



имеет небольшое усиление по сравнению с усилением мод высших порядков (рис. 8, в). Мода под номером 9 имеет максимальное усиление в волокне с двумя активными сердцевинами (см. рис. 8, в, пустые квадраты). Мода с номером 14 имеет максимальное усиление в волокне с шестью активными сердцевинами (см. рис. 8, в, круги черного цвета). В микроструктурных волокнах динамика мод лазера будет определяться потерями и усилением лазера. При определенном соотношении между усилением и потерями можно добиться возбуждения только одной моды с максимальным значением мнимой части эффективного показателя $\text{Im}(n_{\text{eff}})$.

ЗАКЛЮЧЕНИЕ

Для исследования усиления в микроструктурных волокнах использовалось приближение комплексного показателя преломления. В таком приближении коэффициент усиления моды пропорционален мнимой части эффективного показателя преломления соответствующей моды. Показано, что в лазерах на основе микроструктурного волокна могут существовать оптимальные условия для генерации основной моды. Изменяя расположение активных областей в поперечном сечении волокна, можно выборочно влиять на усиление мод высших порядков.

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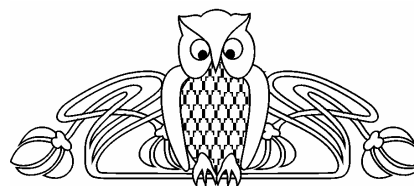
INVESTIGATION OF THE INFLUENCE OF THE HYDROGEN BONDING ON THE STRUCTURE AND VIBRATIONAL SPECTRA OF BIPHENYLMETHANOLS

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Using density functional method (B3LYP/6-31G*), the structures of the biphenylmethanols, their h-bond complexes and methanol h-bond complexes, energies, dipole moments, polarizabilities, frequencies of normal vibrations (in harmonic approximation) and their intensities in vibrational spectra were simulated. The effect of methanol group location in the molecules of 2-, 3- and 4-biphenylmethanols and the influence of the hydrogen bonding on their geometry and vibrational spectra of the molecular systems due to H-bonding have been studied on the basis of molecular modeling.



Исследование влияния водородной связи на структуру и колебательные спектры бифенилметанолов

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С использованием метода теории функционала плотности (B3LYP/6-31G*) были рассчитаны структуры молекул метанола, бифенилметанолов и их H-комплексов, энергии, дипольные моменты, поляризуемости, частоты нормальных колебаний в гармоническом приближении, их интенсивности в колебательных спектрах. На основе молекулярного моделирования изучено влияние положения группы метанола в молекулах 2-, 3- и 4-бифенилметанола, а также влияние водородной связи на их геометрические параметры и колебательные спектры.

I. INTRODUCTION

Recently, 2-biphenylmethanol (hereafter 2BPM) has been the object of our detailed investigations [1–6]. We have studied the IR transmittance spectra of crystalline, glassy, and supercooled liquid phases of 2BPM and their temperature dependencies [1–3]. Also, the crystal structure of the stable (triclinic) [4] and metastable (monoclinic) [6] modifications of 2BPM have been studied by X-ray crystallography at room temperature. It has been shown that the monoclinic structure with four molecules per unit cell can be described as hydrogen-bonded chains of molecules, while triclinic structure can be described as cyclic tetramers of hydrogen-bonded molecules.

In the work [1] the room-temperature Raman and IR spectra of 2BPM have been measured and the calculations of the frequencies of normal vibration and their intensities in the IR spectrum of the free 2BPM molecule by means of the method of fragments [7] realized in the complex of programs 'LEV-100', have been carried out. Also the interpretation of the vibrational spectra of the crystalline 2BPM was given, the conclusion about the formation of the H-bonds was made, and the most probable model of a molecular conformer at room temperature was proposed. In the next paper [4], the 6-31 + G(d) basis set at the B3LYP level of the density functional theory [8] has been applied to the calculation of the structures and the vibrational spectra of the free molecules of 2BPM, biphenyl, methanol, and cyclic tetramer of hydrogen-bonded methanol molecules. These results were improved in [5], where hydrogen-bonded complex: tetramer of 2BPM molecules was optimized and the vibrational spectrum of tetramer

of hydrogen-bonded 2BPM molecules was calculated. On the basis of the analysis of the experimental and computer simulation results, an interpretation of the room-temperature vibrational spectra of the triclinic modification of 2BPM and the role of the H-bond in the structure formation were given.

