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Electronic Structure of π Systems: XIX.[1] Keto–Enol Tautomerism of Dihydrofurocoumarinones

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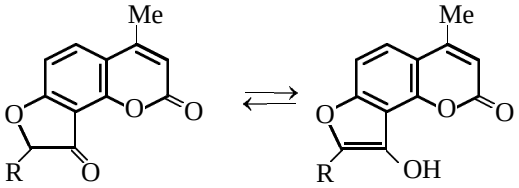
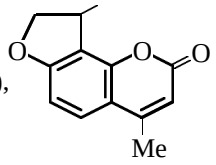
Abstract — Tautomeric transformations of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one and its 8-substituted derivatives were studied by ^{1}H NMR, electronic absorption spectroscopy, and quantum chemistry. The ^{1}H NMR spectra of these compounds in $CDCl_3$ show that they exist in the ketone form, and in more polar solvents they can pass into the enol form. By electronic absorption spectroscopy it was established that the derivatives containing electron-acceptor substituents in the 8 position of the furanone ring undergo tautomeric transformations as the composition of the solvent is varied from 100% methanol to 100% CCl_4. At the same time, the derivatives with electron-donor substituents in the same position do not show any specific alterations in the absorption spectra with solvent. Analogous pattern was observed in the enolization of substituted dihydrofurocoumarinones by acetylation: In presence of electron-donor substituents in the 8 position, no acetylation occurred, while with the compounds containing electron-acceptor substituents, the corresponding 9-acetoxy-4-methylangelicins were prepared in high yields. Calculations by the PPP/CI method of the electronic absorption spectra 4-methyldihydrofuro[2,3-*h*]coumarin-9-one showed that in polar solvents (methanol) it prefers the enol form. Data of spectral measurements were compared with results of semiempirical (MNDO, AM1, and PM3) and nonempirical quantum-chemical calculations (with 3-21G, 6-31G*, and 31G** basis sets).

Coumarins are widely distributed natural compounds. Many of coumarin derivatives exhibit biological activity. For example, furocoumarins are used in the therapy of skin deseases [2, 3]. In our previous works we developed a new method for preparing furocoumarins, based on the the Fries rearrangement of chloroacetoxycoumarins [4, 5]. The rearrangement proceeds in an unusual fashion to form dihydrofurocumarinones whose subsequent reduction and dehydration smoothly provide the corresponding furocoumarins. It was found that dihydrofurocoumarinones are sufficiently reactive. They are easily halogenated to α-halo derivatives, acylated by the carbonyl group, and undergo condensation with aldehydes and ketones, dimerization, etc. [4–7]. All the above-mentioned reactions involve both the oxygen and the carbon atoms of the dihydrofurocoumarinone ring and are underlied by keto–enol transformations.

The ketone (**Ia**) and enol (**Ib**) forms of 4-methyldihydrofuro[2,3-h]coumarin-9-one, as well as the tautomeric forms of its derivatives **II**–**VII** are presented below.



Ia–**VIIIa** **Ib**–**VIIIb**

R = H (**I**), Cl (**II**), Br (**III**), OAc (**IV**), OMe (**V**), OH (**VI**), CH=N–NHC$_6$H$_3$(NO$_2$)$_2$ (**VII**),  (**VIII**).

In this work we have studied keto–enol transformations for a series of dihydrofurocoumarinones **I**–**VIII** by means of spectral methods (^{1}H NMR and electronic absorption spectroscopy) and semiempirical (MNDO, AM1, PM3, PPP/CI) and nonempirical (3-21G, 6-31G*, and 6-31G**) calculations.

Inspite of the fact that 4-methyldihydrofuro[2,3-*h*]-coumarin-9-one (**I**), according to ^{1}H NMR data

[1] For communication XVIII, see [1].

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(in $CDCl_3$, acetone-d_6, and DMSO-d_6) exists only in the ketone form, we could detect its keto–enol transformations by means of electronic absorption spectroscopy. It was found that the electronic absorption spectra of **I** are much solvent-dependent. Specifically, in nonpolar solvents (hexane, carbon tetrachloride) this compound gives a strong long-wave absorption band at 285 nm, while in polar solvents (methanol, ethanol), at 330 nm. As the composition of the solvents is gradually changed from 100% CCl_4 to 100% methanol, the spectral curves show isobestic points, implying mutual transformations of different tautomeric forms. Figure 1 displays the electronic absorption spectrum of 4-methyldihydrofuro[2,3-h]coumarin-9-one in CCl_4–CH_3OH mixtures of varied composition. Analogously, as the composition of the solvent is varied from 100% CCl_4 to 100% methanol, the absorption spectra of compounds **II, III, VII**, and **VIII** show isosbestic points. Contrary to that, no isobestic points were observed in the spectra of compounds **IV**–**VI**, suggesting a weaker tendency of their ketone forms to enolization.

