Tautomeric transformations of arylidenebarbiturates in solutions

G. A. Gavrilova, N. N. Chipanina,* A. F. Gogotov, and V. K. Turchaninov

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: 007 (395 2) 35 6046

IR and UV spectroscopy and quantum chemistry were employed to investigate the structure of arylidenebarbiturates able to undergo tautomeric transformations. The composition of tautomeric mixtures depends on the properties of the solvent and on the concentrations of the solutions.

Key words: arylidenebarbiturates, tautomerism, IR spectra, UV spectra, quantum-chemical calculations.

Arylidenebarbiturates resulting from condensation of barbituric acid (BA) with aldehydes like vanilline[1] can undergo tautomeric transformations in solutions in aqueous dioxane at various pH (4—13). In the case of 4-hydroxy-3-methoxybenzylidenebarbituric acid (**1**), these transformations occur presumably according to Scheme 1.

For 4-hydroxy-3-methoxybenzylidenebarbituric acid, the existence of several more tautomeric forms (**4**—**9**) can be theoretically assumed.

In this work, IR and UV spectroscopy and quantum-chemical calculations were used to study the structure of arylidenebarbiturates in solution in more detail; in addition, the data obtained for related compounds (**10**—**12**) under similar conditions were analyzed.

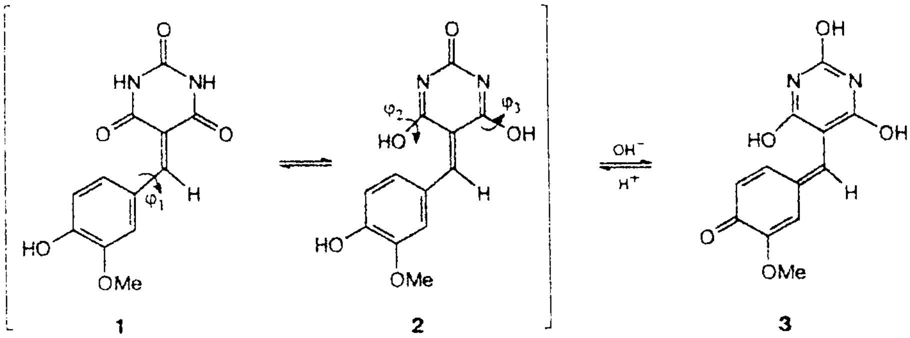
Since compound **10** and its *O*-methyl ether **11** form no tautomers with quinoid structures, the total number of their tautomers is smaller than that in the case of isomeric compounds **1** and **12**, and this simplifies somewhat the situation.

The IR spectra of (hydroxy)methoxy- and dimethoxybenzylidenebarbituric acids (HMB and DMB) were interpreted taking into account the corresponding data for BA, whose structure and vibrational spectra in various aggregative states have been studied fairly comprehensively. For example, according to X-ray diffraction data,[2] anhydrous BA exists in the crystalline state as the triketo-form. The triketo-form is also characteristic of solutions in low-polarity aprotic solvents.[3,4] Quantum-chemical calculations in the AM1 approximation have shown that the triketo-form is also the most stable state for free BA molecules.[5] In the gaseous state, BA exists as a mixture of the triketo-form and the mono-, di-, and trihydroxy-forms, the proportion of the triketo-form being ~95%.[6]

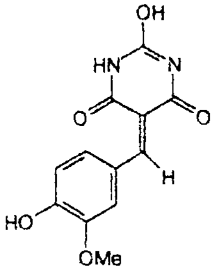
Experimental

Arylidenebarbiturates were obtained by mixing equimolar amounts of an aromatic aldehyde and BA in a minimum quantity of a solvent (water in the case of vanillines or aqueous dioxane in the case of veratric aldehyde). The condensation was accompanied by the appearance of a more intense yellow color of the solution and resulted in the formation of a colored precipitate. To intensify the reaction, in some cases the mixture was brought to boiling for a short period or several drops

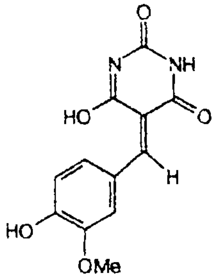
Scheme 1



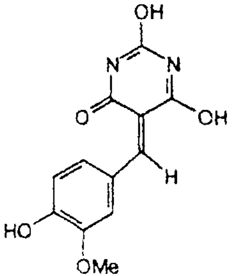
Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 769—775, April, 1997.



