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MOLECULAR STRUCTURE OF COMPLEXES WITH A BIFURCATED HYDROGEN BOND.

5*. DIMERS OF 3-HYDROXY-2-METHYL-4-PYRONE IN INERT MEDIA*[2]

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*According to the data from IR spectroscopy and quantum-chemical calculations (B3LYP/6-31G**, B3LYP/6-311G*), in the vapor and in dichloroethane the synperiplanar conformer of 3-hydroxy-2-methyl-4-pyrone (maltol) exists in equilibrium with two types of dimers. The hydrogen atom of the hydroxy group of one them participates in the formation of a three-center bifurcated hydrogen bond. The second isomer is formed by means of two such H bonds, the intramolecular component of which is substantially weakened while the intermolecular component is so strong that it approximates in character to a two-center hydrogen bond.*

Keywords: 3-hydroxy-2-methyl-4-pyrone, dimers, maltol, bifurcated hydrogen bond, DFT quantum-chemical calculations, IR spectra.

The biological activity of many natural compounds, such as flavonoids, is due to the formation of rings closed by a hydrogen bond in their structure [2]. The presence of intramolecular hydrogen bonds in the structure of a substance often determines the supramolecular structure of the substance in the condensed state. Thus, the molecules of tropolone in its solid aggregate state are linked into centrosymmetric dimers [3]. In chloroform solution these dimers dissociate with the formation of monomers, which are characterized by a strong intramolecular hydrogen bond accompanied by resonance [4]. In nonpolar carbon tetrachloride citrinin, the molecules of which in the solid phase contain two intramolecular hydrogen bonds, exists in the form of an equilibrium mixture of monomeric forms with two and one hydrogen bond [5]. The conformational isomer of 2,5-dihydroxy-1,4-benzoquinone with two intramolecular hydrogen bonds is stable in the gas phase and in chloroform solution. In the crystalline state the molecules of this compound are linked into infinite bands through OH groups participating in three-center bifurcated hydrogen bonds [6]. In the crystalline state the molecules of 3-hydroxy-2-methyl-4-pyrone (maltol) have two polymorphous modifications, representing cyclic

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* For Communication 4, see [1].

*[2] Dedicated to Academician of the Russian Academy of Sciences M. G. Voronkov on his 85th birthday.

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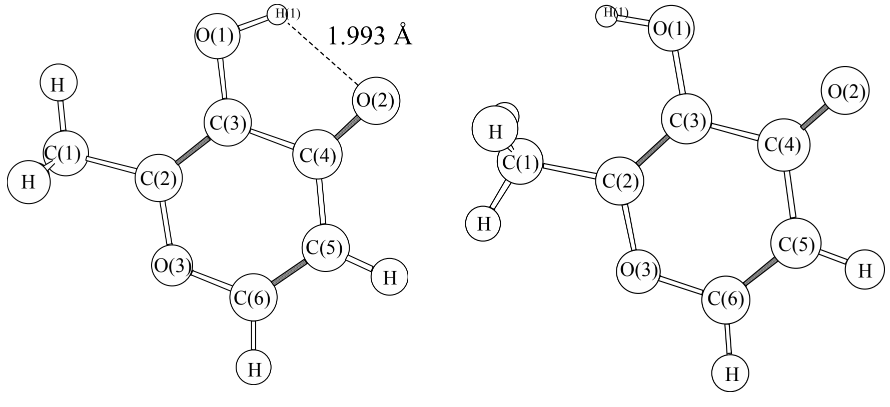
dimers and chain polyassociates [7]. In the present work the structure of maltol molecules was studied in the gas phase and in solution. Greatest attention was paid to the structure of the self-associates, which were characterized by a set of DFT quantum-chemical calculations and by IR spectroscopy.

Satisfactory data on the geometric parameters of the compounds with intramolecular hydrogen bonds leading to polarization of the π-electronic system of the molecules were obtained during quantum-chemical calculations by the B3LYP/6-31G** method [6, 8, 9]. The energy characteristics of the formation and structure of the synperiplanar (*sp*) and antiperiplanar (*ap*) conformers of maltol **1** (Fig. 1) and also of its dimers (Fig. 2), data on the structure of which were obtained from X-ray crystallographic data [7], were studied by this method (the Gaussian-98 software [10]).

