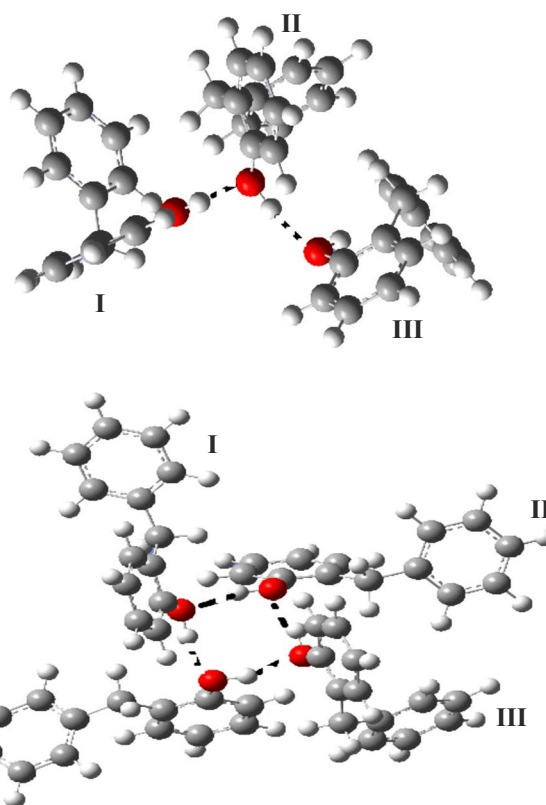

Figure 2. Structure of H-complexes II and III of 2-benzolphenol.

in the process of proton collectivization by oxygen atoms of hydroxyl groups of neighboring molecules. The model of cyclic tetramer is consistent with the XRDA results [1]. Structure of H-complexes II and III is shown in Fig. 2. Roman numerals I, II, III and IV show fragments of H-complexes in Fig. 2 and their correspondent columns in Table 1.

Discussion of results

Structure

Minimum energy of an isolated molecule was -577.831072 Hartree. Its optimized structure is consistent with the data of [2] for a conformer implemented in a stable modification. Dipole moment was 1.385 D. Minimum energies of H-complexes are -1733.525552 Hartree (II) and -2311.380966 Hartree (III). The energy of hydrogen bond is $-6.8 \, \text{kkal/mol}$ (II) and $-8.8 \, \text{kkal/mol}$ (III), which allows it to be classified as a bond of medium force. Geometry parameters of H-complexes II and III are within the limits allowed by the structural chemistry and are considered as reliable values. Table 1 illustrates changes in geometry parameters of the molecule in the process of complex formation. The changes take place only in the vicinity of hydrogen bridge. Length of the O1...H2 hydrogen bond is not greater than 1.851 Å in II and 1.780 Å in III. Length of the O1−H2 bond increases within

Table 1. Geometry parameters of molecule and H-complexes of 2-benzolphenol

Bond, Å	Molecule	H-complex II			H-complex II			
		I	II	III	I	II	III	IV
O1...H2	−	−	1.851	1.809	1.780	1.774	1.777	1.756
O1-H2	0.970	−	0.984	0.978	0.991	0.989	0.990	0.989
C3-O1	1.372	1.364	1.376	1.387	1.382	1.385	1.385	1.386
C3-C8	1.407	1.409	1.407	1.407	1.405	1.406	1.406	1.406
C3-C4	1.397	1.400	1.398	1.394	1.396	1.396	1.396	1.395
C8-C7	1.397	1.397	1.398	1.400	1.399	1.398	1.398	1.398
C8-C9	1.518	1.514	1.515	1.519	1.514	1.524	1.527	1.525
Angle, deg								
H2-O1...H2	−	−	113	−	99	102	100	102
H2...O1-C3	−	−	113	125	120	129	118	119
O1...H2–O1	−	−	162	102	168	165	166	164
C3-O1-H2	109	110	111	109	110	110	110	110
O1-C3-C8	117	117	118	122	118	117	117	117
O1-C3-C4	122	122	121	117	121	121	121	121
C3-C8-C4	121	120	121	122	121	122	122	122
C3-C8-C9	121	120	121	121	121	119	119	119
C7-C8-C9	121	121	121	122	123	123	124	123
C8-C9-C12	114	115	115	115	115	116	116	116

