Electronic structure of π-systems. Studies of electronic structures and tautomeric transformations of a series of 4-methyl-8-(R-phenylazo)dihydrofuro[2,3-*h*]coumarin-9-ones

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Tautomeric transformations of a series of 4-methyl-8-(R-phenylazo)dihydrofuro[2,3-*h*]-coumarin-9-ones were studied by ^{1}H NMR, IR, electronic absorption spectroscopy, mass spectrometry, and quantum chemistry methods. The obtained results suggest that (*p*-R-phenyl)-derivatives exist in the quinone hydrazone form, while (*o*-R-phenyl)derivatives exist as a mixture of quinone hydrazone and azo enol tautomers with domination of the former. The *anti*-quinone hydrazone tautomers with a strong intramolecular hydrogen bond are more favorable than the *syn*-quinone hydrazone tautomers.

Key words: coumarin derivatives, dihydrofurocoumarinones, azo coupling, tautomerism, azo enol, azo ketone, quinone hydrazone, solvatochromism.

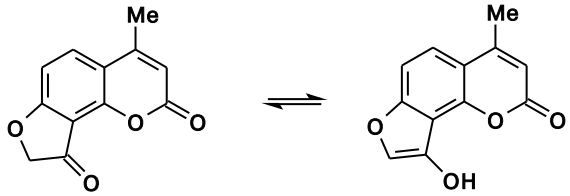
Coumarins are widespread in nature. Many coumarin derivatives exhibit biological activities. Particularly, furocoumarins are used to treat the skin diseases: alopecia circumscripta, psoriasis, mycosis, vitiligo, and a number of other diseases.[1,2] Psoralens are efficient in the photopheresis therapy of such diseases as dermal lymphoma, progressive systemic sclerosis (sclerodermatitis), lupus erythematosus, and rheumatoid arthritis.[3] Here, furocoumarins can serve as both mono- and bifunctional reagents with respect to DNA of viruses and microorganisms.

Earlier,[4,5] with the aim of search for new biologically active compounds in the furocoumarin family we have performed azo coupling of 4-methyldihydrofuro-[2,3-*h*]coumarin-9-one (**1**) with arenediazonium salts $[RC_6H_4N^+{\equiv}N]Cl^-$ to synthesize 4-methyl-8-(R-phenylazo)dihydrofuro[2,3-*h*]coumarin-9-ones **2—14**.

In studies of reactions and tautomeric transformations of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**1**), we found[6—8] that it is smoothly halogenated to α-halo derivatives and O-acetylated, undergoes dimerization and coupling with aldehydes and ketones. All the above-mentioned reactions involve both the oxygen and the carbon atoms of the dihydrofuranone ring and in line with the keto-enol tautomerism of compound **1** (Scheme 1).

The keto-enol equilibrium in the solutions of compound **1** was detected by means of electronic absorption spectra (EAS). Thus, in solutions of compound **1** with gradual change in their composition from CCl_4 to EtOH,

Scheme 1



1A **1B**

the ketone **1A** and enol **1B** forms undergo interconversions as evidenced by the existence of an isosbestic point in EAS of the solutions with different percentage of EtOH. The quantum chemical calculations using the semi-empirical methods MNDO, AM1, and PM3 confirm the existence of the equilibrium between ketone **1A** and enol **1B** tautomeric forms; the ketone form **A** being more stable.

In the present work, we studied the electronic structures and tautomeric transformations of substituted 4-methyl-8-(R-phenylazo)dihydrofuro[2,3-*h*]coumarin-9-ones **2—14** using methods of ^{1}H NMR, IR, and UV spectroscopy, mass spectrometry, their quantum chemical calculations were also carried out by both the semi-empirical (the Pariser—Parr—Pople configuration interaction (PPP-CI) method, AM1, PM3) and nonempirical (the self-consistent field method using the 6-31G* (6-31GF*) basis set) methods.