In the present paper the further two biphenylmethanols: 3-biphenylmethanol and 4-biphenylmethanol (hereafter 3BPM and 4BPM), which are differ by the location of the methanol group (CH₂OH) within the molecule, the IR spectra of which were reported in the set of data on vibrational spectra of the organic compounds [9], have called our attention. Our interest to biphenylmethanols has been stimulated by the fact, that the existence of the isomers provides a unique opportunity to study the influence of the substitution in the 2, 3 and 4 positions of the methanol group in molecules on the vibrational spectra.

It is the main goal of the present investigation to study the effect of methanol group location in isomers of biphenylmethanols on their vibrational spectra and to reveal the role of the H-bond on the structure formation and on the vibrational spectra on the basis of molecular modeling and experimental IR spectra [6, 9].

The molecular modeling of the investigated compounds was performed using density functional theory (B3LYP/6-31G(d)) basis set with the GAUSSIAN'03 software for Windows [8]. Earlier this method was used in [4, 5]. In the course of calculations, the energy minimization and geometry optimization were performed followed by the calculation of the electro optical and mechanical parameters, and the vibrational spectra of the free molecules of 2-, 3- and 4-BPM. Also, this procedure was performed for the H-complex (cyclic tetramers and fragments of the H-bonded chains of biphenylmethanols) calculation. Further we have optimized the geometry and performed the modeling of the vibrational spectra of the methanol molecules and their H-complexes. The discrepancy between calculated and experimental frequencies of the vibrational spectra does not exceed 4%. To remove of this discrepancy we used the frequency scaling procedure [10].



2. RESULTS AND DISCUSSION

In Fig.1 experimental room-temperature IR spectra of the stable and metastable modifications of 2BPM obtained in our earlier publication [6] are compared with experimental IR spectra of 2-, 3- and 4-BPM reported in Ref. [9] (curves 1', 1'' and 1a, 1b, 1c, correspondingly). It should be noted that to our knowledge, no information about the structures of biphenylmethanols studied in [9] is available in the literature. The existence of strong absorption bands in the region $3450\text{--}3150\text{ cm}^{-1}$ with anomalously large width suggests the presence of the H-bonds in these crystals. These wide bands are usually related to the OH stretching vibrations. The comparison of the OH bands observed in the spectra of 2-, 3- and 4-BPM reported in [9] (Fig. 1, curves 1a, 1b and 1c) with the OH band observed in the spectrum of monoclinic modification of 2BPM (Fig.1, curve 1'') shows their similarity. On the other hand, there is a fairly large difference between the frequency of the OH stretching band observed in the spectrum of monoclinic modification (curve 1'') and triclinic

modification (curve 1'). The curve 1'' is red-shifted on 60 cm^{-1} as compared to the curve 1'. The similarity of the IR spectra of the compounds investigated in [9] with that of the monoclinic modification of 2BPM [6] allowed us to conclude, that the cores of the H-complexes in these compounds are similar and close to the monoclinic structure. This suggestion was of fundamental importance for modeling of the 2-, 3- and 4BPM compounds.

According to our previous results [4, 5] the free molecule of 2BPM can be realized in two conformers **A** and **B**, which are differed by the angles between planes of the phenyl rings and by the orientation angles of the methanol group with respect to the nearest phenyl ring. There is a difference in the orientation angles of the O–H bond relative to the CH_2 in the methanol group. They are equal to 5.2° for conformer **A** and 77.9° for conformer **B**. On the basis of the modeling it has been found that the free molecules of 3BPM and 4BPM can be realized only in one conformer. The calculated values of the O–H bond length in the 3BPM and 4BPM molecules