$0.008 - 0.021$ Å, and length of the C3-O1 bond increases within $0.004 - 0.015$ Å. Fragment I of H-complex II turned to be an exclusion. where bond length has decreased by 0.008 Å. Bond lengths are different depending on fragment of H-complex. Lengths of C−C bonds change insignificantly: C3−C8 changes within ± 0.002 Å, C3−C4 changes within ± 0.003 Å, C8−C7 increases by no more than 0.003 Å, C8−C9 decreases by 0.004 Å in fragment I of complexes II and III, and increases in the rest of fragments within 0.009 Å. The changes in angles are such that hardly can affect the spectrum: their values are within $\pm 2°$, and only in fragment III of the chain associate the change achieves 5° for O1-C3-C8 and O1-C3-C4 angles, which may be partly due to the choice of the option of chain associate fragment model. Dipole moments of H-complexes are 5.113 D (II) and 0.418 D (III).

Infrared spectra

Results of modeling of IR spectra of 2-benzolphenol molecule and its H-complexes are shown in Table 2. The table is presented in a short form because the initial version with full calculation of IR spectra of molecule and its H-complexes is cumbersome. The table contains information on some vibrations, which are noticeably affected by the complex formation process. It shows numbers of normal vibrations, their frequencies, ν, intensities, I and vibration waveforms, which can be the basis for assignment. Most of normal vibrations manifested in the region of $400 - 1650$ cm^{-1} are delocalized to a significant extent, which is typical for compounds containing cyclic fragments. The data in Table 2 illustrates the fact that complexation has an effect on some regions of the molecule's IR spectrum. The analysis of table data shows that this effect consists in splitting of molecule vibration frequencies, their shifts and change in intensity to a greater or lesser extent. It is of interest to compare the data of Table 2 with the measured spectra of crystalline modifications and liquid in order to answer the main question: the structure and composition of 2-benzolphenol samples.

The region of $3150 - 3600$ cm^{-1} is the most informative to find out the effect of hydrogen bonding on the structure and IR spectrum because it is the most sensitive to its formation. The presence of hydrogen bond forming H-complexes in the experimental spectra of crystalline modification and liquid measured at different temperatures is indicated by the abnormally wide intensive bands in this region (Fig. 3, curves *1−4*), which centers are shifted