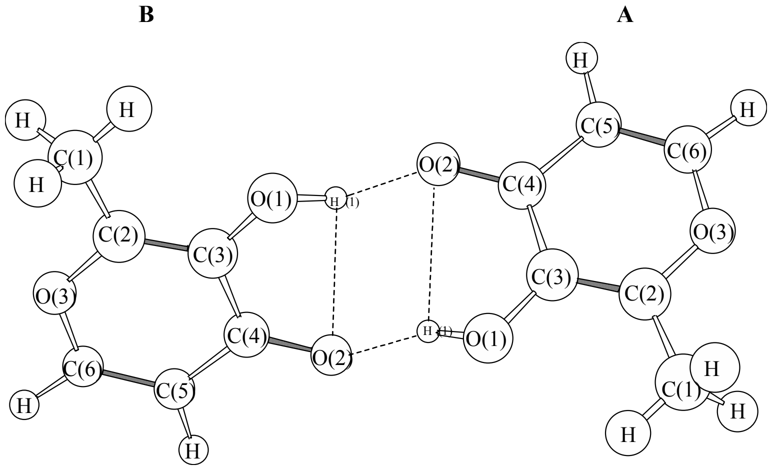
The Conformers of the Maltol Molecule. The energy of formation of the ring with intramolecular hydrogen bonds in the isolated molecule of maltol (Δ*E*) was determined as the difference between the total energies of its *sp*-**1a** and *sp*-**1b** conformers (Fig. 1) and amounted to 48.24 kJ/mol. The theoretical values of the lengths of the valence bonds in conformer **1a** differ little from those obtained by X-ray crystallographic analysis for the subunits of its self-associated (Table 1). In contrast to the valence bonds, the calculated distance between the O(1) and O(2) oxygen atoms of its ring, closed with a hydrogen bond, is substantially shorter (by 0.13 Å) than the value characteristic of the maltol self-associates (Table 1). Obviously, this distance in the latter is increased on account of weakening of the intramolecular hydrogen bond. The length of the nonvalent bond O(1)···O(2) in conformer **1a** is typical of molecules with a strong H bond accompanied by resonance [11]. The heavy atoms in the heteroring of the maltol molecule in form **1a** and the atoms of the ring closed by the hydrogen bond lie in one plane. The heavy atoms of the *ap* form **1b** also lie in one plane, while the hydroxyl group deviates from it by only 6°. The conformational transition *ap* → *sp* leads to a decrease of the bond angles O(2)C(4)C(3) and H(1)O(1)C(3) by 5 and 7° respectively. As a result of the formation of the intramolecular hydrogen bond the distance between the carbonyl and hydroxyl oxygen atoms in conformer **1a** becomes 0.083 Å shorter than in conformer **1b**. In addition to the decrease of this distance, the formation of the intramolecular hydrogen bond gives rise to a sharp increase (by 0.017 and 0.014 Å) of the lengths of the OH and C=O bonds. Altogether, during the formation of the hydrogen-bonded ring in conformer (**1a**) the π-system is affected in such a way that the carbon–carbon bond lengths are equalized, while the aromaticity of its heterocycle is increased in comparison with conformer **1b**.



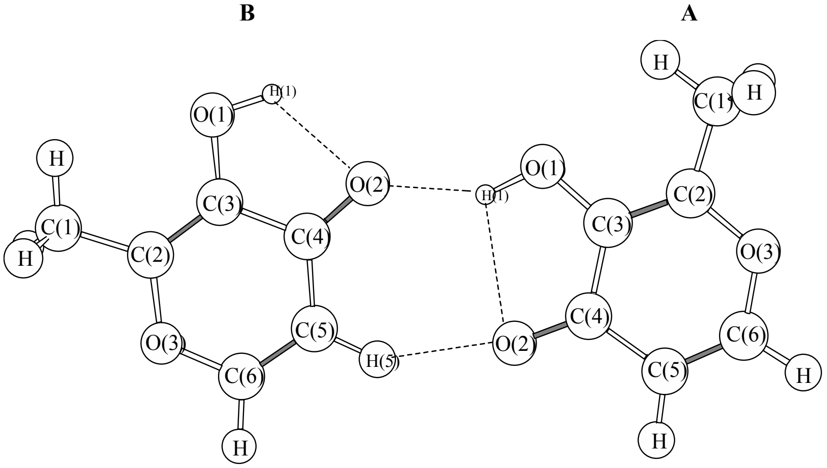
1a (*sp*)

1b (*ap*)

Fig. 1. The molecular structure, energy of formation (Δ*E*), and dipole moment (μ) of the *sp*-**1a** and *ap*-**1b** conformers of maltol (B3LYP/6-31G**). **1a** (*sp*): Δ*E* = 0.0 kJ/mol, M = 5.28 D. **1b** (*ap*): Δ*E* = 48.24 kJ/mol, μ = 3.36 D.