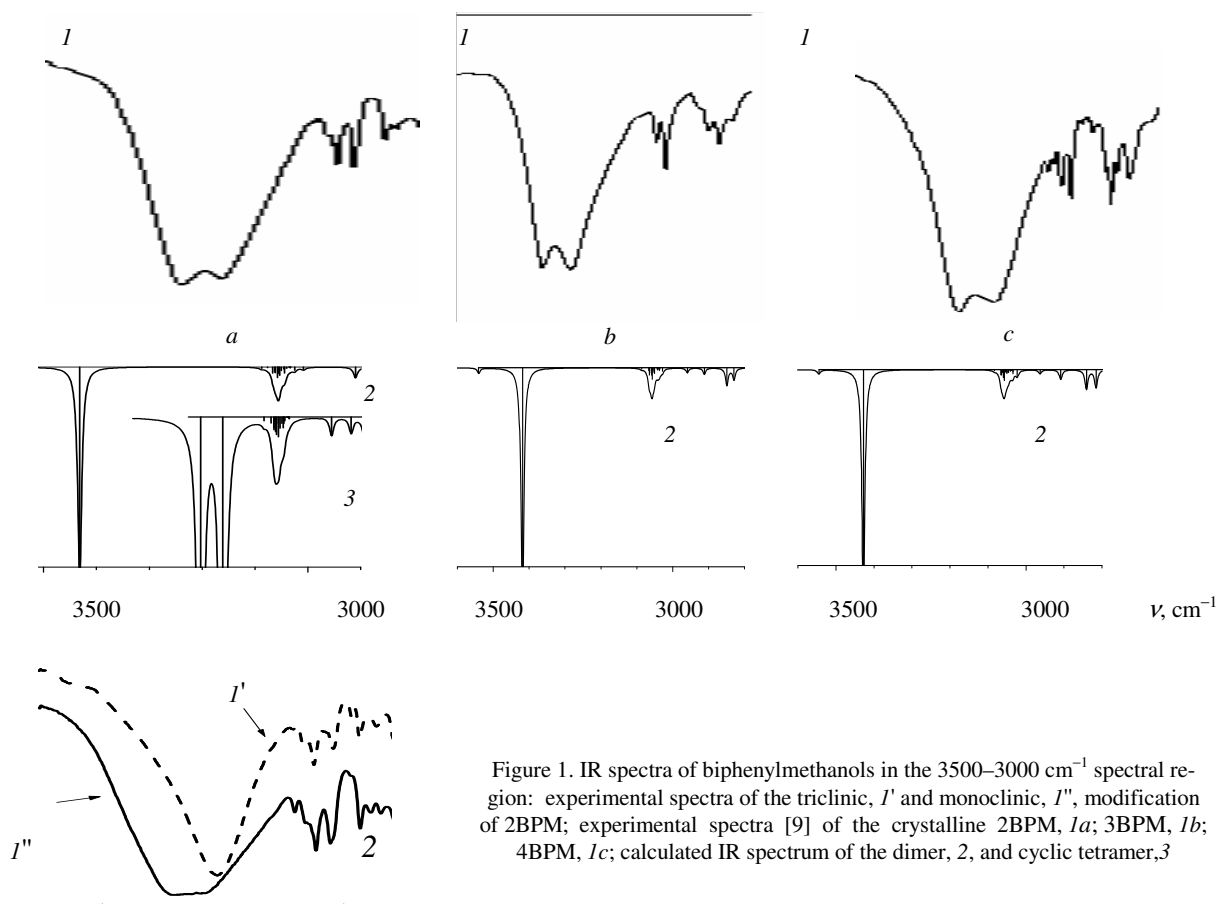


Figure 1. IR spectra of biphenylmethanols in the $3500\text{--}3000\text{ cm}^{-1}$ spectral region: experimental spectra of the triclinic, 1' and monoclinic, 1'', modification of 2BPM; experimental spectra [9] of the crystalline 2BPM, 1a; 3BPM, 1b; 4BPM, 1c; calculated IR spectrum of the dimer, 2, and cyclic tetramer, 3



are equal to 0.969 Å; the values of the angles between phenyl rings are: 38.3° for 3BPM and 40.9° for 4BPM; the values of the orientation angles of methanol group relative to the plane of the nearest phenyl ring (CCCO) are: 27.2° for 3BPM and 27.9° for 4BPM; dihedral angles between the planes CCO and COH (CCOH) of the methanol group are: 10.0° for 3BPM and 10.5° for 4BPM.

The comparison of the calculated IR spectra of 2-, 3- and 4BPM molecules (Fig.2, Table 1) allowed us to estimate the influence of the position of the methanol group in the molecule on the vibrational spectra. The fragments of the IR spectra are shown in Fig.2, and the assignments of their normal vibrations are given in Table 1. In the spectral region 1500–1400 cm⁻¹ there is a sequence of vibrations, which are related to the deformational vibrations of the phenyl rings in biphenyl.

The absorption band of moderate intensity centered at 1479 cm⁻¹ in the spectrum of 2BPM is by 6 cm⁻¹ and by 12 cm⁻¹ red shifted as compared to its position in the spectra of 3BPM (1485 cm⁻¹) and 4BPM (1491 cm⁻¹), correspondingly. At the same time, the intensity of the band centered at 1479 cm⁻¹ slightly increases.

The low-frequency band in the spectrum of 2BPM is by 20 cm⁻¹ blue shifted as compared to its position in the spectrum of 3BPM, while moving from 3BPM to 4BPM the position of this band does not change. At the same time, the intensity of this band slightly decreases.