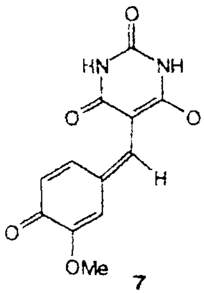
4



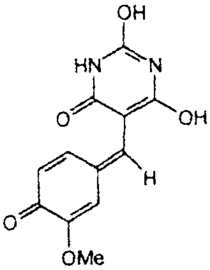
5



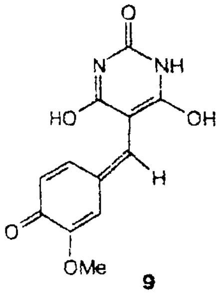
6



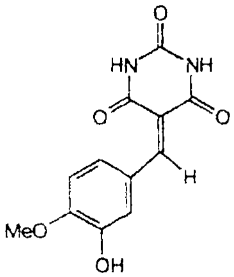
7



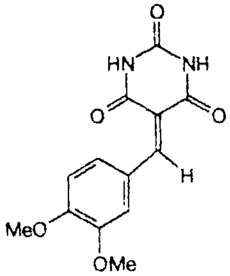
8



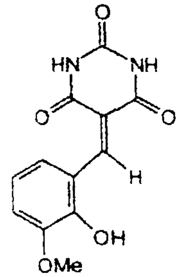
9



10



11



12

of 0.1 *M* HCl were added as a catalyst. The yields of the condensation products were nearly quantitative, and their purities were determined by the GC/MS method.

IR spectra were recorded using a Specord 75-IR spectrometer, and UV spectra were obtained using a Specord UV-VIS spectrophotometer; the concentrations of solutions were $1 \cdot 10^{-1}$—10^{-3} mol L^{-1}. The UV spectra were recorded in the same solvents as the IR spectra.

Results and Discussion

The IR spectra of HMB and DMB were analyzed mostly in the carbonyl absorption region (1500—1800 cm^{-1}). A well-resolved system of bands with maxima at 1740—1670 cm^{-1} is observed in dioxane (Table 1). The triketo-form of BA (a solution in diethyl ether) is characterized by similar absorption with close νC=O frequencies equal to 1755, 1740, and 1710 cm^{-1}.[3,4]

Joint analysis of the characteristics of the IR and Raman spectra of BA and some of its derivatives, using the calculations of frequencies and modes of normal vibrations for the triketo- and monohydroxy-forms of BA, permitted the highest-frequency band (1755 cm^{-1}) to be assigned to the νC(2)O stretching vibrations of the triketo-form.[3,4]

The two other bands at 1740 and 1710 cm^{-1} correspond to the asymmetrical and symmetrical vibrations of the C(4)=O and C(6)=O groups. In the IR spectra of the tetradeutero- and 5,5-dichlorobarbituric acids, absorption bands corresponding to the C=O groups of the triketo-form are located at 1740, 1710, and 1631 cm^{-1} and at 1758, 1717, and 1696 cm^{-1}, respectively.[3] The νC=O frequencies of these BA derivatives are fairly close to those of HMB and DMB, which gives grounds to believe that these compounds exist in dioxane as the triketo-forms. The fact that the νC=O values for the tetradeutero- and dichloro-derivatives and HMB are lower than those for BA is apparently due to kinematic factors and to the effect of the medium (see Table 1). This assignment is also supported by several other facts. First, the IR spectra of solutions of HMB and DMB in dioxane exhibit no bands associated with vibrations of C=N bonds (the band at 1550—1580 cm^{-1} is due to the δNH vibrations of the amide fragments). Second, the IR spectra in dioxane contain a doublet of bands corre-

Table 1. Vibration frequencies of the carbonyl groups of tautomers of HMB and DMB (ν/cm^{-1})