1c



1d

Fig. 2. The molecular structure, dipole moment (μ), and energy of formation (Δ*E*) of dimers **1c** and **1d** in relation to the *sp* conformer of maltol (B3LYP/6-31G**). **1c** Δ*E* = -45.19 kJ/mol, μ = 1.00 D. **1d** Δ*E* = -35.35 kJ/mol, μ = 1.93 D.

The changes in the geometric parameters of the maltol molecule, taking place as a result of the conformational transition *ap* → *sp*, are reflected in the values of the frequencies of its normal vibrations. The vibrational spectrum of the conformational isomers **1a**,**b** (Table 2) was calculated by the B3LYP/6-311G* method, since it better reflects the change in one of the most important parameters of the IR spectra of H complexes, i.e., the frequencies of the stretching vibrations of the OH group [12]. According to the calculations, as a result of the transition from conformer **1b** with the free OH group to conformer **1a**, in which the OH group is bonded, the frequency of the stretching vibration of the hydroxyl group is shifted toward lower frequencies by 217 cm^{-1}, indicating the formation of a strong hydrogen bond. As seen from the data presented above, it polarizes the π-system of the maltol, i.e., it is accompanied by resonance.

TABLE 1. The Bond Lengths (*l*) and Angles (ω) of the *sp*- and *ap*-Conformers of Maltol and its Dimers According to Data from Calculation (B3LYP/6-31G**) and X-ray Crystallographic Analysis [7]

	sp-**1a**	*ap*-**1b**	**1c (A,B)***	**1c (A)**	**1d (B)**	**1c (A)**	**1d (A)**
	B3LYP/6-31G**					PCA [7]	
Bond	*l*, Å						
H(1)–O(1)	0.983	0.966	0.998	0.987	0.981	0.82	0.86
O(1)–C(3)	1.350	1.360	1.343	1.342	1.351	1.356	1.350
O(2)–C(4)	1.241	1.227	1.248	1.240	1.251	1.248	1.254
O(3)–C(2)	1.376	1.374	1.370	1.374	1.371	1.365	1.366
O(3)–C(6)	1.346	1.351	1.343	1.344	1.347	1.347	1.351
C(1)–C(2)	1.490	1.498	1.491	1.491	1.490	1.484	1.482
C(2)–C(3)	1.357	1.359	1.368	1.365	1.359	1.359	1.354
C(3)–C(4)	1.467	1.481	1.466	1.470	1.461	1.441	1.444
C(4)–C(5)	1.446	1.462	1.448	1.451	1.441	1.438	1.433
C(5)–C(6)	1.353	1.346	1.351	1.351	1.353	1.338	1.325
H(1)···O(2)	1.993		2.516	2.318	1.997		
O(1)···O(2)	2.631	2.714	2.822	2.770	2.626	2.754	2.765
O(2)···H(5)				2.139			2.410
O(2)···C(5)				3.116			3.193
H(1)**A**···O(2)**B**			1.663	1.847		1.949	2.035
H(1)**B**···O(2)**A**						1.876	2.102
O(1)**A**···O(2)**B**			2.640	2.718		2.718	2.738
O(1)**B**···O(2)**A**						2.700	2.752
Angle	ω, deg						
H(1)O(1)C(3)	103	110	111	112	103		
O(2)C(4)C(3)	118	123	123	121	117		
O(1)**A**H(1)**A**O(2)**B**			165	145		156	146

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* **A** and **B** are the subunits of the dimers.

