Dihydrofuran ring opening in the reactions of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one with arylhydrazines

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2,3-Dihydrofuro[3,2-*c*]coumarin-3-one reacts with arylhydrazines *via* two routes. The corresponding hydrazones are formed from arylhydrazines in alcohol and nitrophenylhydrazines in acetic acid or toluene. With phenylhydrazine and *para*-tolylhydrazine in toluene, 2,3-dihydrofuro[3,2-*c*]coumarin-3-one reacts unusually undergoing dihydrofuran ring opening and the formation of the corresponding 3-(2-imino-1-(2-arylhydrazinyl)ethylidene)-chromane-2,4-diones. The solvatochromic properties of the synthesized compounds were studied using electronic absorption spectra and quantum chemical calculations.

Key words: furocoumarinones, hydrazones, tautomerism, isomerization, labeled nitrogen atom, electronic absorption spectra.

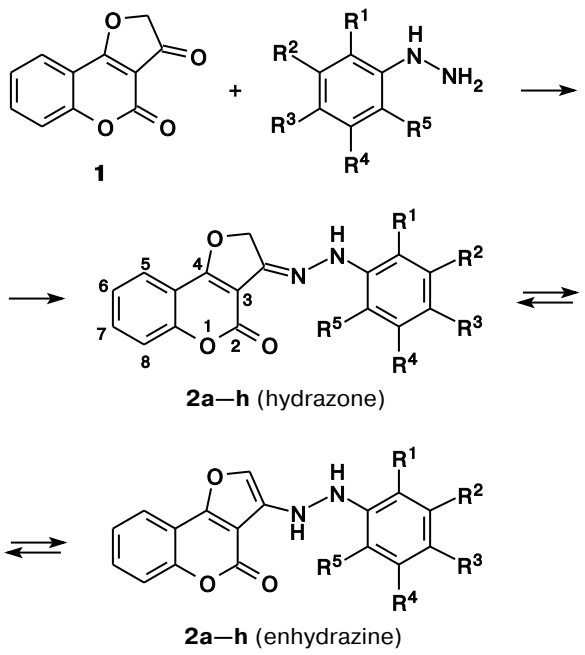
Derivatives of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one (**1**) are of interest, being analogs of a series of natural compounds, for example, fercoprolone and pterophyllines.[1,2] At the same time, coumarin derivatives found wide use as optically bleaching agents, for the creation of active media of frequency-controlled lasers and luminescent labels. Photosensitive coumarins are promising for use in electronic photography as photosensitizers and in the construction of new devices of information recording and storage.

We have earlier[3] studied the reactions of coumarinone **1** with aromatic aldehydes and amines. Compound **1** reacts actively to the both methylene and carbonyl group of the dihydrofuran cycle. It is interesting that the reaction with substituted anilines at the carbonyl group is accompanied by the corresponding tautomeric transformations with aromatization of the dihydrofuran cycle. Continuing the systematic investigation of the reactions of coumarinone **1** and its acyclic analog 3-acetyl-4-hydroxycoumarin[4—7] having the purpose to obtain compounds with valuable spectral properties, we carried out the reactions of compound **1** with arylhydrazines. Arylhydrazines were used as both hydrochlorides and free bases. These experiments gave different results.

Results and Discussion

The results of the reactions of coumarinone **1** (see Ref. 8) with substituted phenylhydrazine hydrochlorides and nitrophenylhydrazines taken as free bases are shown in Scheme 1.

Scheme 1



2a: $R^1 = R^2 = R^3 = R^4 = R^5 = H$
2b: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = F$
2c: $R^1 = R^5 = Cl$, $R^2 = R^3 = R^4 = H$
2d: $R^1 = R^4 = Cl$, $R^2 = R^3 = R^5 = H$
2e: $R^1 = R^3 = Cl$, $R^2 = R^4 = R^5 = H$
2f: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = Me$
2g: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = NO_2$
2h: $R^2 = R^4 = R^5 = H$, $R^1 = R^3 = NO_2$

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Table 1. Chemical shifts of protons (δ) of the NH and CH_2 groups in the ^1H NMR spectra (DMSO-d_6) of compounds **2**

Hydrazone **2**	Yield (%) (ratio of isomers)	δ	
		NH	CH_2
2a (*E*,*Z*)	45 (50 : 50)	11.00/9.14	5.50/5.51
2b (*E*,*Z*)	25 (50 : 50)	10.97/9.13	5.52/5.49
2c (*E*)	41.4	10.60	5.48
2d (*E*,*Z*)	64.1 (30 : 70)	11.39/8.53	5.58/5.74
2e (*E*)	68	11.06	5.54
2f (*E*,*Z*)	50 (5 : 95)	10.91/9.03	5.51/5.49
2g (*E*)	94	10.15	5.6
2h	46	—	—

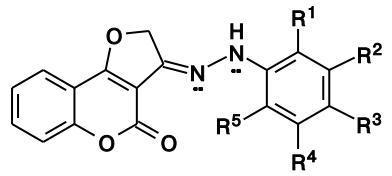
Hydrazones **2a—e** were synthesized by the reactions with arylhydrazine hydrochlorides in ethanol with the addition of sodium acetate. Hydrazone **2f** was obtained under similar conditions, but with triethylamine instead of sodium acetate. The reactions of coumarinone **1** with nitrophenylhydrazines taken as bases are accompanied by the formation of the corresponding hydrazones. The reactions of *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine with coumarinone **1** afford hydrazones **2g,h**. All hydrazones are formed in good yields, except for compound **2b**, which was isolated in 25% yield (Table 1).