Table 2. Measured and calculated IR spectra of 2-benzolphenol

№	ν_{exp}, cm^{-1}	Molecule		Tetramer		Trimer		Vibration waveforms**
		ν_{theor}, cm^{-1}	I, kkal/mol	ν_{theor}, cm^{-1}	I, kkal/mol	ν_{theor}, cm^{-1}	I, kkal/mol	
20		733	1.7	719	0.7	729	12.8	χ_{R1}(CCCH), χ_{R1}(CCCC), χ_{RR1R3}(CCCO), χ_{R1R3}(CCOH), χ_{RR1}(CCCH), χ_{R1RR2}(CCCC), χ_{R1}(HCCH), χ_{R1R}(HCCC)
				721	0.3	734	30.8	
				721	2.3	738	8.7	
				737	1.0			
	725 (s.)*					745	77.7	Deformation vibrations of H-complex core
21	734 (med.)	748	23.6	744	53.1	748	29.1	χ_{R2}(CCCH), χ_{RR2}(CCCH), χ_{R2}(CCCH), χ_{R1}(CCCH), χ_{R2R}(CCCH), χ_{R1}(CCCC), χ_{R1R}(CCCH), χ_{RR1R3}(CCCH)
				747	11.8	752	31.2	
				748	11.1	765	37	
				748	9.7			
22	770 (v.s.)	761	51.7	769	78.3	767	42.2	χ_{R1}(CCCH), χ_{R1R3}(HCCO), χ_{R1}(HCCH), χ_{R1R}(CCCH), χ_{R1}(CCCC), χ_{R1R3}(CCOH), χ_{RR1R3}(CCCO)
				770	69.6	770	50.0	
				771	1.2	785	46.4	
				772	14.7			
23	794 (w.)	798	6.2	792	25.2	794	18.4	χ_{R2}(CCCH), χ_{R2R}(CCCH), χ_{RR2}(CCCH), χ_{R2}(CCCC), Q_{R1}(CC), χ_{R1}(CCCH), χ_{R1RR2}(CCCC), χ_{R2}(HCCH), Q_{R1R3}(CO), Q_{RR2}(CC), Q_{RR1}(CC), γ_{R}(CCC), χ_{R1}(HCCH), γ_{R1RR2}(CCC), γ_{R2}(CCC), χ_{RR2}(CCCC), χ_{R1}(CCCC), χ_{RR1R3}(CCCO)
				809	41.9	796	23.9	
				810	17.2	801	14.9	
				810	53.8			
24	818 (med.)	829	0.8	822	21.3	828	3.9	χ_{R1R3}(HCCO), χ_{R1}(HCCC), χ_{R1}(HCCH), Q_{RR2}(CC), χ_{R2}(CCCH), γ_{R1RR2}(CCC), χ_{RR1}(CCCC), χ_{RR1R3}(CCCO), χ_{R2}(HCCH), χ_{R1R}(CCCC), χ_{R1R}(HCCC)
				823	91.9	829	6.4	
				831	47.5	830	3.4	
				838	98.0			
25	852 (med.)	852	2.2	871	24.1	862	6.6	χ_{R1R3}(HCCO), χ_{R1}(HCCC), χ_{R1}(HCCC), χ_{R1R2}(CCCC), χ_{R1}(CCCC)
				874	29.2	864	8.4	
				875	51.7	865	7.4	
				881	14.5			
				1228	223.7	1212	113.1	
45	1208 (s.)			1230	298.7	1228	85.6	β_{R1R3}(COH), Q_{R1}(CC), β_{R1}(CCH), β_{R1R}(CCH), γ_{R1}(CCC)
		1202	37.9	1234	208.2	1244	49.6	
	1223 (v.s.)			1240	15.3			
46	1254 (med.)	1264	54.7	1248	1.8	1244	44.9	Q_{R1R3}(CO), β_{R1R3}(COH), Q_{R1}(CC)
	1273 (shl.)			1252	6.4	1255	65.1	
				1253	11.5	1275	82.5	
				1257	2.7			
47	1278 (med.)	1300	11.2	1277	76.4	1306	0.3	γ_{R1RR2}(CCC), β_{R2R}(CCH), χ_{RR2}(HCCH), χ_{RR1}(HCCC), β_{R1}(CCH) Q_{R2}(CC), β_{R1R}(CCH), β_{R2}(CCH), β_{R1R3}(COH), χ_{R1RR2}(CCCC), Q_{RR1}(CC)
				1278	42.6	1310	5.2	
				1279	20.4	1311	5.5	
				1281	5.5			

Table 2. (*contd.*)