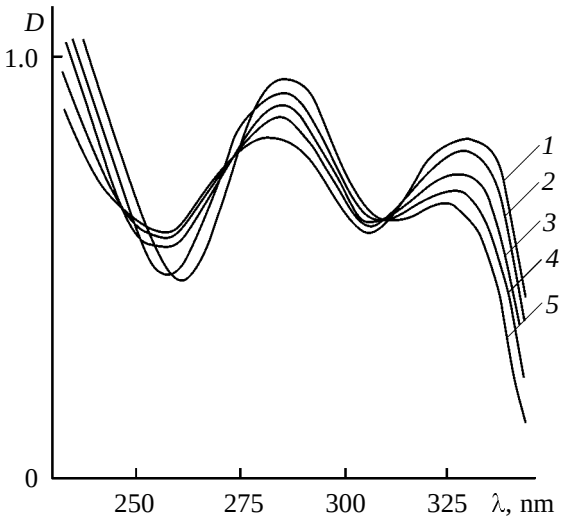


Fig. 1. Electronic absorption spectra of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**I**) in methanol–carbon tetrachloride mixtures: (*1*) 100% methanol, (*2*) 80% methanol + 20% CCl_4, (*3*) 50% methanol + 50% CCl_4, (*4*) 20% methanol + 80% CCl_4, and (*5*) 100% CCl_4.

The electronic absorption spectra of the enol forms of 8-substituted 4-methyldihydro[2,3-h]coumarin-9-one **Ib, IIb, IVb, Vb**, and **VIb** were explored by means quantum-chemical calculations by the PPP/CI method in π approximation.

As a rule, the PPP/CI method fairly reproduces the electronic absorption spectra of complex π-conjugated systems. At the same time, the calculation results often depend on proper choice of atomic and bond parameters. In detail, in our study of the electronic structure of 3-acetyl-4-hydroxycoumarin and a series of substituted coumarins [8] we showed that the reliability of analysis for such systems depends on proper allowance for intramolecular hydrogen bonds. The electronic absorption spectra of 8-substituted 4-methyldihydrofuro[2,3-*h*]coumarin-9-ones **Ib, IIb, IVb, Vb**, and **VIb** were calculated by the PPP/CI method with standard parametrization and allowance for intramolecular hydrogen binding for the carbonyl and hydroxy groups [9].

The results of the PPP/CI calculations are given in Table 1. From a comparison of the experimental and calculated electronic absorption spectra of the tautomeric forms of **I** and **II** it follows that in polar solvents (methanol) enol forms **Ib** and **IIb** are preferred. The calculated absorption maxima are 328 and 334 nm, respectively (experimental values 330 and 332 nm). Figure 2 shows the electronic absorption spectrum of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**I**) in methanol. As seen from the figure, the PPP/CI calculations nicely fit experimental positions and relative intensities of bands.

At the same time, for the enol forms of compounds **IV**–**VI** whose electronic absorption spectra do not contain isobestic points, the PPP/CI calculations with the same parameters strongly overestimate the long-wave absorption maxima (by 33–56 nm) compared with experiment. It is evident that the enol forms of 4-methyldihydrofuro[2,3-h]coumarin-9-ones with strong electron-donor substituents ($OCOCH_3$, OH,

Table 1. Experimental absorption maxima (λ_{max}, nm) and PPP/CI calculation results for the first transitions in the electronic absorption spectra of the enol forms of a series of dihydrofurocoumarinones: HOMO and LUMO energies (ε_{HOMO} and ε_{LUMO}, eV), oscillator strength (*f*), contribution of the HOMO–LUMO transition (φ, %), and absorption maximum (λ_{max}, nm)

Comp. no.	Calculation					Experiment (λ_{max})	
	ε_{HOMO}	ε_{LUMO}	*f*	φ	λ_{max}	MeOH	CCl_4
Ib	–8.85	–2.20	0.31	91	328	330	285
IIb	–8.66	–2.17	0.26	90	334	332	280
IVb	–8.24	–2.15	0.26	92	358	325	
Vb	–7.91	–2.06	0.17	94	378	340	
VIb	–7.68	–2.02	0.15	95	394	338	