As shown in Scheme 1, hydrazones **2a—h** can exist in two tautomeric forms: hydrazone and enhydrazine. For compounds **2g,c,e**,* the presence of the hydrazone form is proved by the ^1H NMR spectral data: a broadened single singlet in a weak field at δ 10.15—11.06 indicates the presence of one NH group and a narrow singlet with an intensity of two proton units at δ 5.5 corresponds to the CH_2 group. These signals are doubled in the spectra of compounds **2a,b,d,f**: two signals of the NH-protons with a total integral of one proton unit are detected at δ 8.53—11.40, whereas two singlets of the CH_2 groups with a total integral value of two proton units are observed at δ 5.48—5.74. The enhydrazine form of compounds **2** should be observed in the ^1H NMR spectra as two broadened downfield signals attributed to the NH group with an integral of one proton unit each and the singlet of the methine proton at δ 7—8, while a signal from the CH_2 group should be absent. No signals of the enhydrazine form were observed in the spectral of all compounds **2**.

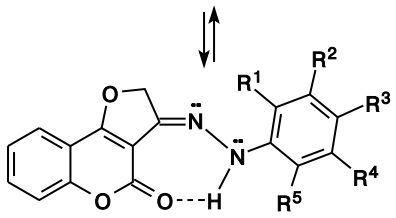
Thus, compounds **2a—h** exist as hydrazones. No five-membered ring aromatization resulting in the formation of the enhydrazine structure is observed. This fact is worth mentioning, the more so the possibility of this aromatization has been observed by us earlier when studying the structures of the condensation products of coumarinone **1** with aromatic amines.[3]

As shown in Scheme 2, hydrazones **2** can exist as *Z*- and *E*-isomers, and in the *E*-isomer the NH-proton and the oxygen atom of the coumarin moiety can be linked by a hydrogen bond, and should result in the downfield shift of the NH-proton. According to the ^1H NMR spectra data, hydrazones **2d**, **2a**, and **2b** are formed as a mixture of *E*- and *Z*-isomers in a ratio of 1 : 2.3, 1 : 1, and 1 : 1, respectively, whereas in compound **2f** the content of the *E*-isomer does not exceed 5%. As already mentioned, in the ^1H NMR spectra of arylhydrazones **2c,e,g**, no doubling of the signals from the CH_2 and NH groups is observed, indicating that these hydrazones exist as a single, most likely, *E*-isomer.

Scheme 2



Z-**2**



E-**2**

The ratio of the *E*- and *Z*-isomers in compounds **2a,b** changes after recrystallization from ethanol. For instance, in compound **2a** the content of the *Z*-isomer increases to 90%, whereas in compound **2b** it reaches 100%.

The Overhauser nuclear effect was studied to confirm the assignment of signals of the CH_2 and NH groups of the *E*- and *Z*-isomers in the ^1H NMR spectra for compound **2d**. This effect was found for the signals with δ 5.74 (CH_2) and 8.53 (NH), indicating that these groups in the *Z*-isomer are spatially close.

The results of PM3 quantum chemical calculations are in agreement with the ^1H NMR spectral data on the structure of compounds **2** (Table 2): the *E*-isomer with the lowest energy of formation is thermodynamically preferential of two hydrazone forms in compounds **2**. The formation of compounds **2** in the enhydrazine form should be considered less probable for thermodynamic reasons.

The ratio of *E*- and *Z*-isomers in hydrazones **2** depends on the solvent. The ^1H NMR spectra of compound **2d** in deuterated chloroform and DMSO were detected

* We failed to detect the ^1H NMR spectrum of compound **2h** because of its low solubility (see Experimental).

for comparison. The character of the ^{1}H NMR spectrum in DMSO-d_6 remains unchanged with time, while a different situation is observed in $CDCl_3$. Two signals of the CH_2 groups in $CDCl_3$ are overlapped and have the form of a single broadened intense singlet at δ 5.44, and the signals of the NH group as two broadened singlets at δ 11.36 and 7.02 correspond to the *E*- and *Z*-isomers, respectively. The doublet-doublet signal corresponding to the 4′-*meta*-proton of the dichloro-substituted benzene ring is doubled and have the corresponding spin-spin coupling (SSC) constants $^{3'}J_{H(3'),H(4')}$ = 8 Hz and $^{4'}J_{H(4'),H(6')}$ = 2 Hz at δ 6.83 (*E*) and 6.7 (*Z*) with intensities of 0.3 and 0.7 proton units. In the spectrum recorded in 1 h, the predominant form becomes almost the single: the content of the *E*-hydrazone form reaches 99%. It is most likely that the *E*-isomer stabilized by the hydrogen bond prevails in chloroform, while in DMSO two forms exist due to the distortion of the intramolecular hydrogen bond.