№	ν_{exp}, cm^{-1}	Molecule		Tetramer		Trimer		Vibration waveforms**
		ν_{theor}, cm^{-1}	I, kkal/mol	ν_{theor}, cm^{-1}	I, kkal/mol	ν_{theor}, cm^{-1}	I, kkal/mol	
51	1355 (s.)	1340	27.6	1374 1375 1384 1386	62.6 68.9 360.9 12.5	1344 1357 1374	14.7 79.6 86.4	Q_{R2}(CC), Q_{R2}(CC), β_{R1R}(CCH), β_{R2}(CCH), β_{R1R3}(COH), χ_{R1RR2}(CCCC)
61	2841 (w.) 2883 (w.) 2901 (w.) 2918 (w.)	2917	27.4	2893 2894 2899 2899	25.1 26.9 28.1 12.7	2896 2901 2906	31.0 13.6 20.1	q_R(CH)
63	3005 (w.)	3019	18.4	3043 3044 3044 3036	1.3 1.0 1.4 10.6	3030 3035 3037	13.1 8.0 6.5	q_{R1}(CH)
				3052 3054 3054 3055	13.1 4.4 12.9 16.8	3040 3042 3051	8.2 6.3 7.8	q_{R1}(CH)
72	3120 (−) 3400 (v.s.)	3570	39.6	3120 3183 3229 3229	50.4 1666.2 1434.2 1434.2	3273 3347	1154.8 774.7	q_{R3}(OH)

* In brackets, in the second column qualitative evaluations of intensities of IR spectrum bands are shown: v.s. — very strong, s. — strong, med. — medium, w. — weak, shl. — shoulder.

** The following common notation of natural vibrational coordinates are used in the table and throughout the text : q(OH), q(CH), Q(CO), Q(CC) — OH, CH, CO, CC stretching vibrations; β(CCH), β(COH), γ(CCC) — plane deformation vibrations of CCH, COH, CCC angles; χ(CCCC), χ(HCCC), χ(CCCH), χ(HCCH), χ(CCCO), χ(HCCO) — out-of-plane deformation vibrations (vibrations of dihedral angles).

toward long wavelengths in relation to the calculated peak of curve I, that corresponds to the q(O-H) stretching vibration of the isolated molecule. With increase in temperature from 11 to 295 K, the band peak in the IR spectrum of a stable crystallographic modification shifts toward high-frequency end by ~ 40 cm^{-1}, its profile transforms (Fig. 3, curve *2*), the intensity of peak of the curve *2* decreases. The results of IR spectra modeling are qualitatively matched to the experimental data in this region. Under packing of the molecules into cyclic tetramers the vibration frequency of $\nu_{72} = 3570$ cm^{-1} is splitting into four components and shifting toward the low-frequency end by 450, 387, 371 and 341 cm^{-1}, respectively. At the same time, the intensity of vibrations increases ~ 1.3, 42, 48 and 36 times, respectively. Under packing of the molecules into chain associates the vibration frequencies are splitting into three components and shifting toward the low-frequency end by 298, 223 and 172 cm^{-1}. The intensity of vibrations is increased ~ 29, 20 and 8 times, respectively. Based on the results of measurements (Fig. 3, curves *1, 2*) and calculations (Fig. 3, curves II, III), a conclusion can be made that at 11 K in the stable phase H-complexes in the form of cyclic tetramers prevail, and at 295 K they are supplemented by H-complexes in the form of chain associates.

With the transition from stable phase to metastable phase at a temperature of 295 K, the profile of this band exhibits yet more transformation (Fig. 3, curve *3*). The band contains three explicit peaks, its center is yet more shifted to the high-frequency end: by ~ 200 cm^{-1} in relation to the peak of curve *1*. The high-frequency peak of this band corresponds to the q(O-H) stretching vibrations of the isolated molecule (Fig. 3, curve I). From the analysis of this region of the spectrum and the results of modeling, a conclusion follows confirming conclusions of [6]: chain H-complexes are present in the metastable phase along with tetramers. It is worth to add that free molecules are present in the sample along with H-complexes.

The liquid sample at a temperature of 330 K corresponds to a structureless wide band (Fig. 3, curve *4*), which center is shifted even further to the high-frequency end, and its peak approaches the calculated peak corresponding to the q(O-H) stretching vibration of the isolated molecule (Fig. 3, curve I). It can be concluded from this that the liquid sample consists of a mixture of free molecules, chain associates, and cyclic tetramers.