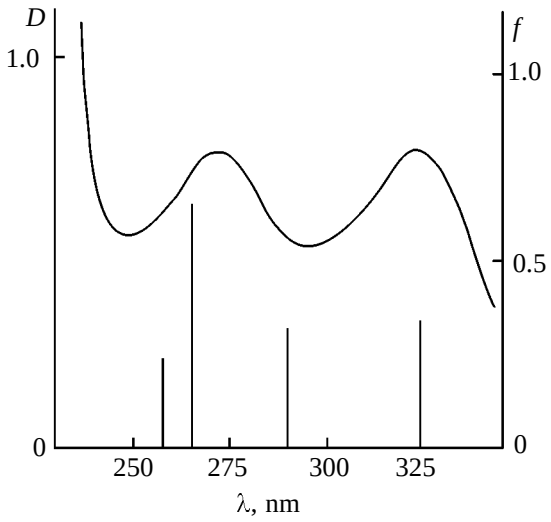
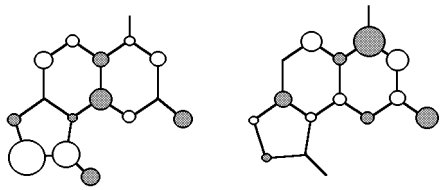


Fig. 2. Electronic absorption spectrum of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**I**) in methanol. Vertical lines show position of absorption maxima and oscillator strengths (*f*) in the spectrum of enol tautomer **Ib**, calculated by the PPP/CI method.

OCH_3) in the 8 position are less stable, and their keto–enol trasnformation are impossible to observe by electronic absorption spectroscopy.

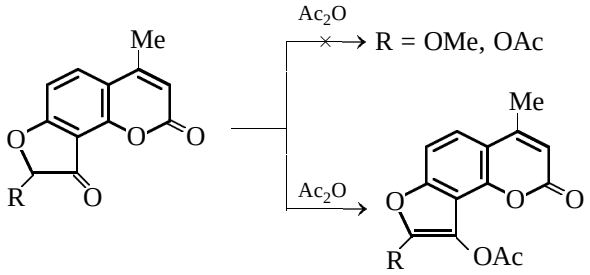
The PPP/CI results allow conclusions as to the nature of bands in the electronic absorption spectra of the enol forms of 8-substituted 4-methyldihydro[2,3-*h*]coumarin-9-ones **Ib, IIb, IVb, Vb**, and **VIb**. Thus, the calculations show that the long-wave absorption band relates to a practically single-configuration π–π^* transition from HOMO to LUMO. The contribution of this configuration is determined by the coefficient ϕ whose value reaches 90–95% (Table 1). Analysis of contributions into the frontier orbitals shows that the first band in the electronic absorption spectra reflects intramolecular charge transfer from the benzofuran to pyranone fragment. Sketches of the frontier orbitals of tautomer **Ib** are given below.



Ib

To gain further insight into the keto–enol transformations of 8-substituted 4-methyldihydrofuro[2,3-h]coumarin-9-ones **I**–**VIII**, we tried to fix their enol forms by acetylation. Note that compounds **IV** and **V**, which bear the electron-donor substituents OAc and OCH_3, respectively, could not be acetylated, while with compounds **I, II, III, VII**, and **VIII** (R = H, Cl, Br , CH=N-NH-$C_6H_3(NO_2)_2$, and 4-methylangelicin-9-yl, respectively), the corresponding 9-acetoxy-4-methylangelicins were obtained in high yields.

Hence, as follows from the electronic absorption spectra, there is a certain correlation between the abilities of 8-substituted dihydrofurocoumarinones to enol acetate formation on acetylation and to tautomeric transformations. Isobestic points were not observed in the electronic absorption spectra of compounds **IV**–**VI** whose enol derivatives could not be obtained.



R = H, Cl, Br, CH=N–NH–$C_6H_3(NO_2)_2$, 4-methylangelicin-9-yl.