Table 2. Enthalpies of formation of *E*- and *Z*-hydrazones **2** and enhydrazines **2** (according to the data of PM3 calculations)

2	H^0_f/kcal mol^{-1}		
	Enhydrazine **2**	Hydrazone **2**	
		E	*Z*
a	0.514	−3.53	−0.624
b	−42.56	−47.24	−44.10
c	−10.70	−12.90	−11.19
d	−11.72	−14.97	−13.50
e	−12.10	−15.04	−13.65
f	−8.94	−12.97	−10.08
g	−8.91	−14.36	−10.36
h	−14.20	−18.62	−16.67

An unexpected reaction route was observed for the reactions of coumarinone **1** with phenyl and *p*-tolylhydrazines taken as bases. For example, when the reaction of compound **1** with phenylhydrazine is carried out in acetic acid or in toluene, a compound different from hydrazone **2a** was isolated as product. This compound is the single product, regardless of the fact whether phenylhydrazone is used in excess or in an equimolar ratio with **1**. The study of the ^{1}H and ^{13}C NMR spectra and the mass spectra suggests the structure of the formed product **3**. The ^{1}H NMR spectrum contains four downfield singlet signals, whereas no upfield signals are observed. The integral intensity of signals in the spectrum corresponds to the presence of 13 protons in the compound (Fig. 1). The ^{13}C NMR spectrum (Fig. 2) exhibits a signal at δ 179.99 corresponding to the carbonyl carbon atom in position 4 of coumarin[9] and signals of the carbon atoms of the phenyl ring. We have previously[9] proved the structures of the *Z*- and *E*-ketoenamines **4** on the basis of analysis of the ^{1}H NMR spectra, quantum chemical calculations, and X-ray diffraction study. As can be seen from Fig. 2, the chemical shifts of the carbon atoms in the ^{13}C NMR spectrum of the new compound designated as **3a** are rather close to the signals of the corresponding carbon atoms in the isomers of ketoenamines **4** shown below.

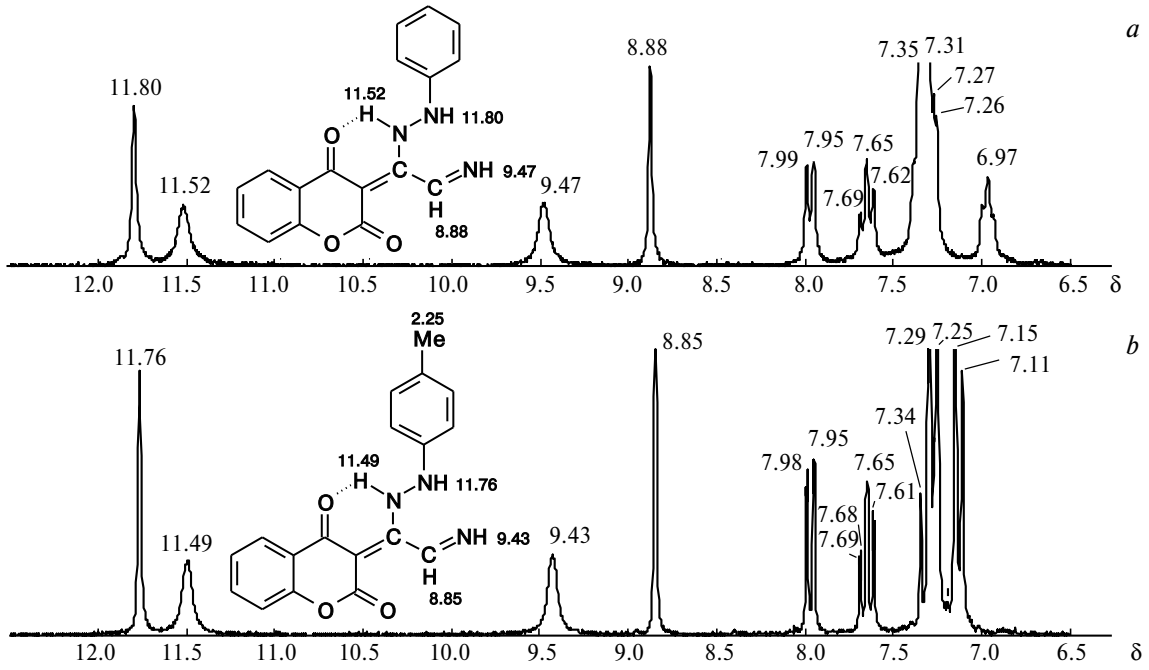


Fig. 1. ^{1}H NMR spectra of compounds **3a** (*a*) and **3b** (*b*).