In the spectrum of maltol vapor, recorded at temperatures above 400 K, the most high-frequency band belonging to the stretching vibrations of the O–H bond lies at 3404 cm^{-1}. In the spectra of solutions of this compound in such inert solvents as carbon tetrachloride, dichloroethane, and methylene chloride the absorption band of the monomer is recorded in the region of 3400-3390 cm^{-1}. Its shift in relation to the corresponding band in the spectra of solutions of the monomer of phenol amounts to 210-220 cm^{-1}. These values agree well with the values calculated theoretically ($\Delta\nu_{OH}$ 222 cm^{-1}). The validity of the use of phenol as reference in this case follows from the proximity of the calculated frequency of its monomer ν_{OH} (3793 cm^{-1}) and the frequency of conformer **1b** of maltol (3788 cm^{-1}). Consequently, the high-frequency band in the region of ν_{OH} in the IR spectrum of maltol vapor and of its solutions in inert solvents belongs to the stretching vibrations of the hydroxyl group involved in the intramolecular hydrogen bond. In accordance with the results of the calculations this indicates a high energy preference for the *sp*-conformer (ν_{OH} 3571 cm^{-1}).

The frequencies corresponding to the region of 1750-1600 cm^{-1} in the calculated spectrum of the *ap*-conformer of maltol **1b** have three types of vibrations of different intensity. Among them the highest frequency (1741 cm^{-1}) is given by stretching vibration of its free carbonyl group, slightly mixed with the deformation vibration of the C–H bond of the heterocycle and the stretching vibration of the C=C bond. The lower frequencies (1679 and 1636 cm^{-1}) correspond to mixed vibrations, i.e., the C=C stretching and C–H and O–H deformation vibrations (Table 2). Such order of variation in the frequencies of the vibrations is typical of α- and γ-pyrones and their derivatives with a free carbonyl group [13, 14]. According to the data from the vibrational spectra, the highest intensity is characteristic of the most high-frequency vibration in the theoretical spectrum of conformer **1b**. In the *sp*-conformer **1a** of maltol the frequencies are in a different order, and its high-frequency vibration (1723 cm^{-1}) is characterized, conversely, by low intensity. It belongs to the deformation vibrations Δ_{OH} with a small contribution from the C=C stretching vibration. The next strongest vibration (1699 cm^{-1}) on the energy scale is mixed, i.e., mostly the C=O stretching vibration, the CH deformation vibration, and to a small degree the C=C stretching vibration. The third vibration at 1620 cm^{-1} with low intensity is also mixed: C=C stretching and CH deformation (Table 2). In the IR spectra of maltol vapor and its solutions in inert solvents ($CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$), recorded under conditions of weak self-condensation, three absorption bands are observed in the above-mentioned range (Fig. 3). The strongest is an intermediate band with a maximum in the region of 1630-1660 cm^{-1}. The first and third absorption bands with maxima at ~1675 and ~1570 cm^{-1} have low peak intensity (Fig. 3, curves 1 and 2). Thus, the results of the experiment agree with the results from calculation of the vibrational spectrum of conformer **1a**. This shows that the most high-frequency in the above-mentioned region of the spectrum of maltol is due to the deformation vibrations of the COH fragment in the *sp*-conformer of its molecule. The nature of the band is confirmed by comparison of the spectra of an aqueous solution (D_2O) of maltol and its solution containing sodium methoxide (Fig. 3, curves 3 and 4).

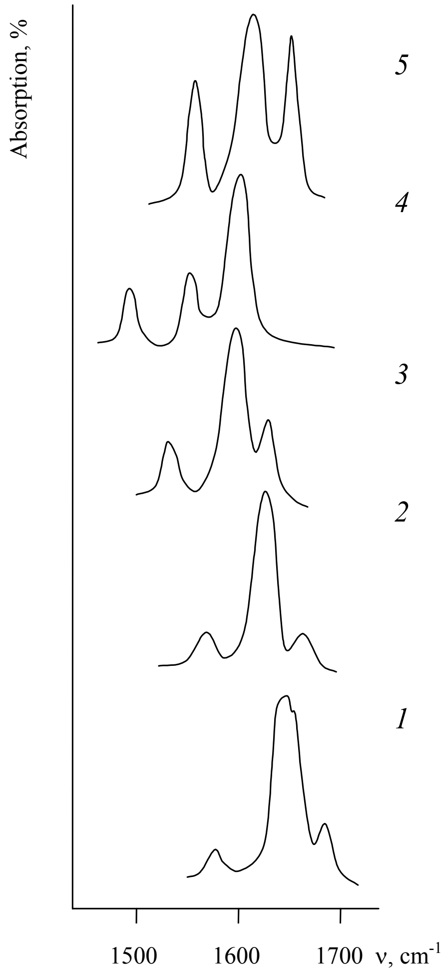

Fig. 3. The IR spectra of maltol in the region of 1750-1450 cm^{-1}. Vapor at 470 K (1). Solutions (c = 0.02 M, 298 K): in dichloroethane (2), in D_2O (3), and in D_2O with an excess of NaOMe (4). Tablet with KBr (5).