The ^{1}H NMR spectra of 8-substituted dihydrofurocoumarinones were recorded in polar deuterated solvents (acetone-d_6, DMSO-d_6) and in the less polar $CDCl_3$. It was found that in $CDCl_3$ all the dihydrofuranones we prepared exist in the ketone form. The ^{1}H NMR spectra of compounds **VII** [R = CH=N–NH–$C_6H_3(NO_2)_2$] and **VIII** (R = 4-methylangelicin-9-yl) in $CDCl_3$ could not be obtained because of an extremely low solubility of these compounds. The most characteristic signal in ^{1}H NMR spectra of 8-substituted 4-methyldihydrofuro[2,3-*h*]coumarin-9-one ($CDCl_3$) is the singlet of H_8 of the furanone ring. Its position depends on the electronic effect of the neighboring substituent: The signal shifts more and more downfied with increasing electron-acceptor power of the substituent. However, the position of the H_8 proton signal is also affected by steric properties of the substituent (Table 2).

The ^{1}H NMR spectra of 8-substituted dihydrofurocoumarinones in polar solvents show that compounds **VII** and **III** exist in the enol form (the signal of the H_8 proton is absent and a downfield broadened signal of the 9-OH proton is observed).

The ^{1}H NMR spectra of the obtained 9-acetoxyfurocoumarines deserve detailed discussion. Table 3 shows that the H_5 and H_6 signals of the coumarin ring

Table 2. Correlation between the relative energies of 8-substituted dihydrofurocoumarinones **I**–**VIII** by the results of quantum–chemical calculations (kcal/mol) and the ^{1}H NMR and electronic absorption spectra

Comp. no.	ΔH_0^f(ketone) – ΔH_0^f(enol), calculation method			δ, ppm ($CDCl_3$) (H^8)	δ, ppm (acetone-d_6)	Presence (+) or absence (–) of isobestic point
	MNDO	AM1	PM3			
I	1.62	10.57	8.82	4.71	4.83 (H^8)	+
II	3.49	10.55	7.76	6.15	6.61 (H^8)	+
III	0.89	7.14	14.46	6.56	9.61 (OH^9)	+
IV	1.5	17.84	13.16	6.25	6.36 (H^8)	–
V	1.48	19.78	13.35	5.35	5.52 (H^8)	–
VI	2.97	19.9	12.9	5.57	5.74 (H^8)	–
VII	6.69	5.79	3.03	–	10.80 (OH^9)	+
VIII	–5.77	9.08	5.73	–	6.27 (H^8)	+

Table 3. Chemical shifts of the H_5 and H_5 protons of the coumarin ring in dihydrofuro[2,3-h]coumarin-9-ones and 9-acetoxyangelicins

Comp. no.	Solvent	Dihydrofuro[2,3-*h*]coumarin-9-one		9-acetoxyfurocoumarines	
		H^5	H^6	H^5	H^6
I	$CDCl_3$	7.80	7.00	7.54	7.39
II	$CDCl_3$	7.91	7.09	7.50	7.32
III	$CDCl_3$	7.91	7.08	7.49	7.34
VII	Acetone-d_6	7.78	7.59	7.85	7.75
VIII	DMSO-d_6	8.10	7.16	7.84	7.61

in the dihydrofurocoumarinone enol acetates are shifted toward each other. The H_5 signal is shifted upfield, and the H_6 signal is shifted downfield, compared with those of the corresponding dihydrofurocoumarinones. Compound **VII** [R = CH=N–NH–$C_6H_3(NO_2)_2$] is the only to drop out of this trend: Its aromatization shifts both the proton signals downfield.

Stabilities of the tautomeric forms of 8-substituted dihydrofurocoumarinones **I**–**VIII** was evaluated by quantum-chemical calculations of their enthalpies of formation. All the semiempirial methods used (MNDO, AM1, and PM3) predict that the ketone forms of all the compounds studied are more stable than enol. Table 2 lists the relative energies of the enol tautomers with respect to the most stable (ketone) form (ΔH_0^f (ketone) – ΔH_0^f (enol), resulting from the calculations.

The experimental data are most reliably correlated with the relative energies given by the AM1 method which is better parametrized to allow for hydrogen binding in the corresponding tautomers. Hence, for example, in the case of the compounds having electron-acceptor substituents in the 8 position of the dihydrofuranone ring (for example Cl, Br, and CHO), the differences in energies of formation are 5.70–10.55 kcal/mol. It is these compounds whose electronic absorption spectra show isosbestic points. The AM1 relative energies are the lowest for compounds **VII** and **III**, which is consistent with the observation of the enol form in their ^{1}H NMR spectra in acetone-d_6 or DMSO-d_6 (Table 2). At the same time, the compounds with electron-donor substituents (OH, OCH_3, and $OCOCH_3$) have rather high relative energies, 17.84–19.90 kcal/mol (AM1). Under these conditions, proton transfer between the ketone and enol forms is hardly probable, which is confirmed by the absence of isobestic points in the electronic absorption spectra of the corresponding compounds.