Since compounds **2—14** are able to undergo both keto-enol and azo enol-quinone hydrazone tautomerisms, the

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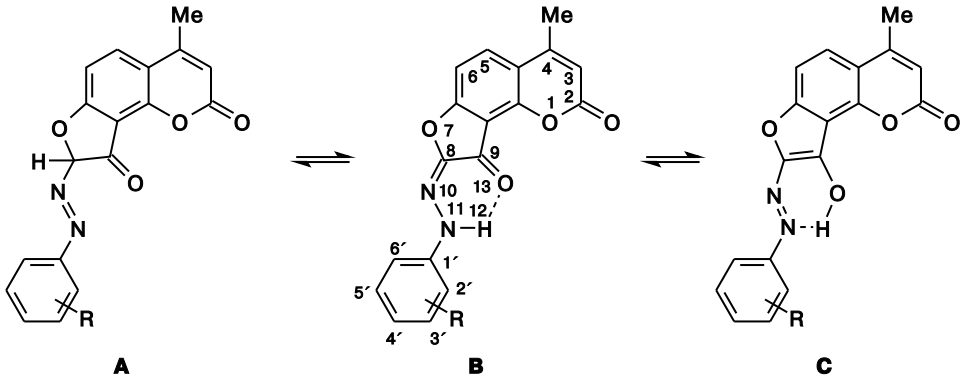
Scheme 2



R = H (**2**), 2-Me (**3**), 4-Me, (**4**), 4-OMe (**5**), 4-Cl (**6**), 4-Br (**7**), 2-NO_2 (**8**), 3-NO_2 (**9**), 4-NO_2 (**10**), 2,4-$(NO_2)_2$ (**11**), 4-Et (**12**), 3-Et (**13**), 2-Et (**14**).

number of possible tautomeric forms is increased as compared with the starting compound **1** (Scheme 2). Theoretically, compounds **2—14** can exist in azo keto (**A**), quinone hydrazone (**B**) and azo enol (**C**) tautomeric forms.

According to ^{1}H NMR spectra, compounds **2—14** exist only as tautomers **B** and **C**. The absence of the azo ketone form (**A**) is confirmed by the absence of signals for H(8) in the range of δ 5.35—6.56 in the ^{1}H NMR spectra of all examined compounds.[9]

In the ^{1}H NMR spectrum of 4-methyl-8-phenylazodihydrofuro[2,3-*h*]coumarin-9-one (**2**), the coumarin fragment has the singlets at δ 2.49 and 6.41 and the doublets at δ 8.13 and 7.36 (^3J = 8.6 Hz) assigned to the protons of the methyl group and protons H(3), H(5), and H(6), respectively. In the low-field region, the singlet at δ 11.05 was observed, which was assigned to proton H(12) of the hydrazone group. It confirms that compound **2** exists in solution in DMSO-d_6 in the quinone hydrazone form **B**. The protons of the phenyl group appear as a multiplet in the range of δ 6.98—7.35.

Table 1. ^{1}H NMR (DMSO-d_6) spectroscopic data of compounds **2—14***

Compound	δ				
	H(3)	H(5)	H(6)	NH	OH
2	6.41	8.13	7.36	11.05	—
3**	6.41	8.12	7.20	9.76	12.02
4	6.35	8.07	7.32	10.90	—
5	6.40	8.10	7.34	10.99	—
6	6.42	8.13	7.37	11.15	—
7	6.35	8.10	7.20	11.05	—
8	6.40	8.15	7.40	11.60	—
9	6.35	8.15	7.35	11.35	—
10	6.40	8.15	7.40	11.60	—
11	6.45	8.25	7.55	11.20	13.65
		(8.05)	(7.45)		
12	6.40	8.12	7.30	11.02	—
13	6.40	8.00	7.30	11.00	—
14**	6.40	8.12	7.21	9.80	12.20

* The chemical shifts of the protons of the azo enol form are shown in parentheses.

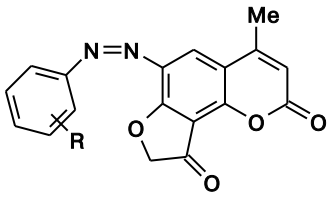
** The chemical shifts of protons H(5) and H(6) of the azo enol form are not shown because of low spectral resolution (low solubility of sample).