Compound	Medium	Triketo-form			Dihydroxy-form	
		ν_1	ν_2	ν_3	ν_1	ν_2
12	Dioxane	1725	1705	1675	—	—
	D_2O	1711	^{a}	^{a}	1686	1668
	Dioxane—D_2O (pH = 7)	1694	^{a}	^{a}	1669	1646
	The same (pH = 10)	1693	^{a}	^{a}	1671	1642
	» » (pH = 12)	—	—	—	1671	1644
10	Dioxane	1741	1707	1677	—	—
	Dioxane—D_2O (pH = 7)	1732	^{a}	^{a}	1690	1674
	The same (pH = 9)	1728	^{a}	^{a}	1687	1669
		1706	^{a}	^{a}		
	» » (pH = 12)	1729	^{a}	^{a}	1686	1669
		1706	^{a}	^{a}		
11	Dioxane (pK_{BH^+} = −2.92)^b	1740	1705	1677	—	—
	The same (pK_{BH^+} = −2.08)	1742	^{c}	^{c}	—	—
	DMSO (pK_{BH^+} = −1.04)	1736	1700	1680	—	—
	Pyridine (pK_{BH^+} = 5.25)	1734	1702	1673	—	—
	EtOH	1742	^{a}	^{a}	1695	1655
	D_2O	1744	^{a}	^{a}	1696	1660
	Dioxane—D_2O (pH = 7)	1740	^{a}	^{a}	1690	1660
		1729	—	—		
	The same (pH = 8)	1740	^{a}	^{a}	1686	1660
		1725				
	» » (pH = 10)	1726	^{a}	^{a}	1686	1668
	» » (pH = 12)	1725	^{a}	^{a}	1686	1670
1	Dioxane (pK_{BH^+} = −2.92)	1740	1704	1676	—	—
	Tetrahydrofuran (pK_{BH^+} = −2.08)	1742	1702	1677	—	—
	MeCN	1744	1702	1680	—	—
	DMSO (pK_{BH^+} = −1.04)	1735	1700	1680	—	—
	Pyridine (pK_{BH^+} = 5.25)	1732	1700	1670	—	—
	Et_3N (pK_{BH^+} = 10.74)	1727	1695	1660	—	—
		1750				
	Dioxane—D_2O (pH = 7)	1723	^{a}	^{a}	1684	1664
	The same (pH = 10)	1720	^{a}	^{a}	1680	1660
	» » (pH = 12)	1704	^{a}	^{a}	1688	—

[a] Overlaps with the spectrum of the hydroxy-form. [b] For pK_{BH^+}, see Ref. 7. [c] The determination of the exact positions of the bands is hampered by the limited solubility of the substance; very weak νC=O bands in the IR spectra.

sponding to the NH stretching vibrations (**10**, 3200 and 3080 cm^{-1}; **1**, 3170 and 3080 cm^{-1}; **11**, 3120 and 3090 cm^{-1}; **12**, 3190 and 3100 cm^{-1}). The second band in the doublet is less intense. In the NH stretching regions of the IR and Raman spectra of the triketo-form of BA and its derivatives, two other bands, at 3200 and 3080 cm^{-1}, are also observed. The intensity of the former band is somewhat higher than that of the latter.[3,4] In keeping with the structure of the triketo-form, the spectra of HMB in dioxane also contain a doublet of bands at ~3560 and 3500 cm^{-1} corresponding to the νOH vibrations of the hydroxyl group in the aromatic fragment. The vibration frequencies in this region virtually coincide with those peculiar, for example, to vanilline (νOH = 3550 and 3490 cm^{-1}).

The presence of two absorption bands corresponding to the NH bonds in the IR spectrum of BA can be interpreted in different ways. In our opinion, the most plausible explanation is the view according to which two types of bonds are present in the triketo-form of BA: the C(2)=O group interacts with the H—N< fragment yielding dimers; the C(4)=O...HN hydrogen bonds join these dimers into ribbons.[3] For the solid phase, this viewpoint has been confirmed by X-ray diffraction data.[2] In terms of this model, the band at 3200 cm^{-1} in the IR spectrum of BA was assigned to the νNH vibrations in the NH...OC(2) fragment, and the band at 3080 cm^{-1} was attributed to vibrations of the NH groups bound to C(4)=O through hydrogen bonds.