Between the low-frequency and high-frequency components of this sequence, a doublet of two weak bands is observed. While moving from 2BPM to 4BPM, the redistribution of intensities of the components of the doublet is observed. The overall intensity of the doublet

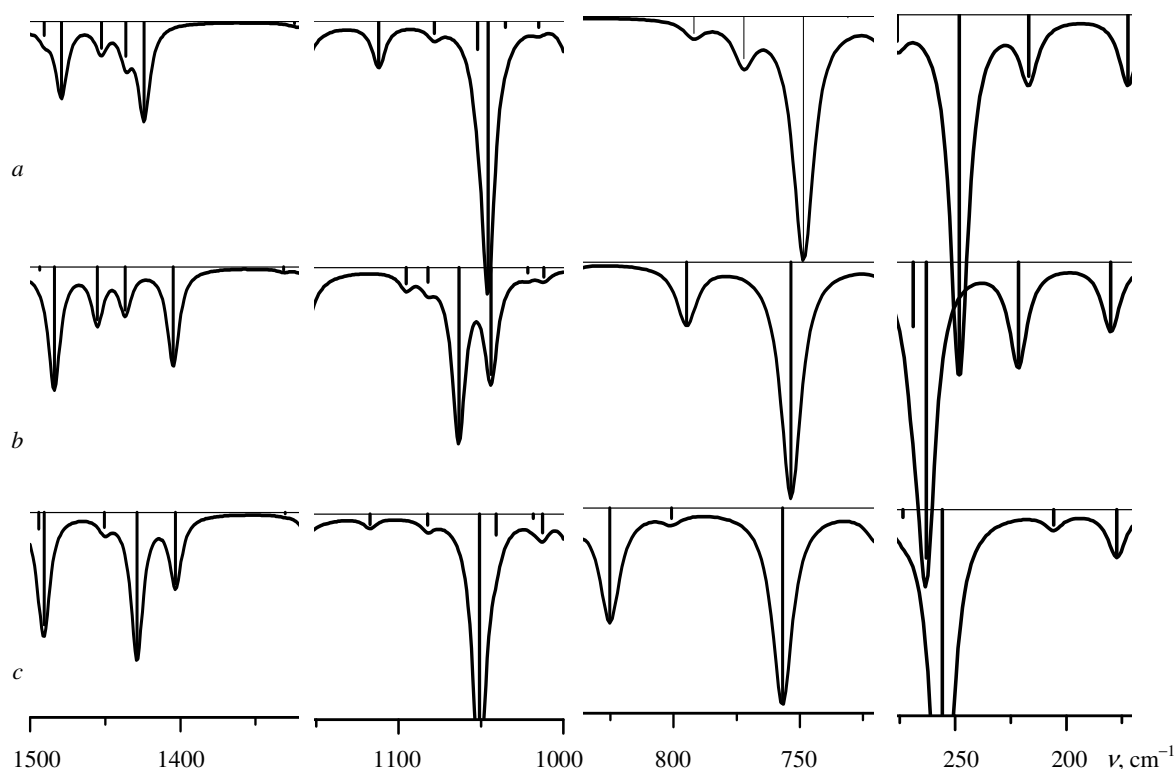


Figure 2. Fragments of the calculated IR spectra of the free molecules: 2BPM (a); 3BPM (b); 4BPM (c)



Table 1
The influence of the substituent location on the IR spectra of biphenylmethanols