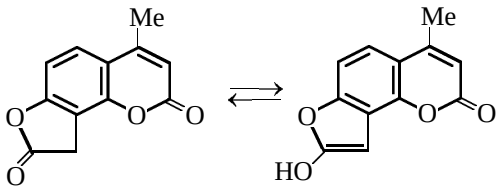
Compound **I**, apart from the two above-discussed forms, ketone **Ia** and enol **Ib**, can exist in their isoeric lactone (**IXa**) and lactone–enol (**IXb**) forms. The latter might be formed by the Fries rearrangement of 7-chloroacetoxy-4-methylcoumarin in the course of the synthesis of dihydrofurocoumarinone **I**.

Table 4. Enthalpies of formation (kcal/mol), total energies (au) and relative energies (kcal/mol, given in parentheses) of tautomers **Ia, Ib**–**VIc** and their isomers **XIa, XIb**, calculated by different methods

Comp. no.	MNDO	AM1	PM3	6-31G*
Ia	–113.98 (11.53)	–91.36 (24.96)	–109.98 (19.49)	–758.5433 (14.56)
Ib	–112.36 (13.15)	–80.79 (35.53)	–101.16 (28.31)	–758.5218 (28.05)
IXa	–125.51 (0.0)	–116.32 (0.0)	–129.47 (0.0)	–758.5665 (0.0)
IXb	–112.82 (12.69)	–80.55 (35.77)	–103.55 (25.92)	–758.5310 (22.28)

Table 5. Enthalpies of formation (kcal/mol), total energies (au), and relative energies (kcal/mol, given in parentheses) of tautomers **VIa**–**VIc**, calculated by different methods

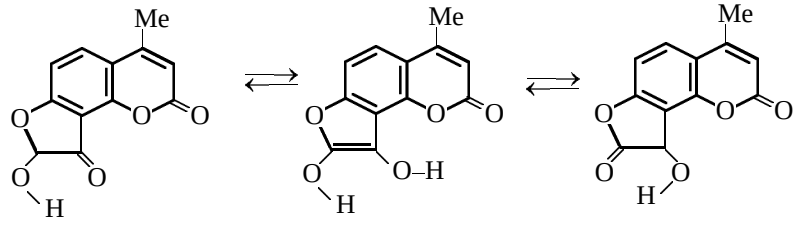
Comp. no.	Calculation method			Basis		
	MNDO	AM1	PM3	3-21G	6-31G*	6-31G**
VIa	–156.77 (1.77)	–132.38 (0.00)	–154.72 (2.29)	–789.9176 (3.42)	–794.3575 (6.88)	–794.3730 (6.85)
VIb	–153.80 (4.74)	–112.48 (19.9)	–145.32 (11.69)	–789.9080 (9.41)	–794.3361 (20.33)	–794.3570 (18.29)
VIc	–158.54 (0.00)	–129.62 (2.76)	–157.01 (0.00)	–789.9230 (0.00)	–794.3685 (0.00)	–794.3839 (0.00)



IXa **IXb**

Stability of the four possible structures we evaluated by semiempirical (MNDO, AM1, PM3) and nonempirical (6-31G*) calculations. By all the methods, the most stable is lactone form **IXa** (Table 4). But neither form **IXa** nor **IXb** could be detected both chemically and by ^{1}H NMR spectroscopy. Convincing evidence for the formation of the ketone rather than lactone isomers was also obtained in a mechanistic study of the Fries rearrangement of 7-chloroacetoxycoumarins [10]. Ketone form **Ia** is impossible to transform to the more stable lactone form **IXa** by varying the solvent, since these compounds are structural isomers.

Compound **VI** which theoretically can exist in three tautomeric forms is of paticular interest.



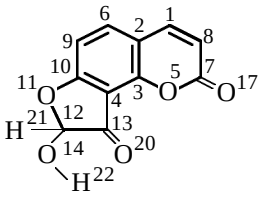
VIa **VIb** **VIc**

The enthalpies of formation of the tautomers and their relative energies with respect to the most stable tautomeric form are presented in Table 5. By the MNDO and PM3 results, the most stable is the lactone form. At the same time, AM1 calculations predict that the most stable is ketone form **VIa**, which is nicely consistent with experimental data: The spectral curves of compound **VI** form no isobestic points in the electronic absorption spectra. The ^{1}H NMR spectra show that this compound exists in the ketone form. Exhaustive acetylation of compound **VI** with acetic anhydride yields compound **IV**.