Studies of ^{1}H NMR spectrum of 8-(2,4-dinitrophenylazo)dihydrofurocoumarinone (**11**) show that the quinone hydrazone form of this compound is in the tautomeric equilibrium with the azo enol form (**11B** : **11C** = 70 : 30). The ^{1}H NMR spectrum of compound **11** contains a low-field signal for the proton of the hydrogen-bonded OH group of the azo enol form **11C** (δ 13.65) along with the signal for the NH-proton of the quinone hydrazone form **11B** (δ 11.20), which is characteristic of this family of compounds. Notably, the transition from the quinone hydrazone form **11B** to the azo enol form **11C** considerably affects only the chemical shifts of protons H(5) and H(6) of the coumarin fragment. Thus, two sets of signals are observed for protons H(5) and H(6) assigned to the quinone hydrazone **B** and azo enol **C** forms of compound **11**, the signals of tautomer **C** being shifted up-field as compared with the signals of tautomer **B** (Table 1). The chemical shift of proton H(3) of the coumarin fragment is not changed, and the chemical shifts of the protons of the benzene fragment of tautomers **B** and **C** are almost the same.

The azo enol-quinone hydrazone tautomerism is also observed in the case of (2-methyl- and 2-ethylphenylazo)-dihydrofurocoumarinones (**3** and **14**). In the ^{1}H NMR spectra of compounds **3** and **14**, the signals for the protons of the OH groups of the azo enol form **C** appear in the low-field at δ 12.02 and 12.20, respectively, while the

signals for the NH protons are shifted up-field as compared with the same signals of azo compounds that can existed only in the quinone hydrazone form **B** and appear at δ 9.76 and 9.80, respectively (see Table 1). Apparently, this shift is connected with the introduction of electron-donating substituents in position 2 of the benzene ring. According to the ^{1}H NMR data, the quinone hydrazone tautomers **3B** and **14B** are prevalent and exist in equilibrium with the azo enol forms, the ratios **B** : **C** = 70 : 30 and 60 : 40, respectively.

According to the data from the ^{1}H NMR spectra of compounds **4—10**, **12**, and **13** in DMSO-d_6, they exist only in quinone hydrazone form **B**. The characteristic signal of these compounds is the signal for the proton of the hydrazone group in the range of δ 10.90—11.60 (see Table 1).

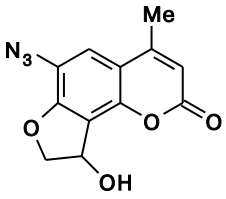


15a—c

R = H (**a**), 4-Me (**b**), 4-Cl (**c**)

That compounds **2—14** exist in the quinone hydrazone form **B** is also confirmed by the fragmentation pattern in the electron impact (EI) mass spectra. The peaks assigned to the R—Ph—NH—N=C fragment were present, while in the EI mass spectra of 6-(R-phenylazo)dihydrofurocoumarinones **15a—c**, knowingly existing in the azo form,[5] only R—Ph—N=N fragments were found.

The quinone hydrazone form of compounds **2—14** was also confirmed by the data from IR spectroscopy. For example, in the IR spectrum of compound **2** the band of moderate intensity is observed at 3230 cm^{-1} assigned to stretching vibrations of the H-bonded NH group. The vibration bands of the carbonyl groups of the lactone and furanone fragments are observed at 1690 and 1735 cm^{-1}, respectively. In the IR spectrum of compound **2**, no stretching vibrations band of the hydroxyl group is present. The unambiguous assignment of the bands observed in the IR spectrum of compound **2** was made on the base of a comparison with the positions of the characteristic bands in the IR spectra of compound **2**, 6-(phenylazo)derivative **15a**, and 6-azido-9-hydroxy-4-methyl-8,9-dihydrofuro-[2,3-*h*]chromen-2-one (**16**) (see Ref. 10).