2BPM		3BPM		4BPM		Assignment
ν , cm^{-1}	I , km/mole	ν , cm^{-1}	I , km/mole	ν , cm^{-1}	I , km/mole	
1491	3.4	1494	0.7	1494	4.0	α ($\text{H}_R \text{C}_R \text{H}_R$), χ ($\text{C}_A \text{C}_A \text{C}_R \text{H}_R$)
1479	17.8	1484	29.3	1491	27.3	β ($\text{C}_A \text{C}_A \text{H}_A$), α ($\text{H}_R \text{C}_R \text{H}_R$)
1453	6.5	1455	12.9	1451	3.5	β ($\text{C}_B \text{C}_B \text{H}_B$), β ($\text{C}_A \text{C}_A \text{H}_A$)
1436	8.4	1437	10.5	1429	35.2	β ($\text{C}_B \text{C}_B \text{H}_B$), Q ($\text{C}_B \text{C}_B$)
1424	23.0	1405	23.8	1403	17.4	β ($\text{C}_A \text{C}_R \text{H}_R$), β ($\text{C}_R \text{O}_R \text{H}_R$)
1112	10.3	1095	3.9	1117	2.5	β ($\text{C}_A \text{C}_A \text{H}_A$), Q ($\text{C}_R \text{O}_R$)
1052	7.0	1064	40.9	1041	5.1	Q ($\text{C}_A \text{C}_A$), β ($\text{C}_A \text{C}_A \text{H}_A$)
1046	63.5	1044	25.9	1051	64.1	Q ($\text{C}_R \text{O}_R$), Q ($\text{C}_B \text{C}_B$)
1035	1.5	1022	1.3	1018	1.0	Q ($\text{C}_B \text{C}_B$), β ($\text{C}_B \text{C}_B \text{H}_B$)
1015	1.4	1012	2.3	1013	4.5	χ ($\text{C}_A \text{C}_A \text{C}_R \text{H}_R$), χ ($\text{H}_R \text{C}_R \text{O}_R \text{H}_R$)
772	10.3	795	14.6	801	2.5	χ ($\text{C}_A \text{C}_A \text{C}_A \text{H}_A$), χ ($\text{H}_B \text{C}_B \text{C}_B \text{C}_B$)
749	58.8	753	57.2	757	47.6	χ ($\text{C}_A \text{C}_A \text{C}_A \text{H}_A$), χ ($\text{H}_B \text{C}_B \text{C}_B \text{C}_B$)
731	0.3	716	1.9	720	6.3	χ ($\text{C}_A \text{C}_A \text{C}_A \text{C}_A$), χ ($\text{C}_A \text{C}_A \text{C}_A \text{H}_A$)
718	3.5	699	5.4	699	7.8	χ ($\text{C}_A \text{C}_A \text{C}_A \text{C}_A$), χ ($\text{C}_A \text{C}_A \text{C}_A \text{H}_A$)
303	1.9	284	0.7	332	3.1	χ ($\text{C}_A \text{C}_A \text{C}_A \text{C}_A$), χ ($\text{C}_B \text{C}_A \text{C}_A \text{C}_A$)
276	6.4	269	15.6	274	1.9	χ ($\text{H}_R \text{C}_R \text{O}_R \text{H}_R$), χ ($\text{C}_A \text{C}_R \text{O}_R \text{H}_R$)
248	87.3	263	71.7	256	106.7	χ ($\text{C}_A \text{C}_R \text{O}_R \text{H}_R$), χ ($\text{H}_R \text{C}_R \text{O}_R \text{H}_R$)
217	14.9	222	24.4	206	3.7	χ ($\text{C}_A \text{C}_R \text{O}_R \text{H}_R$), χ ($\text{H}_R \text{C}_R \text{O}_R \text{H}_R$)
172	16.6	180	16.3	177	11.1	χ ($\text{C}_A \text{C}_A \text{C}_A \text{C}_R$), χ ($\text{H}_R \text{C}_R \text{O}_R \text{H}_R$)

Abbreviations. Q – stretching vibration of C-C or C-O bonds, χ – out of plane deformational vibrations (torsion, deviation of the C-H out of phenyl ring, deformation of the phenyl ring), β and α – variation of the angle formed by two C-C or C-H bonds. The atoms of the phenyl ring with the substituent are signed with A index, the atoms of the phenyl ring without the substituent are signed with B index, the atoms of the methanol group are signed with R index.

in the spectra of 3BPM is larger as compared to that of 2BPM. In the spectra of 4BPM, the intensity of the high-frequency component of the doublet is close to zero, while its low-frequency component is rather strong. The distance between the components of the doublet increases, too.

According to our computer simulation in the spectral region 1040–1070 cm^{-1} the vibra-

tions of the C-C bond in the phenyl ring are observed. In the spectra of 2BPM one strong band centered at 1052 cm^{-1} is observed (Fig. 2a), while in the spectra of 3BPM a clear doublet of two bands centered at 1064 and 1044 cm^{-1} is seen (Fig. 2b). In the spectra of 4BPM only one intense band centered at 1051 cm^{-1} is observed (Fig. 2c).

Weak absorption band observed in the spectral region 830–760 cm^{-1} is assigned to the out-of-plane vibration of the C-H bond of the phenyl ring. The position of this band is blue shifted for 3BPM (794 cm^{-1}) and for 4BPM (825 cm^{-1}) as compared to its position in the spectra of 2BPM (772 cm^{-1}). The intensity of this band is practically the same in the spectra of 2BPM and 3BPM, while it increases in 4BPM spectra.