The analysis of other regions of the measured spectra, taking into account the results of modeling, also indicates the effect of complexation on the spectrum of the molecule.
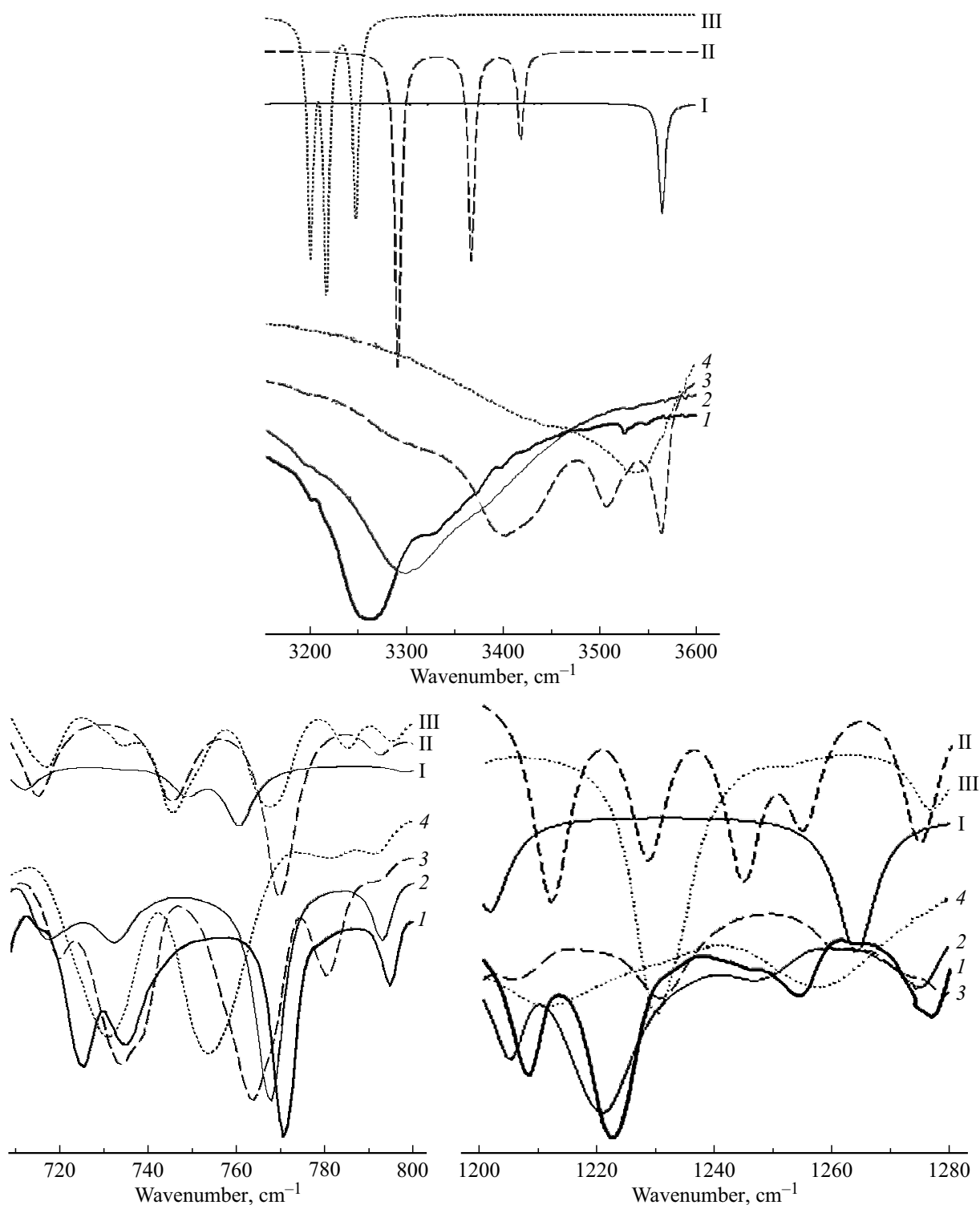
Figure 3. Infrared spectra of 2-benzolphenol: experimental (stable phase at 11 (*1*) and 295 K (*2*), metastable phase at 295 K (*3*), liquid at 330 K (*4*)) and theoretical (isolated molecule (I), chain associate (II), cyclic tetramer (III)).