The high-frequency band of maltol (D_2O) has a maximum at 1632 cm^{-1}. It disappears completely in the spectrum of the anion (D_2O, NaOMe). In the transition from the neutral molecule ($\nu_{C=O}$ 1600 cm^{-1}, D_2O) to its anion the absorption band of the carbonyl group retains its position ($\nu_{C=O}$ 1605 cm^{-1}, D_2O, NaOMe). Here the most low-frequency band (1535 cm^{-1}) is split into two (1560 and 1496 cm^{-1}) (Fig. 3, curve 4). Thus, the bands observed in the region of frequencies for the C=O and C=C bonds differ in nature from the bands characteristic of conformer **1b** and of α- and γ-pyrones with a free carbonyl group. The decrease in the $\nu_{C=O}$ frequency of conformer **1a** compared with the frequency of conformer **1b** and α- and γ-pyrones results from participation of the carbonyl group of the maltol in intramolecular hydrogen bond formation.

Maltol Dimers. By virtue of the fact that opening of the hydrogen-bonded ring of maltol requires large expenditures of energy the dimeric forms of this compound can only be formed with the participation of the *sp*-conformer of its molecule (Fig. 2). According to the data from X-ray crystallographic analysis [7], the symmetrical dimer **1c** is formed through two intermolecular hydrogen bond of the same type OH···O=C. The dimer **1d** is a fragment of a second polymorphous form [7], formed by means of one OH···O=C bond. Both dimers are conformational isomers with mutual *sp* and *ap* orientation of the intramolecular H···O bonds.

The energy of formation of the H complexes **1c** and **1d** (Fig. 2), the subunits **A** and **B** of which are the *sp*-conformer, was determined as the difference between the total energy of the dimer and twice the energy of the monomer. The obtained values demonstrate the higher (by 9.84 kJ/mol) energy stability of dimer **1c**. We note that the structure of the dimer **1d** in the isolated state, as also in the solid state, is determined by the presence of the additional CH···O=C hydrogen bond in this compound (Fig. 2). The calculated distance between the heavy atoms C(5)···O(2) is ~0.08 Å shorter than the distance in the crystal (Table 1).

The nonbonding O···O and H···O distances between the subunits of both isomers obtained during the calculations are shorter than the values measured in the crystal (Table 1). Both in the isolated state and in the crystal they are shorter in the dimer **1c**, indicating that its intermolecular hydrogen bonds have greater strength. This dimer has C_S symmetry and is formed by two three-center bifurcated hydrogen bonds (Fig. 2). The appearance of strong intermolecular H bonds (1.663 Å) in it leads to sharp weakening of the intramolecular

TABLE 2. The Frequencies of the Vibrations in the Region of 4000-1500 cm^{-1} for the Conformers of Maltol and its Dimers

Assignment	IR spectrum, cm^{-1}*				IR, cm^{-1} (gas 470 K)
	1a	**1b**	**1c**	**1d**	
ν_{OH}	3571 (83)	3788 (28)		3585 (81)	3404 s.
ν_{OH}				3445 (1394)	3304 w.
ν_{OH}			3350 (3950)		3220 w.
ν_{OH}			3318 (64)		
$\nu_{C=O}$, δ_{CH}		1741 (403)			
δ_{OH}, $\nu_{C=C}$	1723 (28)			1717 (38)	1684 w.
$\nu_{C=O}$, δ_{CH}, $\nu_{C=C}$, δ_{OH}	1699 (435)			1696 (629)	1658 vs.
$\nu_{C=C}$, δ_{CH}, δ_{OH}		1679 (54)			
$\nu_{C=C}$, $\nu_{C=O}$, δ_{OH}			1688 (767) 1688 (50)	1693 (65)	
$\nu_{C=O}$, δ_{CH}, $\nu_{C=C}$, δ_{OH}			1675 (713) 1672 (1)	1674 (583)	
$\nu_{C=C}$, δ_{CH}, δ_{OH}		1636 (18)			
$\nu_{C=C}$, δ_{CH}, δ_{OH}, $\nu_{C=O}$	1620 (1)		1618 (1) 1617 (79)	1622 (12) 1610 (6)	1570 w.