The O–H vibration band in the low-frequency region is related to O–H banding vibration. This band centered at 248 cm^{-1} in the spectra of 2BPM is blue shifted on 15 cm^{-1} and on 8 cm^{-1} as compared to its position in the spectra of 3BPM (263 cm^{-1}) and 4BPM (256 cm^{-1}), respectively. The intensity of these bands is comparable.

The optimized structures of the fragments of the H-bonded chains of biphenylmethanols are shown in Fig. 3 (5, 6, 7). Fig. 3 also shows the fragments of the H-bonded chains: dimer (1), trimer (2), tetramer (3); and cyclic tetramer (4) of methanol molecules.

The calculated data needed for the analysis of the influence of the H-bonding on the IR spectra are summarized in Table 2. In the triclinic modification cyclic tetramer of 2BPM molecules has a C_i symmetry and built up of two pairs of similar molecules [5]. One pair contains the molecules, which structure is close to that calculated for the conformer A. The second pair contains the molecules, in which structure is intermediate between the structures of A and B conformers. The lengths of the O–H bonds in this tetramer are equal to 0.993 and 0.994 Å. The lengths of the H-bonded bridges (O–H... O) are 2.726 and 2.700 Å (Table 2). The number of the normal vibrations in the cyclic tetramer is equal to 306 (in the free molecules of biphenylmethanols this number is equal to 72). They are divided into two blocks according to C_i group: 153 a_g + 153 a_u . The vibrations of the a_g type are