The replacement of dioxane by tetrahydrofuran, acetonitrile, dimethyl sulfoxide, pyridine, or triethylamine has virtually no effect on the absorption profile of the carbonyl groups in **1** and **11** and does not lead to any new absorption in the 1800—1500 cm^{-1} region. This indicates that in polar aprotic media, these compounds also exist predominantly as the triketo-forms. At the

Table 2. UV spectra of HMB and DMB

Compound	Medium	Electron transition (ν/cm^{-1})				
			Triketo-form			
1	Dioxane	25500	30000 sh	39000 sh	40500	45500
	THF	25400	30000 sh			
	Acetonitrile	25400	30000 sh	40000 sh	41000	43000—46000
	Pyridine	24000	28000 sh			
	Water	24200			^{a}	
	Ethanol	24600	30000 sh	39000 sh	40000 sh	43000
11	Dioxane	25400	30000 sh	39000	40000	43000
	THF	25500	30000 sh			
	Acetonitrile	25400	30000 sh	39000—41000		43400
	Water	25500 sh		^{a}		
	Ethanol	25000		^{a}		
10	Dioxane	25600	29000 sh	39000	41000 sh	45000
	Water	24000—26000			^{a}	
12	Dioxane	29000	35000 sh	37000	>43000	>48000
	Water	29000			^{a}	
			Hydroxy-form			
1	Water	32500	36000 sh	38800	43500	43500
11	D_2O	32000	36000 sh	38400	44000	44000
	Ethanol	32300	36000 sh	39800	43500	43500
10	Water	32000 sh	35000 sh	38000	43800	43800
12	Water	35000 sh		38000	45000 sh	47000
11	Aqueous dioxane (pH = 7)	31600	36000 sh	38200	43500	43500
	The same (pH = 8)	32200	36000 sh	38200	43400	43400
	» » (pH = 10)	32200	36000 sh	37400	43400	43400
	» » (pH = 12)	32000	36000 sh	37200	43300	43300
10	Aqueous dioxane (pH = 7)	^{b}	36000 sh	38200	43400	43400
	The same (pH = 9)	31000 sh^b	36000 sh	38000	43400	43400
	» » (pH = 12)	31500	36000 sh	37350	43400	43400
12	Aqueous dioxane (pH = 7)	34500 sh		38000	44300 sh	~47000
	The same (pH = 12)	34500		38500	45300	45300
			Quinoid form			
1	Water^c	20800		^{a,b}		
	Ethanol	21000		^{b}		
	Aqueous dioxane (pH = 12)	21000		^{a}		
12	Water	23000 sh		^{a,b}		
	Aqueous dioxane^{c,d} (pH = 12)	23000 sh		^{a,b}		

[a] Overlaps with the spectrum of the hydroxy-form. [b] Overlaps with the set of bands due to the triketo-form.
[c] Low concentrations. [d] At high concentrations, an absorption band at ~20000 cm^{-1} that disappears with time is observed.

same time, as the basicity of the solvent increases, the C(2)=O vibration frequency regularly decreases (see Table 1). This is due to the increase in the strength of the hydrogen bonds involving the NH groups of the amide fragments of the molecules and, correspondingly, to the decrease in the strength of their C=O bonds. In the spectrum recorded in aqueous dioxane containing a small amount of alkali, the high-frequency band corresponding to vibrations of the C(2)=O bond in **11** acquires a doublet structure, and the ratio of its components depends on the properties of the medium: the higher the basicity of the medium, the larger the relative intensity of its low-frequency component. This implies that in highly basic polar media, the triketo-forms of **1** and **11** can exist as ensembles of two types of complexes, namely, dimers bound through hydrogen bonds involving one of the NH groups and monomers in which two NH groups are involved in the interaction with the solvent or NaOD; the latter results in even a larger decrease in the νC=O frequency. The dimer is responsible for the high-frequency component of the doublet, while the monomer accounts for its low-frequency component.

The UV spectra of the triketo-forms of HMB are shown in Fig. 1, *a,b*; the frequencies are listed in Table 2. The spectra consist of two sets of absorption bands in the 44000—36000 and 36000—22000 cm^{-1} regions. The Franck—Condon profiles of the bands depend only slightly on the polarity of the aprotic solvent used and are slightly perturbed when the hydroxyl group in **1** (**10**) is replaced by a methoxy group (**11**). The transition from *para*- to *meta*-isomers also has no effect on these bands. However, the spectra of the 4′- and 2′-hydroxy-isomers (**1** and **12**) are markedly dissimilar. In fact, the most intense component of the long-wavelength set of bands shifts to the blue region by more than 3500 cm^{-1} and its relative intensity sharply decreases. The low-intensity component of the first group of bands in the UV spectrum of 2-HMB (**12**) is displaced to the blue region to even a greater extent. As a result, this component is quite clearly manifested. Conversely, the short-wavelength set of bands undergoes a bathochromic shift in the case of the *ortho*-isomer (**12**). The substantial shifts of the longest-wavelength absorption band corresponding to the triketo-form of HMB following the introduction of substituents to the atom that participates in the formation of the interfragment single bond and the sharp decrease in the intensity of this band indicate that it corresponds in its nature to a K-band and its energetic position depends on the molecular conformation.