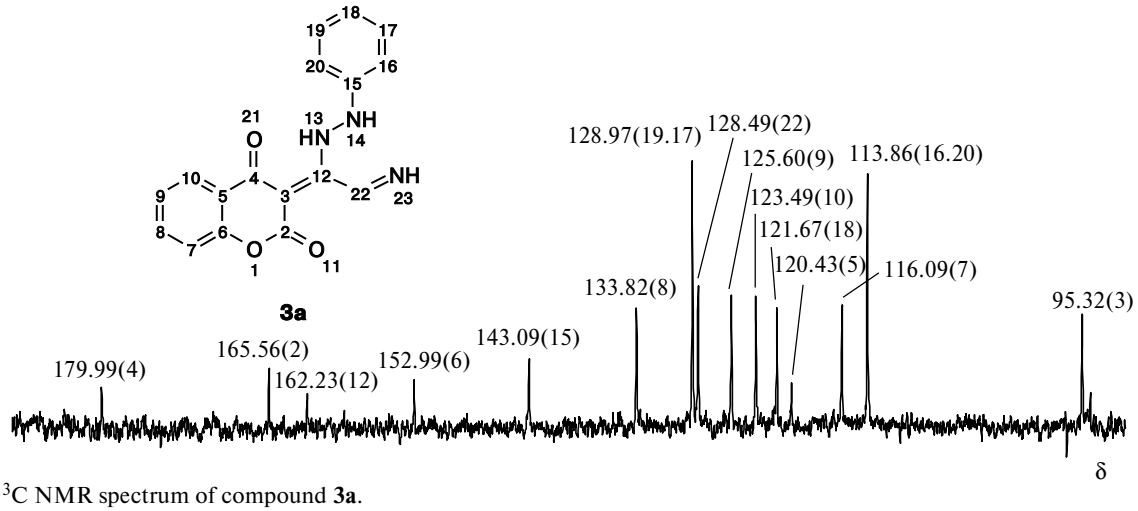
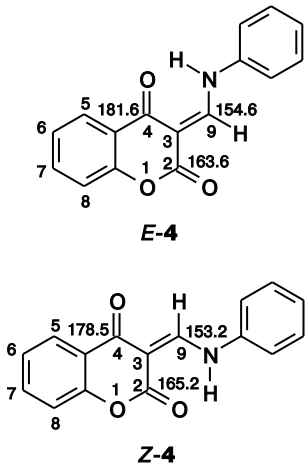


Fig. 2. ^{13}C NMR spectrum of compound **3a**.



The 2D COSY spectrum (Fig. 3) demonstrates the long-range spin-spin coupling along the CH(8.88 ppm)—NH(11.80 ppm) bonds. The spatial closeness of these groups is also indicated by the experiment on the Overhauser effect: the intensity of the signal of the NH—Ph group (δ 11.80) increased upon the suppression of the CH signal (δ 8.88), and *vice versa*, the suppression of the signal with δ 11.80 increases the intensity of the signal with δ 8.88.

Along with the molecular ion peak, the mass spectra of compound **3a** show peaks corresponding to the [M – CH=NH] and [M – NHNHPh] fragments, which also confirms the structure proposed.

Thus, it can be suggested by the data of ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry that the reaction of coumarinone **1** with phenylhydrazine affords a compound with structure **3a**.

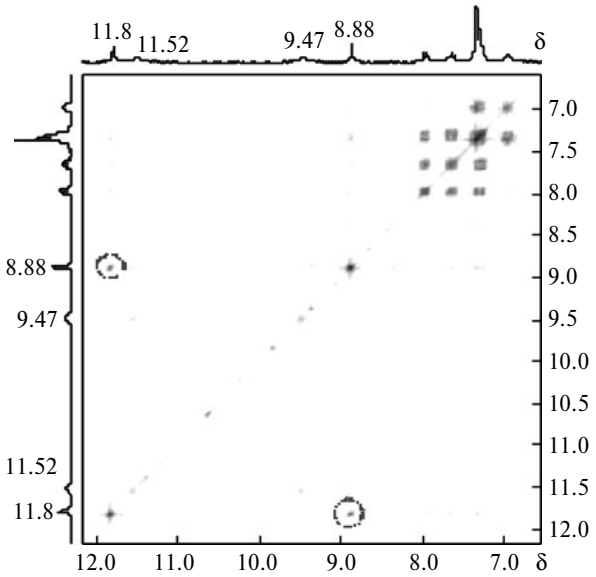
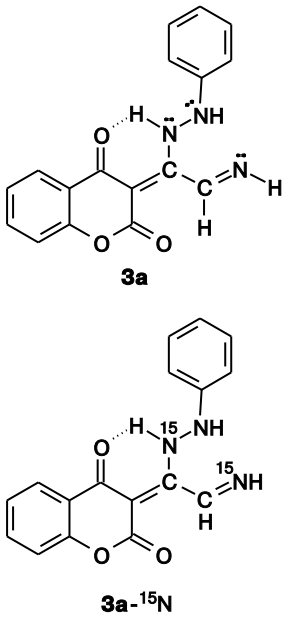


Fig. 3. ^{1}H—^{1}H COSY 2D spectrum of compound **3a**.