16

In the IR spectrum of compound **16**, a broad band of stretching vibrations of the hydroxyl group linked by the intermolecular hydrogen bond is observed at 3340 cm^{-1}, a narrow vibration band of the azido group is at 2050 cm^{-1}, and a vibration band of the carbonyl group of the lactone fragment is at 1680 cm^{-1}. The IR

Table 2. The enthalpies of formation (H_f°) and relative energies (E_{rel}) of the tautomeric forms of compounds **2—14** according to the calculations by the AM1 and PM3 methods

Tautomer	AM1		PM3		Tautomer	AM1		PM3	
	$-H_f^\circ$	E_{rel}	$-H_f^\circ$	ΔE		$-H_f^\circ$	E_{rel}	$-H_f^\circ$	ΔE
	kcal mol^{-1}					kcal mol^{-1}			
2A	4.94	0.00	38.92	0.00	**8C**	—	—	38.52	6.01
2B	3.48	1.46	37.01	1.91	**9A**	—	—	45.32	1.16
2C	1.22	6.16	27.20	11.72	**9B**	—	—	46.48	0.00
3A	15.42	0.00	46.82	0.00	**9C**	—	—	40.22	6.26
3B	10.96	4.46	45.63	1.19	**10A**	—	—	46.62	0.00
3C	3.88	11.54	40.14	6.68	**10B**	—	—	46.53	0.09
4A	12.83	0.00	48.51	0.00	**10C**	—	—	40.26	6.36
4B	11.35	1.48	46.65	1.86	**11A**	—	—	49.57	0.44
4C	6.32	6.51	41.86	6.65	**11B**	—	—	50.01	0.00
5A	43.45	0.00	77.50	0.00	**11C**	—	—	44.00	6.01
5B	41.09	2.36	74.94	2.56	**12A**	17.22	0.00	51.42	0.00
5C	36.92	6.53	70.73	6.77	**12B**	17.07	0.15	51.35	0.07
6A	11.78	0.00	45.48	0.00	**12C**	12.07	5.15	47.06	4.36
6B	10.54	1.24	43.82	1.66	**13A**	20.59	0.00	52.22	0.00
6C	3.81	7.97	38.82	6.66	**13B**	17.09	3.50	51.32	0.90
7A	—	—	30.80	0.00	**13C**	11.35	9.24	46.47	5.75
7B	—	—	29.35	1.45	**14A**	20.13	0.00	47.25	0.00
7C	—	—	24.29	6.51	**14B**	15.18	4.95	47.22	0.03
8A	—	—	44.53	0.00	**14C**	7.46	12.67	41.75	5.50
8B	—	—	43.29	1.24					

spectrum of compound **15a** has the vibration bands of the carbonyl groups of the lactone and furanone fragments that strongly overlap and are observed at 1725 cm^{-1}. A comparison of the IR spectra of compounds **2**, **15a**, and **16** suggests that compound **2** exists in the quinone hydrazone form **B**.

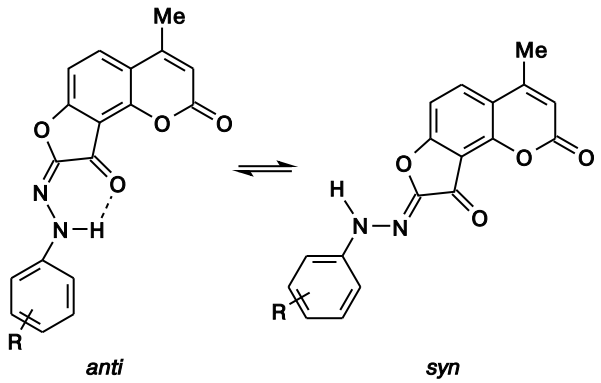
The fact that compounds **2** and **4—7** easily undergo *N*-acetylation with acetic anhydride in the presence of pyridine to give respective *N*-acetyl derivatives also corroborates the quinone hydrazone form **B**.

The enthalpies of formation of three possible tautomeric forms of 4-methyl-8-(R-phenylazo)dihydrofuro-[2,3-*h*]coumarin-9-ones **2—14** were calculated by the AM1 and PM3 methods (Table 2).