This analysis requires much more effort than in the previous case and still allows us to come to the main conclusion regarding the composition of the samples. For example, the effect of hydrogen bonding in the 1200−1280 and 710−800 cm^{-1} regions of the IR spectrum takes place,

however, it is not so significant compared to the region of 3150−3600 cm^{-1} (Table 2). The measured spectrum in these regions is transformed upon transition from the stable phase to the metastable phase and to the liquid (Fig. 3). However, shifts of band peaks are small, they do not exceed

$\sim 20\,\text{cm}^{-1}$, the intensities and shapes of the bands undergo slight changes.

The calculated frequencies of $\nu_{45} = 1202\,\text{cm}^{-1}$ and $\nu_{46} = 1264\,\text{cm}^{-1}$ are referred to the stretching $q(\text{C-O})$ and deformation $\beta(\text{COH})$ vibrations. In the spectrum of the cyclic tetramer, frequency ν_{45} is splitting into four components, the splitting is $12\,\text{cm}^{-1}$. Frequencies of the components are shifted by 26, 28, 32, and $38\,\text{cm}^{-1}$ to the high-frequency end, the intensity of three of them is increased by ~ 5.9, 7.9, 5.5 times, and the intensity of the high-frequency component is decreased by 2.5 times. The peak of curve III, which is the most intense in the calculated spectrum of the cyclic tetramer, corresponds to the peak of curve *1* of the measured spectrum of the stable modification. In the triplet, the frequency splitting ν_{45} was $32\,\text{cm}^{-1}$, its components were shifted to the high-frequency end by 10, 26, $42\,\text{cm}^{-1}$, their intensity increased not so significantly: by ~ 3, 2.3, 1.3 times. The frequency $\nu_{46} = 1264\,\text{cm}^{-1}$ in the tetramer spectrum is splitting in the interval of $9\,\text{cm}^{-1}$ into four components shifted to the low-frequency end by 16, 12, 11 and $7\,\text{cm}^{-1}$. The intensities of the components are decreased by ~ 30.3, 8.6, 4.8 and 20.3 times. In the spectrum of the chain associate, the frequency ν_{46} is splitting into three components in the interval of $31\,\text{cm}^{-1}$. The frequencies of two components are decreased by 20 and $9\,\text{cm}^{-1}$, the frequency of the third one is increased by $11\,\text{cm}^{-1}$. Changes in the intensity in this case are insignificant (Table 2). It is worth noting that vibration frequencies ν_{45} and ν_{46} are different from each other in the free molecule spectrum by $62\,\text{cm}^{-1}$, and components of their splitting in the spectra of the chain associate and cyclic tetramer become closer to each other, remaining nearly in the same interval of $63\,\text{cm}^{-1}$.

In the measured spectrum, the peak of the $1223\,\text{cm}^{-1}$ band (curve *1*) corresponding to the ν_{45} vibration is shifting insignificantly with the transition from the stable crystalline phase to the metastable phase and liquid, within $\sim 17\,\text{cm}^{-1}$, toward low frequencies, approaching the peak $1202\,\text{cm}^{-1}$ of the calculated curve I corresponding to the free molecule. From the qualitative agreement between the experimental and theoretical curves of the intensity distribution in the region of $1200-1280\,\text{cm}^{-1}$ of the IR spectra, it follows the conclusion made earlier regarding the composition of the samples: with the transition from the stable phase to the metastable phase and liquid, in addition to cyclic tetramers, chain associates and free molecules appear.