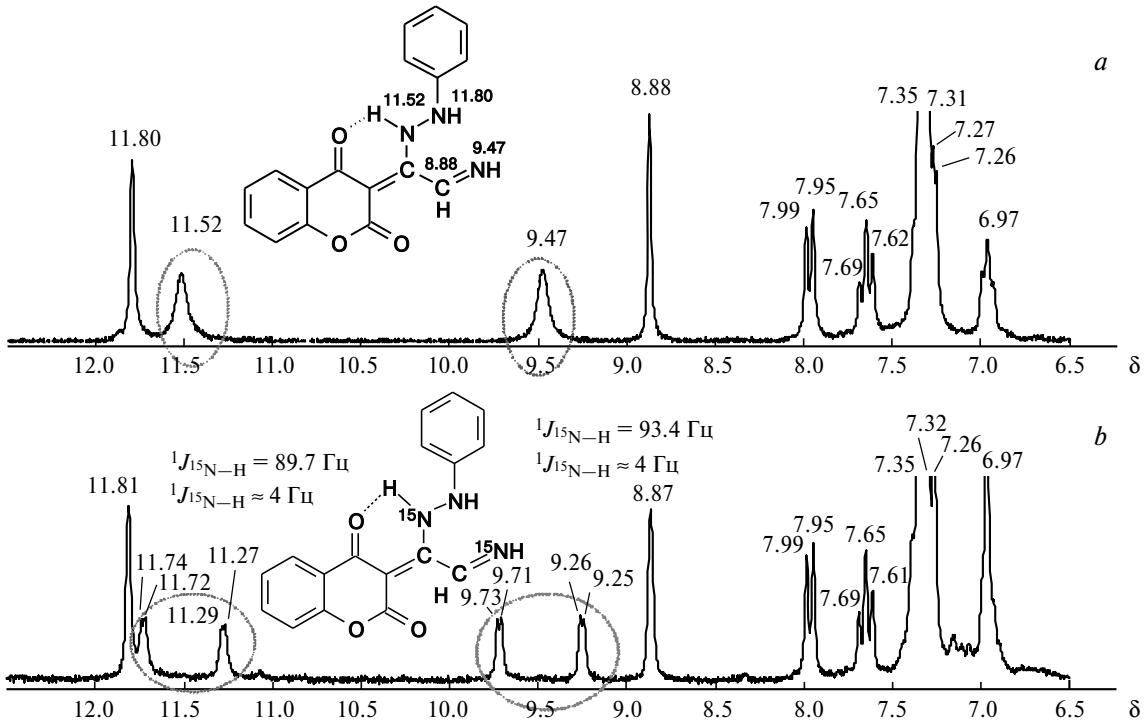


Fig. 4. ^{1}H NMR spectra of compounds **3a** (*a*) and **3a**-^{15}N (*b*).

To confirm structure **3a**, we carried out the reaction of compound **1** with labeled phenylhydrazine $C_6H_5NH^{15}NH_2$, which was prepared by the diazotization of aniline using sodium ^{15}N-nitrite. If proposed structure **3a** is valid, two labeled nitrogen atoms should appear in the molecule, which would reflect the character of the ^{1}H NMR spectrum. The spectrum of compound **3a**-^{15}N is shown in Fig. 4.

As can be seen from the spectrum (see Fig. 4), upon the introduction of labeled ^{15}N atoms, the signals with δ 11.52 and 9.47 are transformed from singlets into two doublets of doublets with the corresponding first-order SSC constants $^1J_{^{15}N-H}$ = 89.7 Hz and the subsplitting of each component of the doublet due to the long-range interaction $^{44}J_{^{15}N-H} \approx 4.6$ Hz.

When ^{15}N atoms are introduced, the signals of the CH (δ 8.88) and NH—Ph (δ 11.80) groups in the spectrum of compound **3a**-^{15}N exhibit signal splitting with $^3J_{CH,^{15}NH} \approx 1$ Hz and $^2J_{NH,^{15}NH} \approx 1.8$ Hz. The long-range SSC constants were estimated by the double resonance experiment with compound **3a**-^{15}N. The long-range constant $^5J_{CH,NH} \approx 1.8$ Hz was established for the signal of CH at δ 8.88, while the constant $^5J_{NH,CH} \approx 1.8$ Hz was found for the signal of NH—Ph at δ 11.80. The suppression of one of the signals results in a change, namely, simplification of multiplicity of another signal, *i.e.*, the effect similar to that detected in the 2D COSY spectrum is observed.

The data of mass spectrometry also confirm the formation of compounds **3a** and **3a**-^{15}N.

The formation of iminohydrazine **3a** is not a single case of such a route of interaction of compound **1** with arylhydrazines. The reaction of compound **1** with *p*-methylphenylhydrazine taken as a base in toluene affords compound **3b**, whose ^{1}H NMR spectrum resembles that of **3a** (see Fig. 1).