The semiempirical quantum chemical calculations that describe the state of a substance in the gas phase predict, for compounds **2—14**, higher stabilities of azo ketone **A** and quinone hydrazone **B** tautomers. The difference in the enthalpy of formation between tautomers **A** and **B** is less then 3.2 kcal mol^{-1}, and for 4′-nitro- (**10**) and 2′-ethyl derivatives (**14**) it is less than 0.1 kcal mol^{-1}, which makes ambiguous the conclusion on the dominant tautomeric form. In the case of 3′-nitro- (**9**) and 2′,4′-dinitro-substituted (**11**) compounds, the quinone hydrazone tautomeric form **B** is the most stable, which is in accord with the spectroscopic data for compounds **2—14** in solution. At the same time, the calculations show that the enol forms **C** for all compounds **1—13** are less stable (relative energy ΔE is 6.01—11.72 kcal mol^{-1}).

The stability of tautomeric forms is known to be largely determined by the existence of intramolecular hydrogen bonds.[11] The energy of these bonds in tautomers **2B—14B** was calculated using the PM3 method by comparing the enthalpies of formation of the quinone hydrazones with (*anti*-isomers) and without (*syn*-isomer) the hydrogen bonds (Scheme 3, Table 3).

Scheme 3



2B—14B

Table 3. The enthalpies of formation (H_f°) and energies of hydrogen bonds ($E_{H...O}$) of the *syn*- and *anti*-isomers of quinone hydrazone tautomeric form **B** of compounds **2—14** according to the calculations by the PM3 method

Tautomer	$-H_f^\circ$/kcal mol^{-1}		$E_{H...O}$ /kcal mol^{-1}
	syn-isomer	*anti*-isomer	
2B	36.04	37.01	0.97
3B	45.63	42.94	−2.69
4B	45.46	46.65	1.19
5B	74.11	74.94	0.83
6B	42.86	43.82	0.96
7B	29.80	30.80	1.00
8B	40.46	43.29	2.83
9B	43.82	46.48	2.66
10B	45.64	46.53	0.89
11B	46.62	50.01	3.39
12B	50.43	51.35	0.92
13B	50.43	51.32	0.99
14B	45.83	47.25	1.42

Due to the intramolecular hydrogen bond, the *anti*-isomers of the quinone hydrazones are more stable than the respective *syn*-isomers (except for compound **3**). According to the calculations, the strongest intramolecular hydrogen bond is the hydrogen bond in compound **11**. Two nitro groups in the benzene ring considerably increase the acidity of the NH group, strengthen the intramolecular hydrogen bond, thereby stabilizing the respective quinone hydrazone form.

For compound **2**, the nonempirical calculations by the 6-31GF* method were also performed. According to the calculations (Table 4), the *anti*-form of the quinone hydrazone is the most stable, which agrees well with the experimental data. One should pay attention to the optimized values of angles and bond lengths calculated for tautomers **2B** and **2C**. These parameters indicate that the intramolecular hydrogen bonds in molecules **2B** and **2C** are possible. Table 5 presents the lengths of O—H, N—H bonds; lengths of intramolecular hydrogen bonds O...H, N...H; angles O—H...N, N—H...O, C—O—H, N—N—H, and C—O...H of the pseudoaromatic ring, and distances between the atoms of nitrogen (hydrazone and azo groups) and oxygen (carbonyl and hydroxyl groups).

Table 4. Total (E_{tot}) and relative (E_{rel}) energies of the tautomeric forms of compound **2** according to the calculations with the 6-31GF* basis set

Tautomer	$-E_{tot}$/au	E_{rel}/kcal mol^{-1}
2A	1096.935738	3.86
2B (*anti*)	1096.941894	0.00
2B (*syn*)	1096.940705	0.75
2C	1096.921989	12.49

Table 5. Several interatomic distances (*d*) and bond angles (ω) in tautomers **2B,C** according to the calculation with the 6-31GF* basis set