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* The IR spectrum, calculated by the B3LYP/6-311G* method (the intensities of the vibrations are given in parentheses).

H bonds. The nonbonding H···O bond in the equivalent subunits **A** and **B** of this dimer is elongated by ~0.5 Å compared with the bond in the free monomer. As a result of this the hydroxy group is rotated by 33° in relation to the plane of the monomer, while the planes of the heterocycle are folded in relation to each other by 59°. The O(1)**A**H(1)**A**···O(2)**B** bond angle (165°) in the three-center bridge of the dimer **1c** tends toward the value characteristic of the complexes with a two-center hydrogen bond. In spite of the weakening of the intramolecular hydrogen bonds (the intramolecular component of the bifurcated H bond) in this dimer the π-electronic system of the *sp*-conformer does not undergo the changes that occur during the conformational *sp* → *ap* transition of maltol. According to the calculations, the lengths of the valence bonds of the heterocycle in the subunits of dimer (**1c**) hardly change at all in comparison with the lengths of those in the free *sp* conformer. This is a specific feature of the three-center complex, due to the transmission of the effect from the intramolecular to the intermolecular component of the bifurcated hydrogen bond.

Both subunits (**A** and **B**) of the second dimer **1d** with the longer (1.847 Å) and, consequently, weaker intermolecular OH···O=C hydrogen bond than in dimer **1c** and a comparatively weak CH···O=C bond lie in one plane. In comparison with the free *sp* conformer in the hydrogen-bonded ring of its fragment **A** the nonbonding O···H distance is increased by ~0.3 Å on account of the appearance of the intermolecular H bond, remaining ~0.2 Å smaller than the sum of the van der Waals radii. According to the calculations the O(1)–H(1)···O(2) bond angle in the three-center bridge amounts to 145°. Its value almost coincides with the X-ray crystallographic data and is 20° smaller than in dimer **1c**. Together with the greater length of the intermolecular OH···O bond this indicates greater stability for the intramolecular component of the given bifurcated H bond compared with dimer **1c**. The conclusions regarding the character of the three-center bifurcated hydrogen bonds in dimers **1c**,**d** can also be extended to the two polymorphic forms of crystalline maltol.

Analysis of the calculated vibrational spectrum of dimer **1d** (Table 2) showed that the frequency of the stretching vibration of the OH group participating only in the intramolecular H bond (fragment **B**) is slightly higher (by 14 cm^{-1}) than the value corresponding to the free conformer **1a**. The weakening of this intramolecular H bond results from the involvement of the oxygen atom of the C=O group in a three-center complex. On the other hand, the formation of the bifurcated hydrogen bond by means of the hydrogen atom of the hydroxyl group in subunit **A** of the given dimer leads to a decrease of 126 cm^{-1} in the ν_{OH} frequency compared with the free *sp*-conformer. This indicates higher stability for the intermolecular component of the three-center H bond.

By virtue of the symmetrical structure of dimer **1c** all the vibrations of its bonds are doubly degenerate. The strong intermolecular hydrogen bonds of **1c** give rise to a larger decrease ($\Delta\nu$ 221 and 253 cm^{-1}) in the frequency of the OH stretching vibrations than in dimer **1d**.

The vibrations in the region characteristic of the carbonyl and carbon–carbon double bonds of both dimers become more complex in nature than in the free *sp*-conformer (Table 2). In this connection theoretical data concerning the change of the ν_{OH} frequencies during dimerization were mainly used as basis for further analysis.

In the IR spectra of maltol vapor at 400-410 K, together with the band at ν_{OH} 3404 cm^{-1} corresponding to the absorption of the free *sp*-conformer, two other bands were recorded, i.e., a broad low-intensity band with a maximum at 3270-3280 cm^{-1} and a strong band centered at 3180 cm^{-1} (Fig. 4, curve 1). Their low-frequency shift in relation to the absorption band of the conformer **1a** amounts to ~130 and 220 cm^{-1}, which agrees well with data from the vibrational calculation of the isolated **1d** ($\Delta\nu_{OH}$ 126 cm^{-1}) and **1c** ($\Delta\nu_{OH}$ 221 cm^{-1}) dimers of maltol. If the temperature is increased to 430 K the intensity of the low-frequency band, corresponding to the energetically more favorable dimer **1c**, decreases while the relative intensity of the absorption band (3294 cm^{-1}) of dimer **1d** on the other hand increases. In the spectrum at 470 K (Fig. 4, curve 2) a strong absorption band is observed for the OH group of the free molecule of maltol, while the absorption bands of its dimers become very weak.