The UV spectrum of the triketo-form of **1**, calculated in the AM1 (KB) approximation (Table 3), is in satisfactory agreement with the experimental results (correlation with a slope tangent close to unity). The results of calculations imply that (a) the lowest-energy π—π*-transition in **1** actually involves intramolecular charge transfer from the aromatic fragment to the barbituric fragment; (b) the next transition must be interpreted as a perturbed benzene transition; (c) both low-energy transitions should actually be quite sensitive to the magnitude of the torsional angle. As the molecule becomes more non-planar, they undergo substantial hypsochromic shifts (see Table 3). It should be noted that the potential curve for the internal rotation in free molecule **1** existing in the triketo-form with torsional angles φ_1 ranging from 30 to 60° is a relatively smooth well with a minimum near 43°. Probably, the medium somewhat flattens the molecules of this compound,

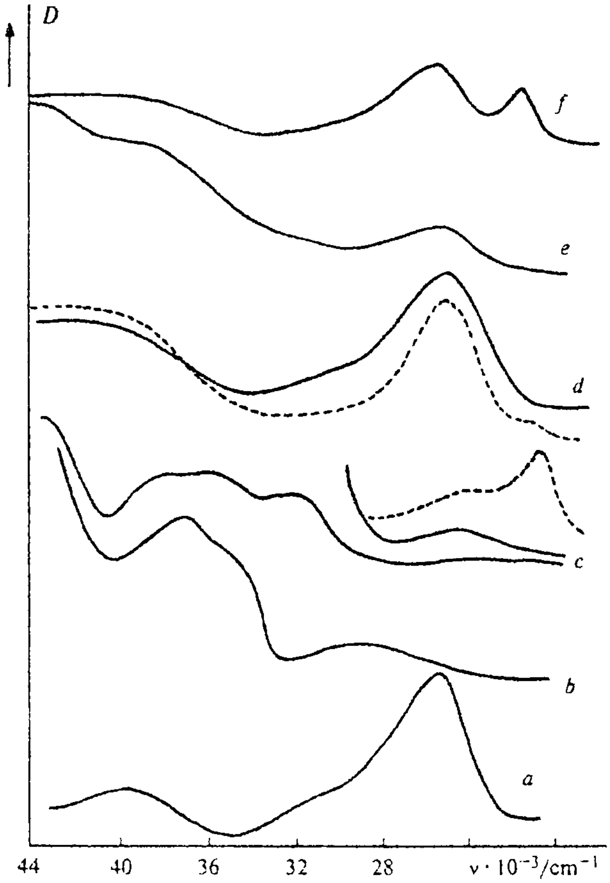


Fig. 1. UV spectra of HMB and DMB: **1** in dioxane (*a*); **12** in dioxane (*b*); **1** in water (*c*) and in ethanol (*d*), the solid line corresponds to a saturated solution, and the dashed line corresponds to a dilute solution; **11** in ethanol (*e*); **1** in an aqueous alkali—dioxane mixture (*f*), pH = 10.