Parameter	**2B**	**2C**
Bond	*d*/Å	
O(13)...H(12)	2.138	0.954
N(11)...O(13)	2.862	2.860
N(11)—H(12)	0.998	2.141
Angle	ω/deg	
N(10)—N(11)—H(12)	119.07	104.40
N(11)—H(12)...O(13)	109.87	131.12
C(9)—O(13)...H(12)	114.03	108.53

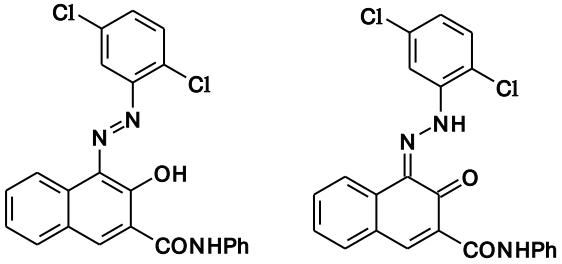
In addition, the tautomeric transformations in the series of azo compounds **2—14** were studied by the EAS method using solvents with different polarity (methanol, DMSO, chloroform, and binary mixtures with different composition). Particularly, the electronic spectra were recorded in mixtures MeOH—CCl_4 with concentration of methanol varying from 100% to 12%.

As the composition of the solvents changed, the EAS of compounds possessing electron-donating substituents in the benzene ring, *i.e.*, **3—5** and **12—14**, show isosbestic points, which implies the equilibrium between tautomeric forms of these compounds (Fig. 1).

At the same time, in the spectra of azo compound **2** and compounds **6** and **10** with electron-withdrawing groups in the *p*-position of the benzene ring, isosbestic points are absent, which implies the presence of only one tautomeric form. This is confirmed by the data from ^{1}H NMR spectra, which show that compounds **2**, **6**, and **10** exist in the quinone hydrazone form **B**. Unfortunately, because of the extremely low solubility we failed to obtain EAS of 2′,4′-dinitro-substituted compound **11**, for which the data from ^{1}H NMR spectroscopy suggest the existence of the tautomeric equilibrium.

The electronic absorption spectra of several tautomeric forms of compounds **2**, **5**, **6**, and **10** were calculated by the PPP/CI method in the π approximation.

There are numerous data of the effective application of the PPP/CI method for the quantum chemical calculation of EAS of different classes of compounds and for the analysis of the structures of electronic levels in molecules of polycycloquinones,[12,13] azo compounds,[14] naphthoquinones,[15] and anthraquinones.[16] With accurate selection of parameters of atoms and bonds, and with allowance for intramolecular hydrogen bonding, the results of calculations agree well with the experimental data. The calculations of the tautomeric forms of azo compounds by the PPP/CI method are of particular interest. For example, the spectroscopic differences between hydroxy azo- (**A**) and quinone hydrazone (**B**) tautomeric forms of compound **17** were adequately predicted by the PPP/CI method.[13]



17A **17B**

$\lambda_{max}(C_6H_{12})$ = 425 nm, λ_{max} = 409 nm

$\lambda_{max}(C_6H_{12})$ = 503 nm, λ_{max} = 506 nm

The results of calculations of EAS of 4-methyl-8-(R-phenylazo)dihydrofuro[2,3-*h*]coumarin-9-ones **2**, **5**, **6**, and **10** are shown in Table 6. A comparison of the experimental EAS and those calculated by the PPP/CI method for *anti*- and *syn*-quinone hydrazone and azo enol tautomers shows that these compounds exist as quinone hydrazones in the *anti*-isomeric form. For this tautomer, the calculated absorption maxima of compounds **2**, **4**, **6**, and **10** are 429, 444, 433, and 433 nm, respectively, which is close to the experimental data, 428, 451, 430, and 431 nm. The differences between the calculated and experimental absorption maxima for the respective azo enol and *syn*-quinone hydrazone tautomeric forms

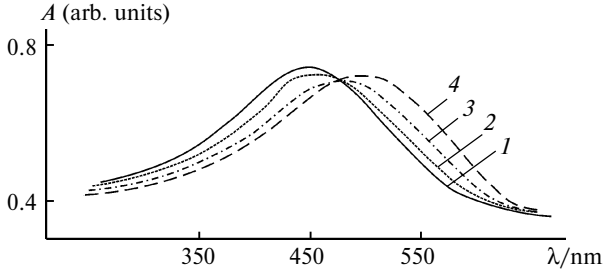


Fig. 1. Electronic absorption spectra of compound **12** recorded in mixtures of MeOH—CCl_4: *1* — MeOH, *2—4* — mixtures MeOH—CCl_4 with ratio 4 : 1 (*2*), 1 : 1 (*3*), 3 : 7 (*4*).