In the spectra of a solution of maltol in polar dichloroethane at 298 K (fig. 4, curves 3-5), in addition to the absorption band of the *sp*-conformer, there is an absorption band for the dimer **1d** (3250 cm^{-1}), shifted toward lower frequencies in relation to the spectrum of the vapor. Its relative peak intensity is increased with increase in the concentration of the solution and with decrease in temperature with a simultaneous decrease in the intensity of the high-frequency band on account of displacement of the equilibrium toward the dimer (Fig. 4, curves 4, 5). In addition to these two clearly defined bands, the spectrum of the solution of maltol in dichloroethane at 298 K contains three weaker bands. One of them has a maximum at ~3200 cm^{-1}. The second appears in the form of a shoulder at ~3280 cm^{-1} on the high-frequency wing of the band corresponding to dimer **1d**. The third creates an inflection on the low-frequency slope of the absorption band of the monomer (Fig. 4, curve 3). The relative intensity of the minor components does not change with increase in the concentration of the solution. Decrease of temperature is accompanied by an increase in the intensity of the band (~3280 cm^{-1}) adjacent to the band of the dimer (**1d**) and by the disappearance of the most low-frequency band (~3200 cm^{-1}) as early as 263 K. The position of the latter gives reason to assign it to the dimer **1c**. In addition, resonance-enhanced Fermi bands, due to overtones or composite tones of the stretching vibrations of the C=O and C=C bonds and the deformation vibrations of the COH fragment, can appear in the frequency region of 3140-3340 cm^{-1}.

In order to determine the nature of the minor bands we studied the spectrum of partially deuterated maltol in the region of 2300-2600 cm^{-1} (the OF:OH ratio was ~1:1). In the spectrum of its vapor (470 K) absorption bands with maxima at 2526 and 2418 cm^{-1} correspond to the stretching vibrations of the O–D bonds of the *sp*-conformer and the dimer **1d** (Fig. 4b). The ν_{OH}/ν_{OF} ratio amounts to 1.347 for the monomer and 1.362 for the dimer **1d**. In the spectrum of a solution in dichloroethane (298 K) (Fig. 4, curve 7) the frequencies at the maximum of the observed bands are 2518 and 2430 cm^{-1}. Here the ν_{OH}/ν_{OF} ratios are as follows: 1.348 for the monomer, 1.337 for the dimer. Bands close to the maximum of the band of the dimer **1d** are not observed in