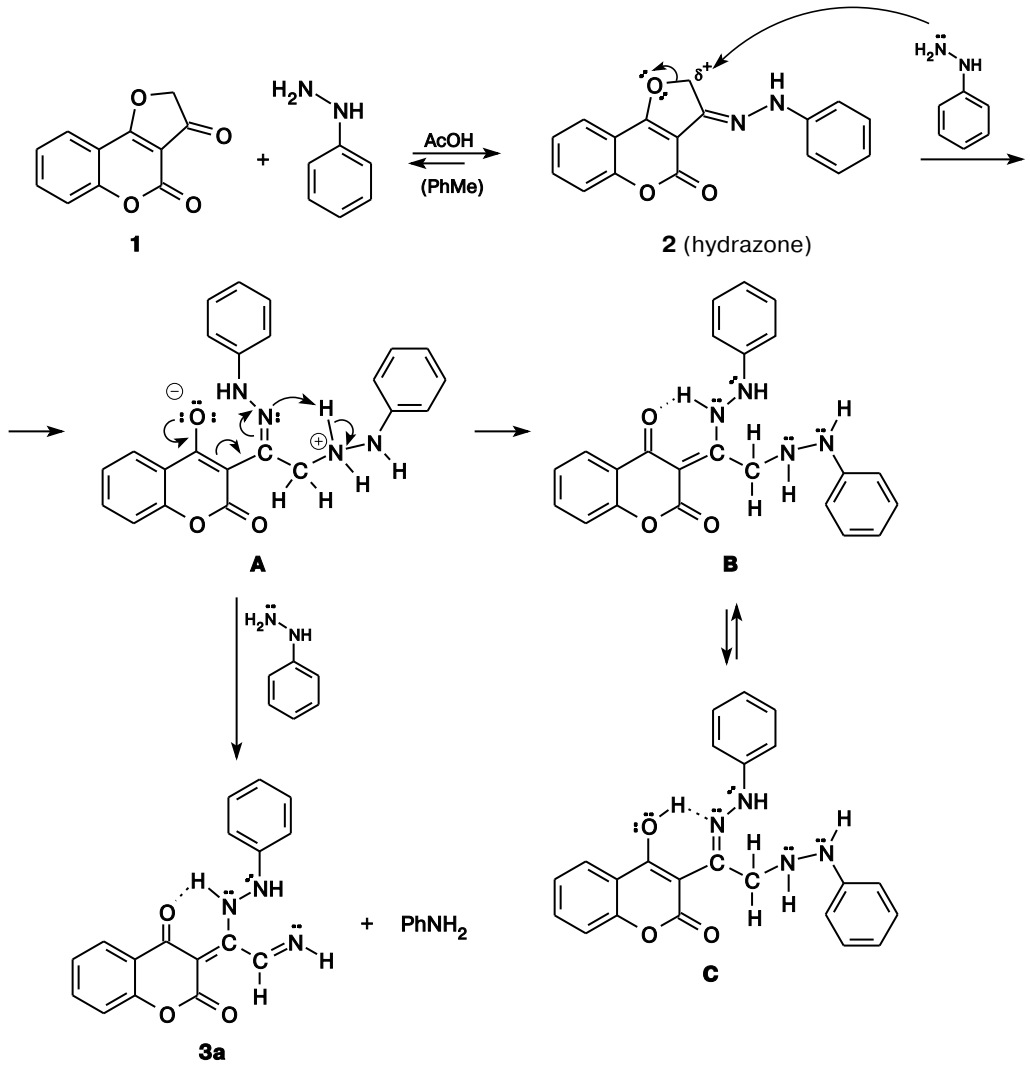
We believe that the formation of compounds **3** follows Scheme 3.

It is most probable that the reaction proceeds through the formation of hydrazone **2**. In a control experiment, hydrazone **2a** was dissolved in toluene, and phenylhydrazine (1 mol) was added during reflux. Compound **3a** was isolated after reflux for 20 min followed by cooling.

Evidently, hydrazone **2** can react with the second phenylhydrazine molecule as a nucleophile with five-membered ring opening and the formation of betaine **A**. Form **A** of betaine is in equilibrium with neutral form **B** and hydroxy form **C**. However, it is most likely that betaine form **A** undergoes subsequent elimination under the action of another phenylhydrazine molecule. Easiness of opening of just the dihydrofuran cycle is determined, most likely, by the stability of the oxide coumarin moiety in betaine **A**. It is known that 4-hydroxycoumarin is considerably acidic. Its pK_a value was experimentally estimated[10] as 5.89. We also found aniline by the ^{1}H NMR study of the reaction mixture.

There are literature data for examples of dihydrofuranone ring opening under the action of arylhydrazine.

Scheme 3



The action of *p*-nitrophenylhydrazine on 3-coumaranone **5** with the intermediate formation of hydrazone **6** and hydrazinohydrazone **7** affords[11,12] ozazone **8** (Scheme 4).

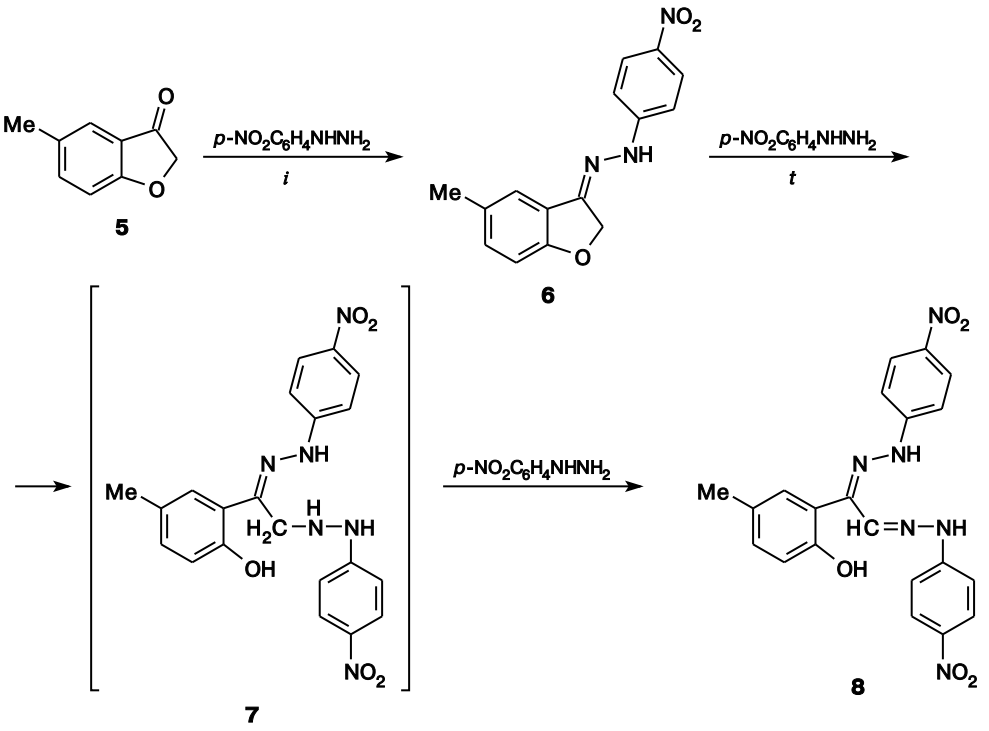
Note that we observed no dihydrofuran ring opening in the reactions of compound **1** with nitrophenylhydrazines.