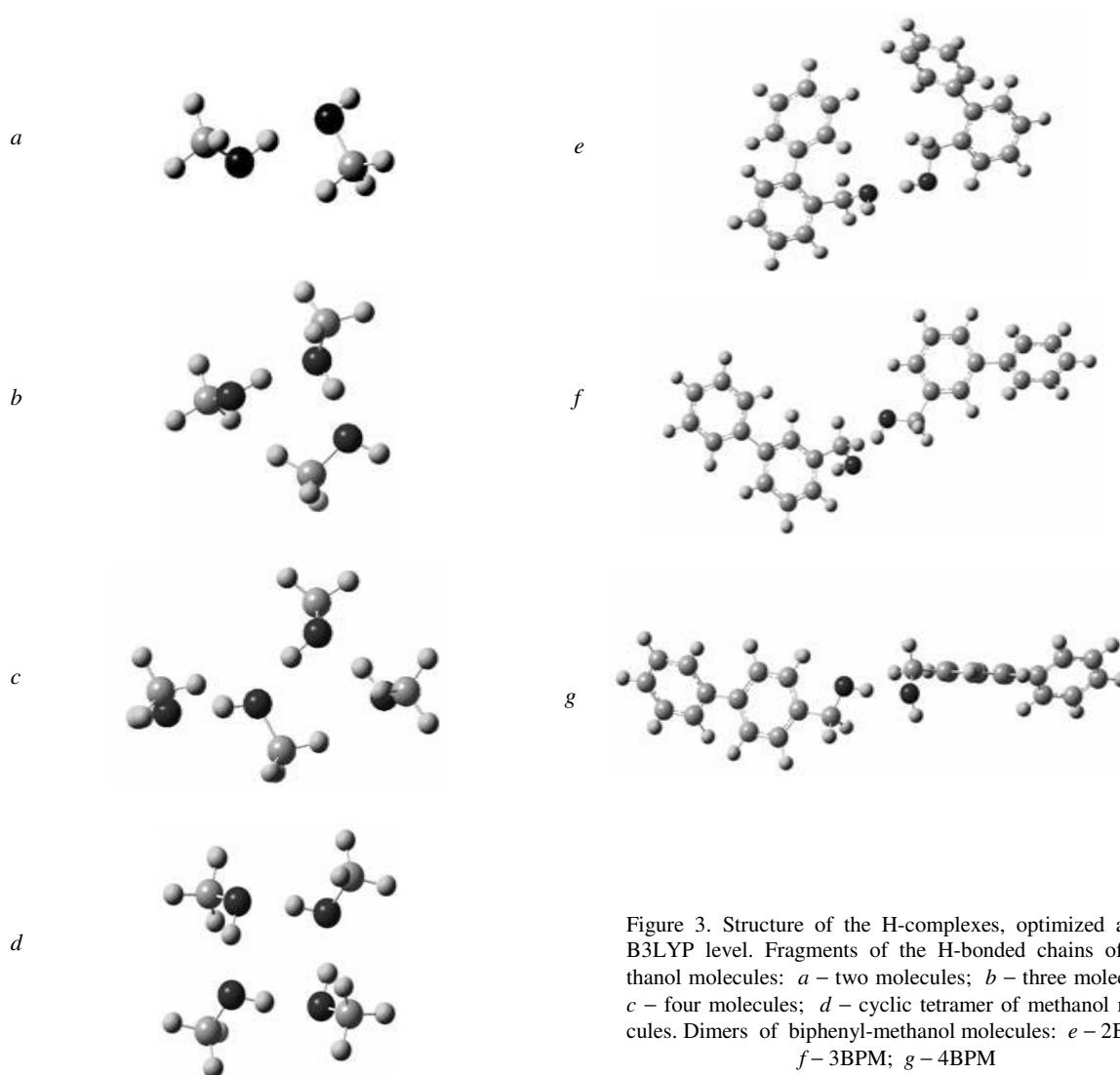


Figure 3. Structure of the H-complexes, optimized at the B3LYP level. Fragments of the H-bonded chains of methanol molecules: *a* – two molecules; *b* – three molecules; *c* – four molecules; *d* – cyclic tetramer of methanol molecules. Dimers of biphenyl-methanol molecules: *e* – 2BPB; *f* – 3BPB; *g* – 4BPB

active in the Raman and a_u are active in IR. Under packing of the molecules into tetramers some normal vibration frequencies of the free molecule are splitting into four components. The largest value of the splitting is 152 cm^{-1} for OH stretching vibration. This value is determined by the difference of the normal vibration frequencies with the symmetry a_g , which are inactive in the IR spectrum. The position of the quartet is substantially red shifted on 380 cm^{-1} . The difference between the frequencies of the two normal vibrations, which are active in the IR spectrum (a_u), is equal to 45 cm^{-1} . These two normal vibrations substantially contributed to the corresponding band in the IR spectrum.

From the analysis of the calculated parameters for the chain fragments (dimers) of 2-, 3-

and 4BPB (Table 2) it follows that the H-bond energy in these cases is smaller than in the case of cyclic tetramers of 2BPB. Moreover, the red shift of the O–H stretching vibration frequency in the case of chain structures is smaller as compared to that of cyclic tetramer of 2BPB (Table 2, Fig. 1, a, b, c, 2, 3). The value of the O–H stretching band splitting caused by formation of the H-bonded chain is comparable with this value in the cyclic tetramer. In the case of H-bonded chain, all vibrations are active, thus the corresponding band is wider as compared to that of cyclic tetramer. This is clearly illustrated by the modeling results of the cyclic tetramer of methanol molecules and the fragments of the chains of methanol molecules: dimer, trimer and tetramer (Table 2, Fig. 4).



Table 2

Calculated parameters of biphenylmethanols, methanol, and their H-bond complexes

Object	$R_{OH}, \text{Å}$	$R_{OH-O}, \text{Å}$	ν_{OH}, cm^{-1}	$\Delta\nu, \text{cm}^{-1}$	$\Delta H, \text{kcal/mole}$	$I_{IR}, \text{km/mole}$	μ, D
2BPM	0.968		3575			18.3	1.707
tetramer	0.993	2.726	3085	490	6.36	0.0	0.000
	0.994	2.700	3161	414	5.80	3036.3	
			3203	372	5.47	2709.0	
			3226	349	5.27	0.0	
dimer	0.977	2.838	3432	143	3.04	845.7	4.134
	0.971		3549			24.2	
3BPM	0.969	-	3572	-	-	16.3	1.651
	0.978	2.838	3418	154	3.20	1015.4	3.710
	0.972		3541			20.9	
4BPM	0.969	-	3571	-	-	15.3	1.730
	0.978	2.848	3427	144	3.06	961.8	4.294
	0.971		3544				
Methanol	0.969	-	3568	-	-	11.2	1.695
chain fragment (2 mol.)	0.976	2.850	3450	118	2.65	383.0	2.885
	0.969		3575			21.7	
chain fragment (3 mol.)	0.976	2.755	3395	173	3.46	590.0	3.152
	0.976		3448			739.7	
	0.976		3481			27.9	
chain fragment (4 mol.)	0.976	2.740	3377	191	3.69	1370.0	8.930
	0.976		3416			42.5	
	0.976		3427			864.8	
	0.976		3487			25.4	
cyclic tetramer	0.993	2.716	3091	477	6.27	0.0	0.000
	0.993	2.734	3192	376	5.50	2005.3	
	0.993	2.716	3199	369	5.44	1798.7	
	0.993	2.734	3237	331	5.12	0.0	

