

Modeling of the structure and vibrational spectra of 2-biphenylmethanol using B3LYP method

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Abstract

Hydrogen-bonded complex of 2-biphenylmethanol molecules in solid state was optimized using the density functional method (B3LYP/6-31G*). The structures, energies, dipole moments, polarizabilities, frequencies of the normal modes in the harmonic approximation (and in the anharmonic one for the free molecule), and their intensities in IR and Raman spectra were calculated. On the basis of the experimental data analysis and computer calculation results, the peculiarities of the crystal structure and dynamics of 2-biphenylmethanol due to H-bonding were clarified.

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1. Introduction

The molecular compound 2-biphenylmethanol (2BPM) is a glass-forming material and, therefore, it can be used as a model system for the study of a glass transition and the dynamics of molecules in a supercooled liquid state [1], which are still far from being completely understood. The investigation of 2BPM began with the study of its Raman and IR spectra at room temperature [2]. In addition, the computer calculation of the molecular structure and IR spectrum was carried out on the basis of the semi-classical theory by means of the method of fragments [3] realized in the complex of programs 'LEV-100'. We reported the interpretation of the vibrational spectra of the crystalline 2BPM, made the conclusion about the formation of the H-bonds, and proposed the most probable model of a molecular conformer at room temperature. The existence of the hydrogen bonds in 2BPM was effectively taken into account. The obtained results were considered as preliminary ones that need a complementary verification. In more details, we have investigated the influence of the H-bonding on the structure of 2BPM in the work [4]. In the next work [5],

the crystalline structure was determined by means of X-ray diffraction and the process of solidification was investigated by means of IR and Raman spectroscopy.

Further, by means of the density functional method (B3LYP/6-31G*) using the program package GAUSSIAN'03 [6], we have optimized the geometries of the fragments from which the H-complex consists in the crystalline 2BPM. Namely, the geometry optimization has been performed for the free molecules of 2BPM, biphenyl, methanol, and H-bonded complexes (cyclic tetramer) of methanol molecules. On the basis of the analysis of the experimental and computer simulation results, an interpretation of the IR spectrum has been given. The other works [7–9], dedicated to theoretical and experimental investigations of the methanol structure and to the influence of H-bond on its vibrational spectrum should also be mentioned.

The main aim of this work is the structure determination for the 2BPM H-complex (tetramer) by B3LYP method and comparing the obtained results with the previous ones [2,4,6]. In particular, our attention will be paid to the study of the influence of H-bond on the structure of 2BPM and of the display of it on the vibrational spectra. For calculations we will use GAUSSIAN'03 program package [10].

2. Experimental and computer simulation

Details concerning the experimental set-up and results are given in our earlier publications [4,5]. The density functional

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calculations for free/isolated molecular systems, such as a monomer and the H-complex (a cyclic tetramer) of 2BPM molecules, have been performed using the program package GAUSSIAN'03 for Windows. The B3LYP level of theory in conjunction with the 6-31 (d) basis set has been used in the calculations. In the course of calculations, the energy minimization and geometry optimization as well as dipole moments and polarizabilities for the corresponding molecular systems have been determined. The wavenumbers and intensities in the IR and Raman spectra of normal vibrations (in the harmonic approximation) have been calculated for each system. Normal mode analysis has been performed in the context of considered DFT method by GAUSSIAN'03 program. An approach reported in [11] was applied to compute Raman differential cross sections. To estimate the influence of the mechanical anharmonicity on the dynamics of the molecular system, the spectrum of normal vibrational frequencies of the free 2BPM molecule was calculated additionally in anharmonic approximation using of third-order normal coordinates derivatives of the potential energy in second-order perturbation theory [10].

3. Results and discussion

The crystal structure of 2BPM is presented in [5,6]. Analysis of the results obtained on the geometry in the course of structure determination by the density functional method suggests that at least two conformers (denoted as **A** and **B**) for the free molecule could be realized. The **A** and **B** conformers [6] differ by the orientational angles of methanol group relative to the nearest phenyl ring (φ_1) and by the orientational angles of phenyl rings relative to each other (φ_2). The values of the angles are: $\varphi_1=20^\circ$, $\varphi_2=55.1^\circ$ (for the conformer **A**) and $\varphi_1'=73.6^\circ$, $\varphi_2'=76.8^\circ$ (for the conformer **B**). The length of the O–H bond is 0.969 Å.

The comparison of the experimental X-ray results with that of the theoretical modeling shows that the crystal structure contains tetramers built up of two pairs of similar molecules. One pair contains the molecules, which structure is close to that calculated for the conformer **A**. The second pair of the tetramer contains the molecules, in which structure is intermediate between the structures of the **A** and **B** calculated conformers.

