STRUCTURE AND VIBRATIONAL SPECTRA OF DIHYDROXYBENZOIC ACID ISOMERS. THEORY, EXPERIMENT

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The purpose of work: to study the effect of the hydrogen bond in dihydroxybenzoic acid (DHBA) dimers on their IR spectrum.
Tasks: to construct structural-dynamic models of DHBA dimers and, on the basis of the results obtained, to interpret the measured IR spectra.
Methods: DFT method and functional and basis sets are B3LYP/6-31G(d).

Objects:

Dihydroxybenzoic acids are a subclass of hydroxybenzoic acids with two hydroxyl groups, the relative position of which determines the properties of the molecules. There are 6 structural isomers of DHBA that differ in the position of the OH groups: 2,3-DHBA (Pyrocatechuic acid), 2,4-DHBA (β-resorcylic acid), 2,5-DHBA (Gentisic acid), 2,6-DHBA (γ-resorcylic acid), 3,4-DHBA (Protocatechuic acid), 3,5-DHBA (α-resorcylic acid). The structure of the DHBA molecules is shown in Fig. 1.

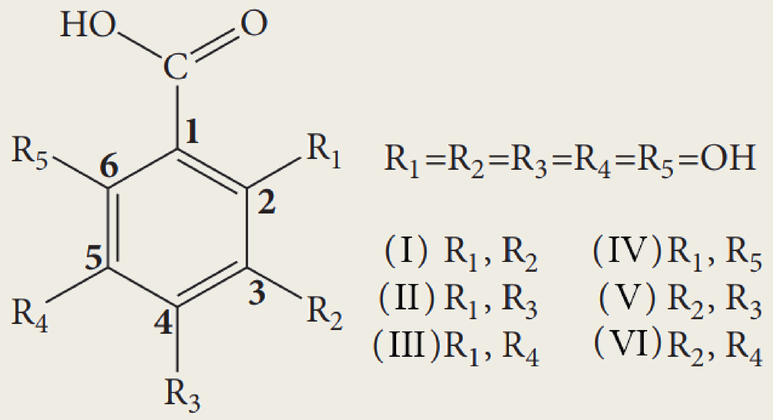
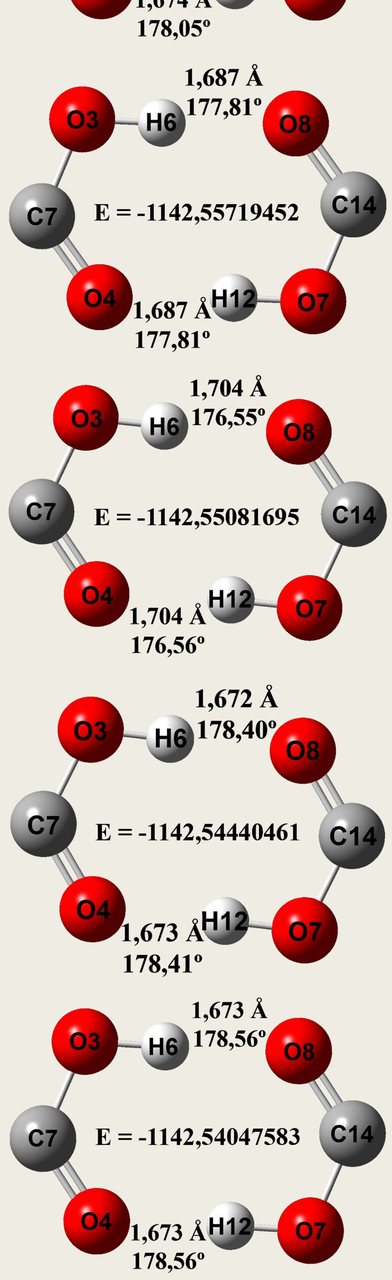
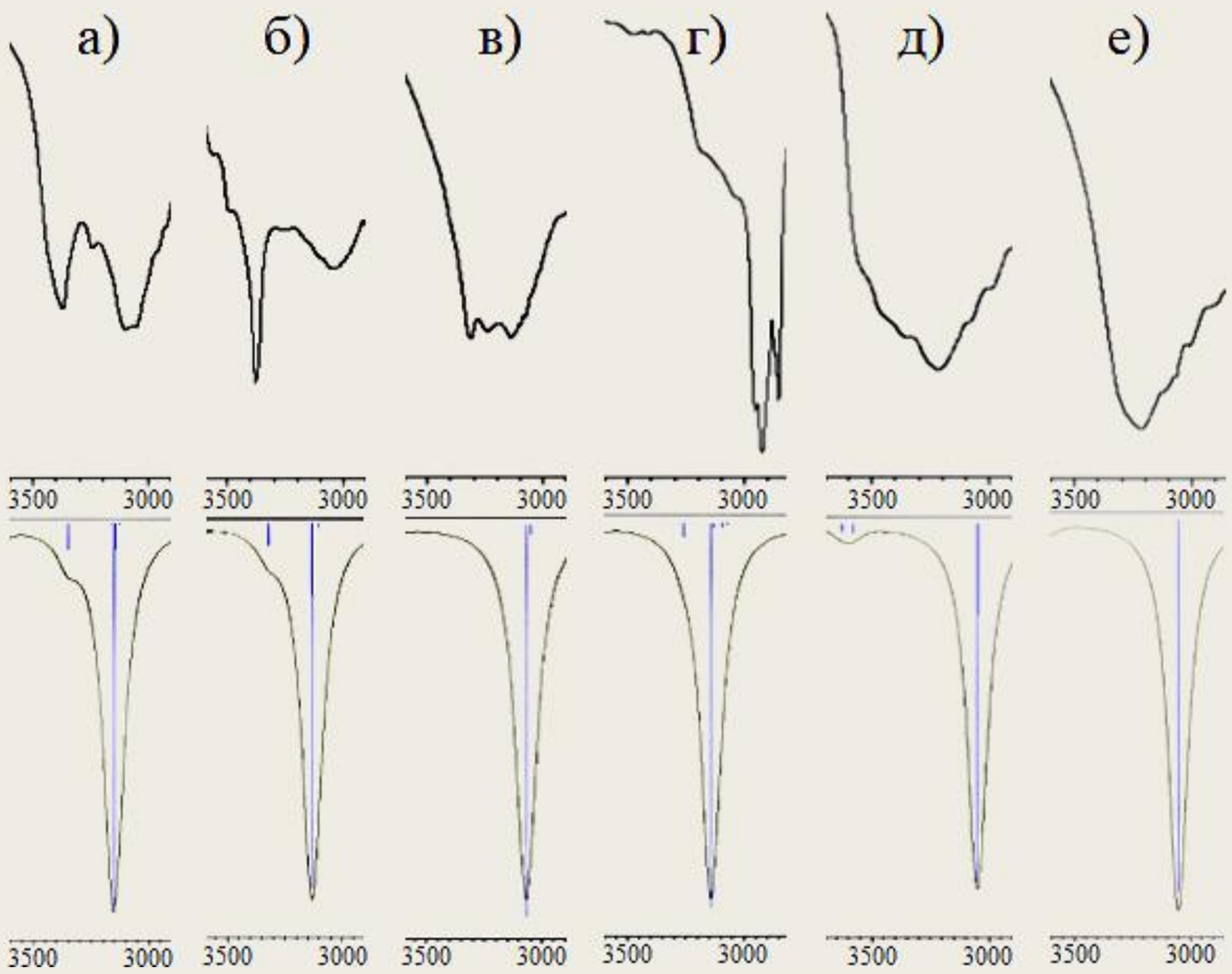