Table 3. Electron transitions of **1** calculated in the AM1 (KB) approximation

Tautomer [$\Delta_f H^0$ /kcal mol^{-1}]	E/eV	Type of transition	Tautomer [$\Delta_f H^0$ /kcal mol^{-1}]	E/eV	Type of transition
1,	3.494[a]	π→π*	**1**,	3.613[a]	π→π*
φ_1 = 30°	3.876[b]	π→π*	φ_1 = 43°	3.924[b]	π→π*
[−137.57]	4.630	π→π*	[−137.80]	4.709	π→π*
	4.990	π→π*		5.041	π→π*
	5.800	π→π*		5.739	π→π*
	5.191	n→π*		5.098	n→π*
	5.537	n→π*		5.165	n→π*
1,	3.732	π→π*	**4**	3.528[a]	π→π*
φ_1 = 60°	4.006[b]	π→π*	[−118.59]	3.786[b]	π→π*
[−137.31]	4.598	π→π*		4.517	π→π*
	5.044	π→π*		5.007	π→π*
	5.866	π→π*		5.149	π→π*
	5.523	n→π*		4.002	n→π*
	5.595	n→π*		4.814	n→π*
5	3.523[a]	π→π*	**6**	3.459[a]	π→π*
[−121.69]	3.869[b]	π→π*	[−88.22]	3.802[b]	π→π*
	4.530	π→π*		4.294	π→π*
	5.108	π→π*		4.680	π→π*
	5.286	π→π*		5.085	π→π*
	4.624	n→π*		3.533	n→π*
	4.921	n→π*		4.539	n→π*
2,	3.473	π→π*	**2**,	3.596	π→π*
φ_2 = 0°,	3.931[b]	π→π*	φ_2 = 180°,	3.832	π→π*
φ_3 = 0°	4.471	π→π*	φ_3 = 0°	4.535	π→π*
[−102.34]	4.862	π→π*	[−102.34]	4.808	π→π*
	5.057	π→π*		4.919	π→π*
	3.560	n→π*		3.429	n→π*
	4.921	n→π*			

[a] Transition with intramolecular charge distribution. [b] Perturbed benzene transition.

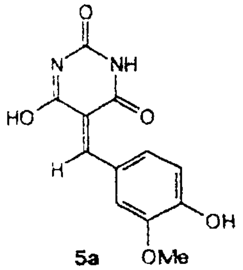
since the spectrum calculated for a smaller torsional angle (30°) is in better agreement with the experimental results for the magnitude of energy transitions.

The calculations performed also indicate that the triketo-form is theoretically the most stable among all the possible tautomeric forms of **1**.

In proton-donating media, especially in aqueous solutions, the UV absorption spectra of HMB and DMB substantially change. The long-wavelength set of bands undergoes a hypsochromic shift by ~6000 cm^{-1} on the average. In the short-wavelength region of the UV spectrum, two individual maxima are normally recorded in these media.

Along with the new spectra, in concentrated aqueous solutions of all three HMB as well as of DMB, there are also absorption bands due to the triketo-forms (Fig. 1, *c*, the low-intensity band in the long-wavelength region). In dilute aqueous solutions of **1**, in addition to the absorption bands mentioned above, one more absorption maximum appears in the red region of the spectrum (20800 cm^{-1}). This maximum is not detected in the case of compound **11** under the same conditions. The UV spectra of dilute solutions of compound **12**, but not of **10**, also contain additional absorption at ~23000 cm^{-1}, although it is much weaker than that in the case of compound **1**.

The UV spectra of saturated ethanolic solutions of **1**, unlike those of aqueous solutions, are completely similar to the spectrum of the triketo-form. However, at low concentrations of **1**, the spectrum contains an absorption band at about 21000 cm^{-1}, which is less pronounced than in the case of aqueous solutions (Fig. 1, *d*). The UV spectra recorded for ethanolic solutions of compound **11** do not have this band. The UV spectrum of **11** in ethanol, unlike that of **1**, is similar to the spectrum in D_2O except that the relative intensity of the absorption band corresponding to the triketo-form (Fig. 1, *e*, the band at about 25000 cm^{-1}) is much higher in the former. Empirical analysis of the typical parameters of the UV spectra recorded in hydroxyl-containing solvents makes it possible to conclude that in this case, both HMB and DMB contain at least one additional tautomer. It is clear that this is a hydroxy-form. The proportion of the hydroxy-form depends both on the chemical structure of the compound studied and on the properties of the solvent. The hypsochromic shift of the long-wavelength set of absorption bands corresponding to the new tautomer with respect to that of the triketo-form and the decrease in the intensity of its lowest-energy component indicate that the spectral changes are mostly due to a change in the molecular conformation rather than in the nature of transitions. This "geometric" requirement is fulfilled for three (two or one) tautomers, **2**, **5**, and **6**. This conclusion is supported by the results of AM1 (KB) calculations of the UV spectra of the hydroxy-forms of **1**. From these calculations, it follows that the orbital and configurational compositions of the long-wavelength electron transitions in these tautomers of **1** are approximately the same as those in the triketo-form. Among the spectra calculated for the tautomers, those calculated for the monohydroxy-form **5** and for one of the rotamers of tautomer **2** are in the best agreement with the experimental spectrum (see Tables 2 and 3). Since along with the structure shown above, the monohydroxy-form **5** can exist as its geometric isomer **5a** (which is degenerate with **5**, as shown by calculations, but is similar to the triketo-form in the nonvalence interactions), the experimental spectrum should consist of the superposition of two sets of long-wavelength bands with approximately equal intensities. Since this superposition is not observed in reality, we give preference to the dihydroxy-form **2**.