Table 6. The experimental (λ_{max}^{exp}) and calculated (PPP/CI) (λ_{max}^{calc}) values of the long-wave absorption maxima of quinone hydrazone (**B**) and azo enol (**C**) tautomeric forms of compounds **2, 5, 6**, and **10**.

Compound	λ_{max}^{exp}/nm ($CHCl_3$)	λ_{max}^{calc}/nm		
		B (*anti*)	**B** (*syn*)	**C**
2	428.0	429.0	392.2	424.6
5	451.0	443.8	404.6	437.8
6	430.0	432.2	396.5	431.3
10	431.0	433.1	394.1	426.9

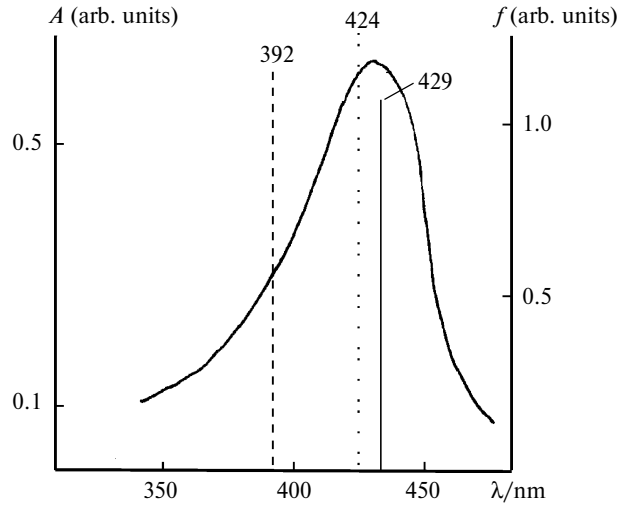


Fig. 2. Electronic absorption spectra of compound **2** in $CHCl_3$. Vertical lines show the positions of absorption maxima (λ_{max}^{calc}) and oscillator strength (*f*) for tautomers: quinone hydrazone (**B**), *anti*-isomer (solid line), quinone hydrazone (**B**), *syn*-isomer (dotted line), azo enol (**C**) (dashed line) calculated by the PPP/CI method.

are considerably higher and, for example, in the case of *syn*-quinone hydrazones achieve 37—39 nm.

The experimental and calculated (PPP/CI) EAS of 4-methyl-8-(phenylazo)dihydrofuro[2,3-*h*]coumarin-9-one (**2**) are given in Fig. 2. This and data from Table 6 show that the quantum chemical calculations by the PPP/CI method of the EAS of *anti*-quinone hydrazones well reproduce both the absorption maxima and relative band intensities.

The calculation by the PPP/CI method allows one to make conclusion about the nature of bands in the EAS. According to the calculations, the first band in EAS of *anti*-quinone hydrazone tautomers **B** of compounds **2**, **5**, **6**, and **10** 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 97%. The sketches of the frontier orbitals (HOMO and LUMO) of tautomers **2B** **10B** are given in Fig. 3.

The analysis of eigenvalues of the frontier orbitals of *anti*-quinone hydrazones **2B** and **5B** shows that they are delocalized over all atoms of the molecule (Fig. 3, *a*). At the same time, for tautomers **6B** and **10B** the most long-wave transition is accompanied by transfer of electron density from the coumarin to arylazofuranone fragment of the molecule (see Fig. 3, *b*). Figure 3 also shows the polarization directions of the first and the second electron transition. For all discussed *anti*-quinone hydrazone tautomers calculated by the PPP/CI method, the polarization direction of the first long-wave transition in EAS is almost parallel to the long axis of the molecule.