In the region of $710-800\,\text{cm}^{-1}$, where out-of-plane deformation vibrations of $\chi(\text{CCCH})$, $\chi(\text{CCCC})$, $\chi(\text{CCCO})$, $\chi(\text{CCOH})$, $\chi(\text{HCCH})$ types are manifested, the measured and calculated spectra qualitatively match each other. From their analysis, a substantiation can also be found for the main conclusion made earlier regarding the composition of 2-benzylphenol samples. Let us consider the intensive band at $770\,\text{cm}^{-1}$ in the measured spectrum, which corresponds to the ν_{22} vibration. With the transition from the stable phase to the metastable phase and liquid, its peak shifts by $\sim 17\,\text{cm}^{-1}$ towards low frequencies,

approaching the peak of curve I of the calculated spectrum corresponding to the vibration $\nu_{22} = 761\,\text{cm}^{-1}$ of the free molecule. The vibration frequency ν_{22} is splitting in the process of complexation into four components in the range of $13\,\text{cm}^{-1}$ in the spectrum of the cyclic tetramer and into three components in the range of $18\,\text{cm}^{-1}$ in the spectrum of the chain associate. In this case, the intensities change insignificantly, the frequency shifts are also small and amount to 8, 9, 10, $11\,\text{cm}^{-1}$ in the spectrum of the tetramer and 6, 9, $24\,\text{cm}^{-1}$ in the spectrum the chain associate. The result obtained coincides with the experimental data and confirms the main conclusion about the composition of 2-benzylphenol samples.

Note that the theoretical analysis of the bands of the measured IR spectra, corresponding to the ν_{22}, ν_{45} and ν_{72} vibrations, is given by us taking into account only one mechanism of their formation, i.e. the formation of a hydrogen bond. However, there is also the second mechanism, which is associated with the conformational mobility of 2-benzylphenol molecules. As already mentioned, according to the data of [2], its molecule exists in the form of three spectrally distinguishable conformers. Frequencies ν_{72} of the stretching vibrations of the O-H bond of conformers differ within $53\,\text{cm}^{-1}$, frequencies of vibrations ν_{46} differ within 24, frequencies of vibrations ν_{45} differ within 8 and frequencies of vibrations ν_{22} differ within $18\,\text{cm}^{-1}$. Only one of three conformers is stable in the stable crystallographic modification. Two other conformers can arise in a sample with increase in temperature and transition to the metastable crystalline modification and liquid, which will be reflected in the measured spectra. The $3100-3600\,\text{cm}^{-1}$ region is little sensitive to the appearance of additional conformers in the samples: changes in the vibration frequency ν_{72} within $53\,\text{cm}^{-1}$ introduce nothing new because these changes are an order of magnitude smaller than the frequency shifts of this vibration during complexation. The intensity and shape of the band in the presence of conformers should not change qualitatively as well. The $1200-1280$ and $700-780\,\text{cm}^{-1}$ regions are more sensitive to the appearance of two additional conformers in the sample because frequency shifts due to the effects of hydrogen bonding and conformational mobility are comparable in magnitude. Accounting for the second mechanism, conformational mobility, may introduce some corrections into the interpretation of the mentioned regions of the IR spectra, however, they cannot affect the main conclusion of the studies.

Conclusions

Based on the analysis of the IR spectra of 2-benzylphenol measured at different temperatures in different phase states and the results of constructing structural-dynamic models of an isolated molecule, a fragment of a chain associate, and a cyclic tetramer, the presence of complexes formed by hydrogen bonding in the samples was theoretically

substantiated. The hydrogen bond energies of H-complexes were determined: -8.8 kkal/mol in the cyclic tetramer, -6.8 kkal/mol in the chain associate. The energy values correspond to medium-strength bonds. It has been established that in the stable crystalline phase at a temperature of 111 K, the sample consists predominantly of cyclic tetramers. As the temperature rises to 295 K, chain associates appear in the stable phase along with cyclic tetramers. Upon transition from the stable phase to the metastable phase at a temperature of 295 K, and to the liquid at 335 K, the sample is a mixture of cyclic tetramers, chain associates, and free molecules.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by Y.Alekseev