5a

The bands in the carbonyl absorption region in the IR spectrum of ethanolic solutions of **11** are broader than those in the spectrum of dioxane solutions and have equal intensities (Fig. 2, *a*). The low-frequency band is broadened to the greatest extent, and its frequency markedly decreases (~20 cm^{-1}). Conversely, the high-frequency band virtually does not shift (~2 cm^{-1}), but its intensity dramatically decreases. The "middle" band, located at 1705 cm^{-1} (in dioxane), undergoes a moderate shift to lower frequencies (~10 cm^{-1}) in an ethanolic solution. In the case of solutions in D_2O, the intensities of the bands under consideration are further redistributed. Now it is the low-frequency component that is characterized by the highest intensity. Simultaneously, this band becomes somewhat narrower. Taking into account the data obtained by UV spectroscopy, the variation of the relative intensities of the bands at ~1740, 1700, and 1660 cm^{-1} should be interpreted as resulting from variations of the proportions of the triketo- and hydroxy-forms of **11**. Since the monoenol forms of BA are characterized by frequencies below 1650 cm^{-1},[4] the doublet of bands at 1700 and 1660 cm^{-1} in the IR spectrum of **11** can be attributed only to dihydroxy-forms (**2** and **6**). An IR spectrum similar to those in ethanolic and aqueous media is also observed when **11** is dissolved in an aqueous alkali—dioxane mixture. At pH 7, the spectrum virtually coincides with that recorded in ethanol except for the doublet structure of the high-frequency band; at pH 8, it resembles the spectrum in D_2O, with the same exception. When the content of alkali in the solvent mixture is very high, the dihydroxy-forms predominate over the triketo-form. In these me-

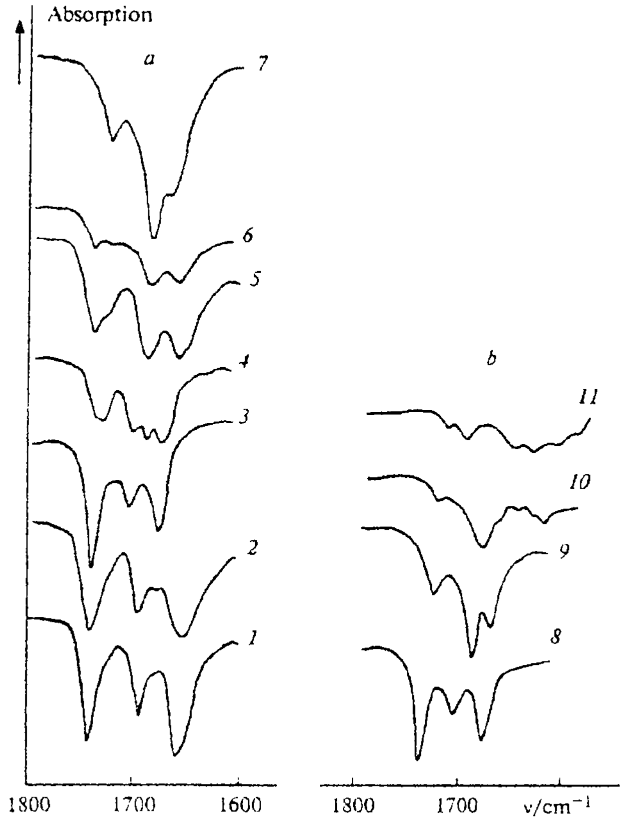


Fig. 2. IR spectra in the νC=O region of **11** (*a*) and **1** (*b*). *a*: in D_2O (*1*); in ethanol (*2*); in dioxane (*3*); in aqueous dioxane ($C_4H_8O_2$—D_2O—NaOD) (*4*—*7*) at pH = 6 (*4*); 7 (*5*); 8 (*6*); 9 (*7*). *b*: in dioxane (*8*); in aqueous dioxane ($C_4H_8O_2$—D_2O—NaOD) (*9*—*11*) at pH = 7 (*9*); 10 (*10*), 12 (*11*).