The theoretically determined tetramer of 2BPM molecules has a C_i symmetry (see Fig. 1). The lengths of the O–H bonds in this tetramer are equal to 0.993 and 0.994 Å. The bridge lengths (i.e. O...O distances) are 2.726 and 2.700 Å (Table 1). The oxygen atoms do not lie on the straight line, which is the prolongation of the O–H bond, but deviate from it by the angles of 14° . The core of the cyclic tetramer is not planar. Note that the calculated geometry parameters are in a good agreement with the crystallographic data. Dihedral angles OHOH (between planes OHO and HOH) in both type of molecules are equal to -47.5° and -9.7° , respectively.

The calculated O–H lengths in 2BPM and methanol are similar [6]. The bridge lengths O–H...O in their tetramers are also similar (Table 1). This result is in agreement with our supposition [6] that the replacement of the hydrogen atom in the methyl group ($-\text{CH}_3$)

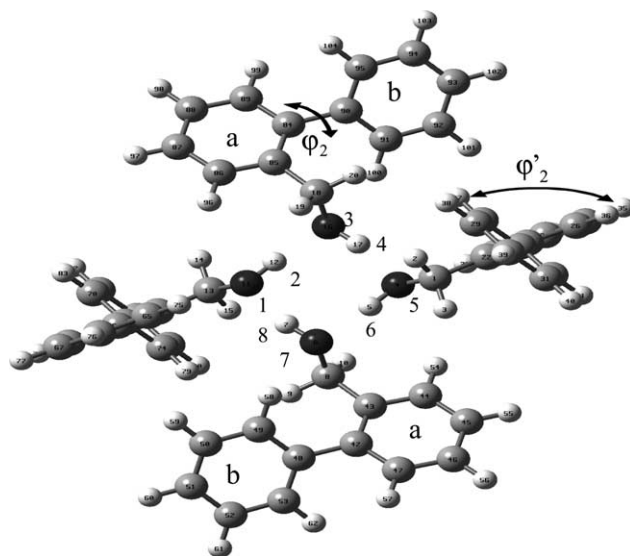


Fig. 1. Structure of 2BPM. H-complex (B3LYP/6-31G*).

of monomer or tetramer by biphenyl (there are four such groups in the tetramer) does not affect appreciably the core of the H-complex. The cores of the H-complexes of 2BPM and methanol molecules, both of which are cyclic tetramers, are similar in structure and analogous in dynamics.

Fig. 2 shows the experimental and calculated vibrational spectra of 2BPM tetramers. In the high-frequency region $3150\text{--}3350\text{ cm}^{-1}$ of the IR spectrum (Fig. 2a, curve 1), OH-stretching band with the peak frequency 3250 cm^{-1} is dominated in the spectrum. Its peak position (the large shift to the low-frequency side), anomalous width and strong intensity (Fig. 3a, curve 1) are the characteristic features of the H-bond in molecular crystals [12,13].

Raman spectra complement the data concerning the dynamics of 2BPM. The stretching and deformation vibrations of the core of the H-complex among other manifest themselves in the low-frequency region ($10\text{--}300\text{ cm}^{-1}$) (Fig. 3b, curve 1). The stretching vibrations of the hydrogen bond $\text{H}\cdots\text{O}$, active in Raman spectrum occur at 250 and 295 cm^{-1} and have low intensity. The deformation vibrations of the H-complex core appear in the region $<100\text{ cm}^{-1}$. The out-of-plane deformation vibrations of the hydrogen bond occur at 87 cm^{-1} $-\chi(\text{HOHO})$, 65 cm^{-1} $-\chi(\text{COHO})$, 56 cm^{-1} $-\chi(\text{HOHC})$, and 42 cm^{-1} $-\chi(\text{HOHO})$. The in-plane deformation vibrations of the hydrogen bond occur at 55 cm^{-1} $-\alpha_1(\text{H}\cdots\text{O}-\text{H})$, and 28 cm^{-1} $-\alpha_2(\text{H}\cdots\text{O}-\text{H})$.

The calculated frequencies of the O–H stretching vibrations in the molecules of methanol [6] and 2BPM are similar. They are also similar in their tetramers. The hydrogen bond energy (ΔH) in the tetramer of 2BPM molecules was estimated using the empirical formula obtained by Iogansen [14]. It connects the down-shift of the stretching vibration OH with the H-bond energy. The value of ΔH lies in the range from 6.64 to 5.52 kcal/mol and is approximately equal to 5.99 kcal/mol, which is close to the H-bond energy in the tetramer of methanol molecules [6] (Table 1). This is further evidence that the

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