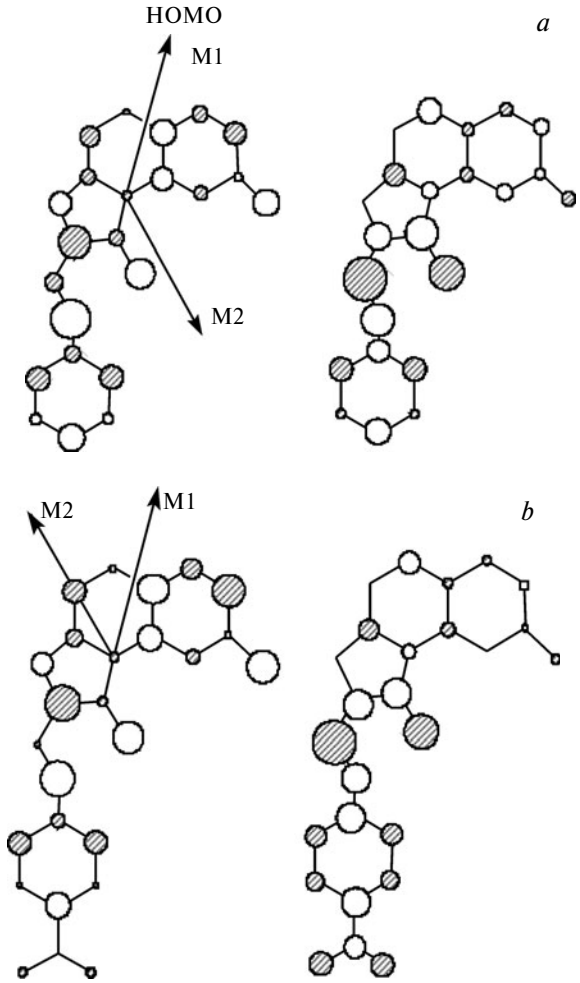


Fig. 3. The sketches of the frontier orbitals (HOMO and LUMO) of the quinone hydrazone tautomers **B** of compound **2** (*a*) and **10** (*b*). The arrows show the polarization direction of the first (M1) and second (M2) long-wave transition.

Thus, the obtained spectral data and results of quantum chemical calculations altogether allow us to state that (*p*-R-phenyl)derivatives exist in the quinone hydrazone form, while (*o*-R-phenyl)derivatives exist in the tautomeric equilibrium of the quinone hydrazone and azo enol forms (the ratio of the tautomers is 70 : 30). The non-empirical quantum chemical calculations by the 6-31GF* method also predict higher stability of the quinone hydrazone form.

Experimental

4-Methyl-8-(R-phenylazo)dihydrofuro[2,3-*h*]coumarin-9-ones **2—14** were prepared according to the known method.[5] The ^1H NMR spectra of compounds **2—14** were recorded on a Bruker-200 spectrometer in DMSO-d_6 using Me_4Si as the internal standard. The electronic absorption spectra were obtained on a Specord UV/VIS spectrophotometer in methanol,

DMSO, and chloroform. The tautomeric transitions were studied in a mixture MeOH—CCl_4. The IR spectra were recorded on a UR-20d spectrometer in KBr pellets. Mass spectra (EI, 70 eV) were recorded on a SSQ-720 (Finnigan MAT) mass spectrometer.

The semiempirical (AM1, PM3) quantum chemical calculations were carried out using MOPAC (see Ref. 17). Preliminary geometry optimization was performed by molecular mechanics MM+ method. The nonempirical quantum chemical calculations were carried using GAUSSIAN-94 with the 6-31 GF* basis set.[18] The geometrical characteristics of all studied structures were fully optimized by the gradient procedure.[19] The quantum chemical calculations of the EAS were performed by the PPP/CI method in the π approximation with standard atomic and bond parameters including intramolecular hydrogen bonding for carbonyl, hydroxyl and amino groups.[13]

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