The electronic absorption spectra of compounds **2** were recorded in various solvents (Table 3). As can be seen from Table 3, the absorption maxima differ insignificantly. The bathochromic shift of the long-wavelength absorption of compounds **2** on going from a polar solvent (alcohol or DMF) to nonpolar carbon tetrachloride is due, most likely, to *E*/*Z*-isomerization with a possibility of formation of the intramolecular hydrogen bond of the NH group with the carbonyl oxygen atom of the lacton moiety in the *Z*-isomer in the nonpolar solvent and its cleavage in polar solvents. The isomerization transition is confirmed by the isosbestic point on going from the polar

Table 3. Long-wavelength absorption maxima (λ_{max}) in the electronic absorption spectra of compounds **2a—h** and **3a,b** in various solvents

Compound	λ_{max}/nm (log ε)		
	CCl_4	EtOH	DMF
2a	413 (4.21)	407 (4.13)	407 (4.20)
2b	410 (4.82)	405 (4.83)	404 (4.84)
2c	407 (4.20)	390 (4.23)	395 (4.21)
2d	406 (4.27)	392 (4.39)	393 (4.35)
2e	435 (4.11)	412 (4.10)	418 (4.11)
2f	419 (4.00)	413 (3.92)	413 (3.86)
2g	438 (4.20)	442 (4.07)	438 (4.58)
2h	415 (4.72)	412 (4.64)	416 (4.30)
3a	423 (4.86)	—	418 (4.86)
3b	429 (4.62)	—	427 (4.59)

Scheme 4



i. EtOH, in cold.

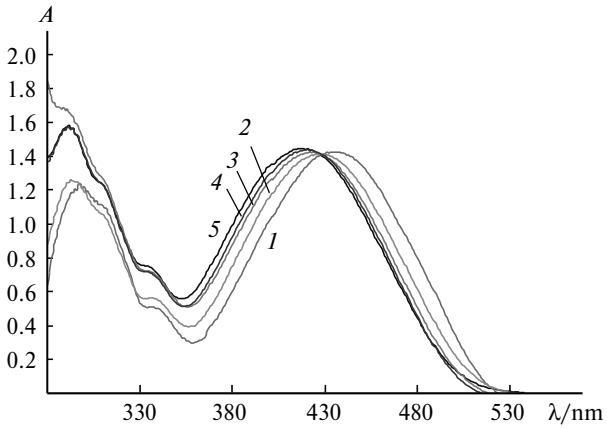


Fig. 5. Electronic absorption spectra of compound **2e** recorded at different ratios of CCl_4 and DMF: 100 : 0 (*1*), 75 : 25 (*2*), 50 : 50 (*3*), 25 : 75 (*4*), and 0 : 100 (*5*).

to nonpolar solvent (Fig. 5). As can be seen from the spectra, the *E*- and *Z*-forms only insignificantly differ by the position of the long-wavelength absorption maxima. No isosbestic points were detected in the absorption spectra of compounds **3a,b**. Therefore, we may conclude that these compounds exist in one stable form and undergo no transitions in solution.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200-SY spectrometer with the working frequency 200 MHz in deuterated solvents (DMSO-d_6 and $CDCl_3$) using Me_4Si as the internal standard.

Mass spectra were obtained on a Finnigan MAT SSQ-710 mass spectrometer with ionizing radiation energy 70 eV. The GC—MS spectrum of compound **3a** was detected on a PE SCIEX API165 (ELSD UV254 spectrometer (EI, 70 eV)), Synergi 2u Hydro-RP Mercury column 20S2.0 mm.

Electronic absorption spectra were measured on an APEL PD-303UV spectrometer. A cell filled with the solvent was used as a reference cell.

The reaction course and individual character of the compounds synthesized were monitored by TLC on Silufol UV-254 plates in the following systems of solvents: (*A*) chloroform—acetone (16 : 1); (*B*) chloroform—acetone (5 : 1); (*C*) hexane—acetone (2 : 1).

Quantum chemical calculations were performed using the HyperChem 6.0 program. Preliminary geometry optimization was carried out using the molecular mechanics method in the MM+ variant.