dia, they absorb at 1686 and 1670 cm^{-1}. The absorption corresponding to the triketo-form is manifested as a single band with a maximum at 1725 cm^{-1}. This indicates that the dimers have completely dissociated and that the C=O...H—N hydrogen bonds have been replaced by N—H...⁻O—D. At pH = 6, the spectrum is a clear-cut superposition of the individual spectra of the triketo-form and dihydroxy-form (see Fig. 2, *a*). Thus, in alkaline solutions, as in solutions in water or ethanol, **11** exists as an equilibrium mixture of the two above-mentioned tautomers.

The results obtained for the triketo- and hydroxy-forms of HMB in proton-donating media are qualitatively similar to those described above and are summarized in Tables 1 and 3.

The conclusion that the dihydroxy-tautomers form in this pH range, which follows from the analysis of the IR spectra, is confirmed by the UV-spectroscopy data shown in Fig. 1.

The UV spectra of alkaline solutions of **1** in aqueous dioxane exhibit an intense band with a maximum at ~21000 cm^{-1}, which has previously been observed only in dilute aqueous solutions (Fig. 1, *f*). It is absent in the case of **11** and **10**, but is observed, although with low intensity, in the UV spectrum of **12**. This combination of experimental facts makes it possible to assign this band to one of the tautomers of **1** with a quinoid structure (**7**—**9**). This assignment is confirmed by the data of IR spectroscopy, *viz.*, by the fact that the intensity of the absorption with a center of gravity near 1620 cm^{-1} that is not a part of the spectra of the triketo- and hydroxy-forms of **1** increases as the pH of the medium increases. At high pH, this absorption becomes comparable with those of the other forms (Fig. 2, *b*). The most intense bands of this absorption with maxima at 1640 and 1620 cm^{-1} are typical of molecules with quinoid structures.[8]

Thus, the results obtained by IR and UV spectroscopy imply that in aprotic media, HMB and DMB molecules exist predominantly in the triketo-forms. The results of AM1 and AM1 (KB) calculations are in full agreement with this conclusion. In proton-donating and alkaline media, an equilibrium between two types of tautomers, *viz.*, triketo- and dihydroxy-forms of the barbiturate moiety of HMB molecules, is established. In the case of compound **1**, one more tautomer is detected reliably in water and alkaline aqueous dioxane. This tautomer is characterized by a quinoid system of bonds. Unfortunately, its UV spectrum lacks necessary details, and the characteristics of the IR spectrum alone are insufficient to judge definitely the fine structure of this tautomer.

References

1. A. F. Gogotov, A. N. Zakazov, and V. A. Babkin, *Khim. Drevesiny* [*The Chemistry of Wood*], 1992, **2/3**, 44 (in Russian).
2. W. Botton, *Acta Crystallogr.*, 1963, **16**, 166.
3. N. A. Smorygo and B. A. Ivin, *Khim. Geterotsikl. Soedin.*, 1975, 1402 [*Chem. Heterocycl. Compd.*, 1975 (Engl. Transl.)].
4. N. A. Smorygo, and B. A. Ivin, *Khim. Geterotsikl. Soedin.*, 1975, 1411 [*Chem. Heterocycl. Compd.*, 1975 (Engl. Transl.)].
5. S. Millefiori and A. Millefiori, *J. Heterocycl. Chem.*, 1989, **26**, 639.
6. T. V. Soldatova, G. Ya. Kabo, A. A. Kozyro, and M. L. Frenkel', *Zh. Fiz. Khim.*, 1990, **64**, 336 [*Russ. J. Phys. Chem.*, 1990, **64** (Engl. Transl.)].
7. *Tablitsy konstant skorosti i ravnovesiya geteroliticheskikh organicheskikh reaktsii* [*Tables of the Rate and Equilibria Constants of Heterolytic Organic Reactions*] Ed. V. A. Pal'm, VINITI, Moscow, 1976, **2** (1), 704 pp.; 1977, **2** (2), 616 pp. (in Russian).
8. *Working Atlas of Infrared Spectroscopy*, Verlag Chem., Weinheim; Butterworths, London; 1972, **5**, 327 pp.

Received May 14, 1996