Fig. 1. Structural formulas of DHBA dimers (I, II, III, IV, V and VI) with indication of atomic labeling and their trivial names

Additionally, the dimer of the 2,5-DHBA' conformer was modeled, which differs from the original 2,5-DHBA molecule by turning the O1-H4 bond towards the O4 oxygen atom (marked with a dash ') and forming an internal hydrogen bond, which is clearly manifested in the spectrum in the region over 3000 cm^{-1}.

Fig. 2. Complexes of carboxyl groups and geometric parameters of DHBA dimers.
E – the minimized energies in Hartree,
d_n – the dipole moment in Debye (n = x, y, z, total)





The simulation results clearly show a strong influence on the IR spectrum of the H6-O8 and H12-O4 intermolecular hydrogen bonds formed in the dimer ring, which manifest themselves in an anomalous broadening of the bands and an increase in intensity from 4888 km/mol in the 3,4-DHBA dimer to 6071 km/mol in the 2,6-DHBA dimer. The oscillation frequencies of OH-bonds of dimers of DHBA molecules differ slightly from each other, being in the range of 3050±35 cm^{-1}. The formation of the band structure of the measured IR spectra in this region is also influenced by the internal hydrogen bonds H4--O4. Their presence is manifested in the spectra of 2,3-, 2,4-, 2,6-DHBA and 2,5-DHBA dimers in less wide bands compared to the bands caused by external OH-bonds, but also quite noticeable in intensity-from 226 km/mol in 2,6-DHBA to 421 km/mol in 2,3-DHBA.

а)	2,3-DHBA;
б)	2,4-DHBA;
в)	2,5-DHBA (2) и 2,5-DHBA' (3);
г)	2,6-DHBA;
д)	3,4-DHBA;
е)	3,5-DHBA.

Fig. 3. Experimental (1) and calculated (2,3) intensities in the IR spectrum of DHOBC dimers.

Conclusions

1. According to the results of constructing structural and dynamic models of H-complexes of DHBA, differences in the vibrational spectra and other parameters of these molecules were revealed due to the position of hydroxyl groups relative to the phenyl ring, as well as the presence or absence of an internal hydrogen bond.
2. A weak intramolecular hydrogen bond was detected in the molecules 2,3-, 2,4-, 2,6-DHBA and 2,5-DHBA', which is manifested in the region over 3000 cm^{-1} by intensity peaks in the IR spectrum.