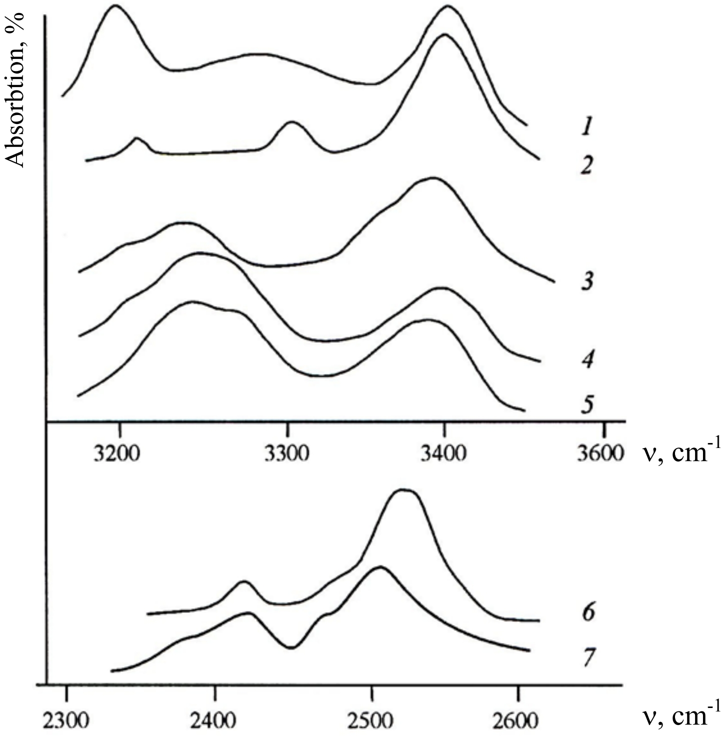

Fig. 4. The IR spectra of maltol and OD-maltol in the region of 3600-2300 cm^{-1}.
Maltol vapor: 410 (1), 470 K (2). Solutions of maltol in dichloroethane: c = 0.06 M, 298 K (3);
c = 0.15 M, 298 K (4); c = 0.06 M, 235 K (5). Vapor of OD-maltol: 470 K (6).
Solution of OD-maltol in dichloroethane: c = 0.06 M, 298 K (7).

these spectra. Consequently, the band with a maximum at ~3275 cm^{-1} in the spectrum of a solution of maltol in dichloroethane is due to one of the overtones. This is most likely an overtone of the stretching vibration of the C=O bond (1630 cm^{-1}). On the other hand, the absorption on the long-wave slope of the band for the vibrations of the O–D bond of the *sp*-conformer becomes clearly defined. In the spectrum of the original maltol it corresponds to the inflection at ~3340 cm^{-1}, which may be due to a Δ_{OH} overtone (1668 cm^{-1}). The band assigned to the dimer **1c** in the spectrum of the original maltol is also observed in the spectrum of the deuterated derivative. It is shifted toward higher frequencies in relation to the dimer **1d** and appears in the form of a shoulder at ~2480 cm^{-1}.

Thus, the investigation has shown that due to the strong intermolecular OH···O=C hydrogen bonds the dimeric forms of maltol exist not only in its solid state of aggregation but also in the gas phase and in dichloroethane solution. Their structure is due to the formation of one or two bifurcated hydrogen bonds. In the symmetrical dimer **1c** the intramolecular component of such a three-center H bond is so weakened that the nature of the intermolecular interaction approximates to two-center. The higher dipole moment (Fig. 2) of the second dimer **1d** leads to increase in nonspecific solvation and increases the population of its state in the solution in comparison with dimer **1c**.

The assignment of the frequencies in the IR spectrum of crystalline maltol to the vibrations of its bonds in [15, 16] was based on data relating to γ-pyrones and the metal chelates of kojic acid [13, 17]. The investigators paid greatest attention to the region of the absorption of carbonyl groups and carbon–carbon double bonds. The strong high-frequency band with a maximum at ~1660 cm^{-1} (Fig. 3, curve 5) was assigned to the stretching vibrations of the C=O group. The decrease of its frequency compared with γ-pyrones and also the low value of ν_{OH} (~3200 cm^{-1}) in this spectrum were explained by the presence of an OH···O=C intramolecular hydrogen bond. However, there are indications of strong mixing of the vibrations of the C=O and C=C bonds in compounds of such a type, which hinders the analysis [18]. In addition, there is an assignment of the high-frequency band in the region of 1700-1550 cm^{-1} in the spectrum of 2,6-dimethyl-γ-pyrone to the vibrations of the C=C bonds [19]. From the combination of data obtained as a result of the present investigation it becomes clear that the low value of ν_{OH} in the spectrum of maltol in the solid phase is due to the involvement of its hydroxy groups in three-center bifurcated hydrogen bonds, on account of which two types of self-associates are formed. The high-frequency band (1666 cm^{-1}) in the spectrum of maltol (Fig. 3, curve 5) is due to the deformation vibrations of the hydroxy groups in its polyassociate, a fragment of which is the dimer **1d** (Table 2). The band characterized by the highest intensity and half-width with a maximum at 1626 cm^{-1} corresponds to the superimposition of the absorption bands of both polymorphic forms of maltol. The vibrations corresponding to them have a preferred contribution from the C=O and C=C bonds. Finally, the absorption with a maximum at 1564 cm^{-1} belongs to vibrations with a preferred contribution from the carbon–carbon double bonds of these forms.

EXPERIMENTAL

3-Hydroxy-2-methyl-4-pyrone (maltol) **1** was isolated from the needles of the Siberian fir (*Abies sibirica* Ledeb.) [20]. Its OH groups were deuterated by repeated boiling of a solution of the compound in D_2O. The IR spectra of the maltol vapor at 400-480 K and of its solutions were obtained on a Specord IR-75 spectrophotometer with a thermostated cuvette.

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