To obtain a more reliable information on the tautomeric form of compound **VIa**, we performed quantum-chemical calculations of its possible tautomeric forms **VIa**–**VIc** nonempirically with the 3-21G, 6-31G*, and 6-31G** basis sets. Table 5 lists the total energies of tautomers **VIa**–**VIc** and the relative energies of the tautomeric forms with respect to the most stable tautomer, obtained by all the calculation methods used.

The nonempirical methods all give the first place in stability to lactone form **VIb**. Ketone form **VIa** ranks next. The difference in their energies is 6.88 kcal/mol. But tautomeric transformations between these forms are possible only via intermediate formation of enol **VIb** which is very unstable and considerably differs in energy from the most stable lactone **VIb**. The corresponding difference in energies is 20.33 kcal/mol. Such a high energy barrier evidently rules out the tautomeric transformation between the ketone and lactone forms of 8-hydroxy-4-methyldihydrofuro[2,3-h]coumarin-9-one.

Of interest are the geometric parameters of ketone isomer **VIa**, obtained by quantum-chemical calculations. Figure 3 presents the molecule of tautomer **VIa** in two projections. The furan ring in this tautomer is nonplanar. The sp^3-carbon atom C^{13} (the numbering of atoms is given in Table 6) deviates from the coumarin ring plane by 4.9°, and the hydroxyl oxygen O^{14} deviates from the same plane by 50° to the opposite side. The deviation of the carbonyl O^{20} is insignificant (4.1°).



VIa

In tautomers **VIa-VIc**, the neighboring OH and C=O groups can form interamolecular hydrogen bond. Therefore, of special interest are the values of angles and bond lengths in hydrogen-bonded cycles of these tautomers, resulting from 6-31G* and 6-31G** calculations. The 6-31G* results for tautomer **VIa** are as follows: O^{14}–H^{22} bond length 0.949 Å, $O^{20}\cdots H^{22}$ distance 2.926 Å, $O^{14}\cdots O^{20}$ distance 2.935 Å, $C^{13}O^{1}\cdot H^{22}$ angle 111.2°, O^{14}–$H^{22}\cdots O^{20}$ angle 81.2°, and C^{12}–$O^{20}\cdots H^{22}$ angle 96.7°. The O···O distances for tautomers **VIa**–**VIc** are 2.936–3.022 Å, which confirms the existence of a weak intramolecular hydrogen bond. Note that ketone form **VIa** which, according to ^{1}H NMR and UV data, 8-hydroxy-4-methyldihydrofuro[2,3-*h*]coumarin-9-one prefers in solution, has the shortest hydrogen bond (the $O_{14}\cdots O_{20}$ distance is 2.935 Å) as compared to the more stable, according to calculations, lactone tautomer **VIc** (2.935Å). At the same time, for the unstable enol tautomer **VIb** quantum-chemical calculations give the longest hydrogen bond (3.022Å), inspite of the fact that the hydrogen-bonded ring in this tautomer lies in the molecular plane, and the molecule is planar.