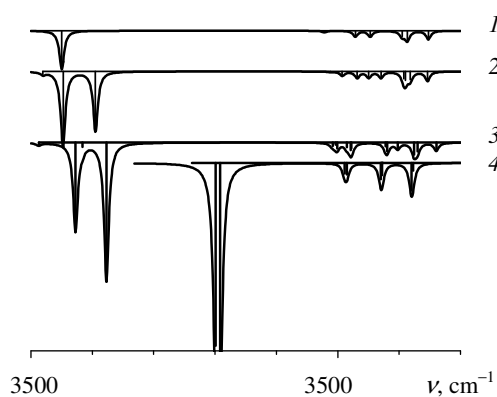


Figure 4. Fragments of the calculated IR spectra of the H-bonded chains of methanol molecules: 1 – two molecules; 2 – three molecules; 3 – four molecules; 4 – cyclic tetramer of methanol molecules

In Ref. [4], the applicability of such modeling was justified for the analysis of the high-frequency region ($3150\text{--}3450 \text{ cm}^{-1}$) of the IR spectrum of 2BPM, because the structure of the cores of the H-complexes formed by 2BPM and methanol molecules are very similar. The results of the modeling of the fragments of the chain of

methanol molecules allowed us to make fairly correct conclusions without the modeling of the huge fragments of the chain of biphenylmethanol molecules. According to the modeling results (Table 2), the length of the free O–H bond in dimers makes up 0.971 Å for 2BPM and 4BPM, and 0.972 Å for 3BPM. The length of the O–H bond in the H-bonded bridge is 0.977 Å for 2BPM, and 0.978 Å for 3BPM and 4BPM; the length of the H-bonded bridge O–H····O is 2.838 Å for 2BPM and 3BPM, and 2.848 Å for 4BPM; the hydrogen atom in 2BPM does not lie on the straight line, which is a prolongation of the O–H bond, but deviates from it by the angle of 3° .

The length of the H-bonded bridge O–H····O in the H-bonded chain involving three and four molecules of methanol is slightly smaller as compared to that of cyclic tetramer of methanol molecules. An increase in the number of the molecules in the chain changes the length of the O–H····O bridge. Namely, for the chain with two molecules this length is equal to 2.809 Å , while for the chain with three molecules it decreases and becomes equal to 2.605 Å . In the



case of the chain of four molecules there are three bridges. The lengths of the two bridges are equal to 2.605 Å, while the length of the third bridge is equal to 2.710 Å, due to the formation of the weak bond O...H–C.

The frequencies of the OH stretching bands in methanol molecules and in 2-, 3- and 4BPM are similar (Figs. 1, 4; Table 2). The H-bond energy (ΔH) in the cyclic tetramers of biphenylmethanol molecules, which was estimated using the empirical formula obtained by Iogansen [11] are approximately 6 kcal/mol and are similar to the H-bond energy in the cyclic tetramer of methanol molecules [4]. The H-bond energy in the H-complexes formed by 2-, 3- and 4BPM and methanol are also similar and are approximately equal to 3 kcal/mol (Table 2). This means that the investigated biphenylmethanols are the molecular crystals with the H-bond energy of a moderate strength.

3. CONCLUSION

On the basis of the analysis of the experimental IR spectra and the results of computer modeling it was established, that the location of the methanol group in 2, 3 and 4 positions in biphenylmethanol molecule influence on the vibrational spectrum. This influence appears as negligible shifts of some bands related to the vibrations of the phenyl ring and as a essential redistribution of the intensities among these bands.

It was established that the experimental vibrational spectrum of 2BPM, studied in [9], belongs to a monoclinic crystalline modification. This modification consists of H-bonded chains. The similarity of the IR spectra of 2-, 3- and 4BPM in the region 3450–3150 cm^{-1} allowed us to conclude, that the 3BPM and 4BPM, studied in [9], also belong to the monoclinic modification. The results of the modeling are in accordance with the X-ray data for the triclinic and monoclinic modifications of 2BPM [6] and with the experimental IR spectra of 2-, 3- and 4BPM compounds [6, 9].

In the case of tetramer two closely spaced O–H vibration bands, which are related to O–H asymmetric stretching vibrations, which are active in the IR spectrum, determine the shape of the corresponding band in the IR spectrum of the triclinic modification. In the case of the

H-bonded chains all stretching vibrations of the O–H bond are active and form a zone. This zone determines the width of the corresponding band in the IR spectrum of the monoclinic modification, which turns out to be wider relative to that in the IR spectrum of the triclinic modification.

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