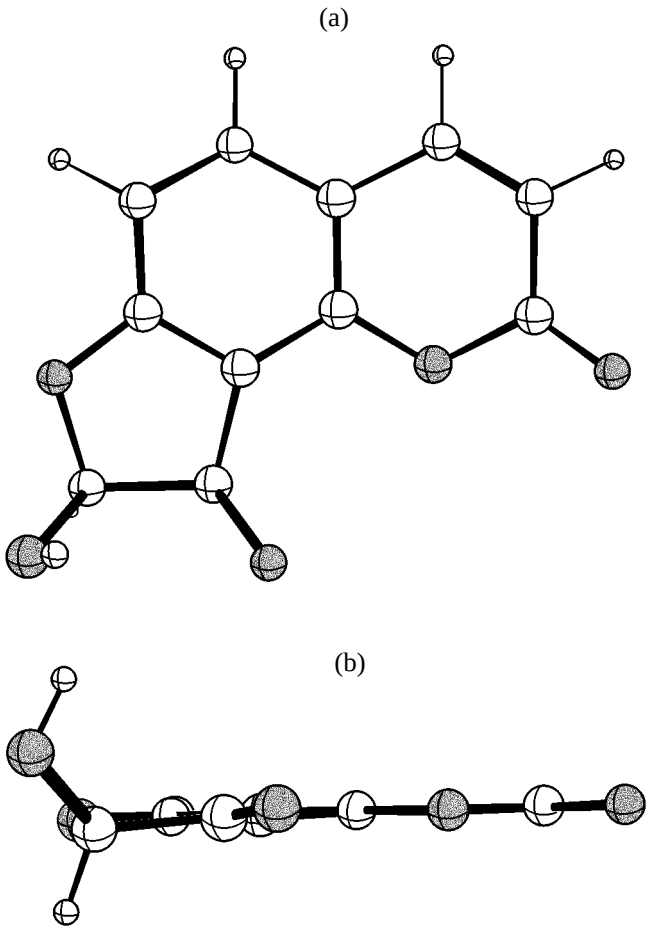


Fig. 3. 6-31G*-optimized steric stuctures of tautomer **VIa**: (a) frontal and (b) horizontal projections.

It is also interesting to note that the $O^{20}\cdots H^{22}$ and $O^{14}\cdots O^{20}$ distances in tautomeric form **VIa** which, according to experimental data, is the most stable form of compound **VI** are almost equal to each other (2.926 and 2.935 Å, respectively). In this respect tautomer **VIa** is clearly distinguished from the others.

Table 6 lists the charges on atoms involved in hydrogen bonding in tautomer **VIa**. The most significant gap between the 6-31G* and 6-31G** values is in the negative charges in the hydrogen bonded hydroxy group. Inclusion of polarization functions on hydrogen atoms decreases the charge on O^{14} by 0.1 *e*

Table 6. Atomic charges (*e*) in the hydrogen-bonded fragment of 8-hydroxy-4-methylhydrofuro[2,3-*h*]coumarin-9-one (**VIa**), calculated with the 6-31G* and 6-31G** basis sets

Atom	6–31G*	6-31G**
C^{12}	0.466	0.460
C^{13}	0.444	0.510
O^{14}	–0.701	–0.603
O^{20}	–0.497	–0.498

(–0.701 to –0.603 *e*). Similar trends were revealed in intramolecular hydrogen bonding in other compounds. In particular, the same results were obtained by nonempirical quantum-chemical calculations of different tautomers of 3-acetyl-4-hydrocoumarin [1]. Comparison of the calculation results showed that inclusion of polarization functions on hydrogen atoms changes the negative charge of the hydroxy group involved in hydrogen bonding by 0.1 *e*. Evidently, hydrogen bonding leads to electron density equalization in the hydrogen-bonded ring.

Hence, the experimental studies of the tautomeric transformations of 4-methyldihydrofuro[2,3-h]coumarin-9-one **I** and its 8-substituted derivatives **II**–**VIII**, together with MNDO, AM1, and PM3 semiempirical calculations, established that the ketone forms of all the compounds studied are more stable than the enol ones. By UV spectroscopy in mixtures of solvents of various polarity and chemically, by acetylation, it was shown that the derivatives containing electron-acceptor substituents in the 8 position of the furanone ring undergo enolization. At the same time, related derivatives with electron-donor substituents exhibit no such ability.

EXPERIMENTAL

The ^{1}H NMR spectra of compounds **I**–**VI** were recorded on a Bruker-200 spectrometer in acetone-d_6, DMSO-d_6, and $CDCl_3$ against internal TMS.

The electronic absorption spectra were obtained on Perkin-Elmer 323 and Specord UV-VIS spectrometers in nonpolar (CCl_4), polar (ethanol, methanol), and mixed (polar plus nonpolar) solvents.

The semiempirical (MNDO, AM1, PM3) quantum-chemical calculations were carried out using MOPAC [11]. Preliminary geometry optimization was performed by molecular mechanics (MM+ method). The electronic absorption spectra were calculated by the PPP/CI method in π approximation with standard atomic and bond parameters [9]. The nonempirical quantum-chemical calculations were carried using GAUSSIAN-94 with the 3-21G, 6-31G*, and 6-31G** basic sets [12]. Full geometry optimization for all the structures was performed by the gradient procedure [13]. The resulting structures were related to local minima on the potential energy surface by 6-31G* calculations of vibration frequences in harmonic approximation.

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