Reactions with arylhydrazine hydrochlorides 2a—e. Coumarinone **1** (0.3 g, 1.5 mmol) was dissolved in ethanol. A solution of hydrochloride of the corresponding arylhydrazine (2 mmol) and anhydrous sodium acetate (1.5 g, 2 mmol) in ethanol (3 mL) was prepared separately. Then a mixture of phenyl-

hydrazine with sodium acetate was added dropwise to a boiling solution of dihydrofurocoumarinone. The reaction mixture was continued to reflux until a precipitate stopped to form. After the reaction mixture cooled, hydrazone was filtered off and recrystallized from acetic acid, ethanol, or dioxane.

(3*E*)- and (3*Z*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-diones (2a) 3-(phenylhydrazones). The yield was 0.11 g (45%), m.p. 200-202 °C (from acetic acid). ^{1}H NMR (DMSO-d_6) δ: 5.50 (s, 0.5 H, CH_2(3*E*)); 5.51 (s, 0.5 H, CH_2(3*Z*)); 6.74—6.75 (m, 1 H, H(4′)); 6.90—6.94 (m, 1 H, H(2′(3*E*)), H(6′(3*Z*))); 7.05—7.30 (m, 3 H, H(6), H(8), H(2′(3*Z*)), H(6′(3*Z*)); 7.35—7.65 (m, 2 H, H(3′), H(5′)); 7.65—7.95 (m, 2 H, H(5), H(7)); 9.14 (s, 0.5 H, NH(3*Z*)); 11.00 (s, 0.5 H, NH(3*E*)). MS, *m/z* (I_{rel} (%)): 292 $[M]^+$ (50), 92 $[NHPh]^+$ (100), 186 $[M - NNHPh]^+$ (42). Found (%): C, 69.79; H, 4.30; N, 9.50. $C_{17}H_{12}N_2O_3$. Calculated (%): C, 69.86; H, 4.14; N, 9.58.

(3*E*)- and (3*Z*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-diones (2b) 3-[(4′-fluorophenyl)hydrazones]. The yield was 0.17 g (25%), m.p. 217—219 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 5.49 (s, 1 H, CH_2(3*Z*)); 5.52 (s, 1 H, CH_2(3*E*)); 6.98—7.06 (m, 4 H, H(2′), H(3′), H(5′), H(6′)); 7.30—7.65 (m, 2 H, H(6), H(8)); 7.65—8.00 (m, 2 H, H(5), H(7)); 9.13 (s, 0.5 H, NH(3*Z*)); 10.97 (s, 0.5 H, NH(3*E*)). MS, *m/z* (I_{rel} (%)): 310 $[M]^+$ (30). Found (%): C, 65.92; H, 3.60; N, 9.13. $C_{17}H_{11}FN_2O_3$. Calculated (%): C, 65.81; H, 3.57; N, 9.03.

(3*E*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-dione 3-[(2′,6′-dichlorophenyl)hydrazone] (2c). The yield was 0.22 g (41.4%), m.p. 176—178 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 5.48 (s, 2 H, CH_2); 6.98—7.06 (m, 1 H, H(4′)); 7.40—7.60 (m, 4 H, H(6), H(8), H(3′), H(5′)); 7.85—7.91 (m, 2 H, H(5), H(7)); 10.6 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 360 $[M]^+$ (22). Found (%): C, 56.57; H, 2.82; N, 7.80. $C_{17}H_{10}Cl_2N_2O_3$. Calculated (%): C, 56.53; H, 2.79; N, 7.76.

(3*E*)- and (3*Z*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-diones (2d) 3-[(2′,5′-dichlorophenyl)hydrazones]. The yield was 0.35 g (64.1%), m.p. 254—256 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 5.58 (s, 0.8 H, CH_2(3*E*)); 5.74 (s, 1.2 H, CH_2(3*Z*)); 6.78 (dd, 0.38 H, H(4′(3*E*)), $^3J_{4',3'}$ = 8.3 Hz, $^4J_{4',6'}$ = 1.8 Hz); 6.88 (dd, 0.62 H, H(4′(3*Z*)); $^3J_{4',3'}$ = 8.3 Hz, $^4J_{4',6'}$ = 1.8 Hz); 7.20—7.70 (m, 4 H, H(6), H(7), H(8), H(5′)); 7.70—8.00 (m, 2 H, H(5), H(3′)); 8.53 (s, 0.62 H, NH(3*Z*)); 11.39 (s, 0.38 H, NH(3*E*)). ^{1}H NMR ($CDCl_3$), δ: 5.44 (s, 2 H, CH_2); 6.70 (dd, 0.7 H, H(4′(3*E*)); $^3J_{4',3'}$ = 8 Hz, $^4J_{4',6'}$ = 2 Hz); 6.81 (dd, 0.3 H, H(4′(3*Z*)); $^3J_{4',3'}$ = 8 Hz, $^4J_{4',5'}$ = 2 Hz); 7.02 (s, 0.3 H, NH(3*Z*)); 7.16—7.46 (m, 4 H, H(6), H(7), H(8), H(5′)); 7.66—7.84 (m, 2 H, H(5), H(3′)); 11.36 (s, 0.7 H, NH(3*E*)). MS, *m/z* (I_{rel} (%)): 360 $[M]^+$ (80). Found (%): C, 56.50; H, 2.83; N, 7.80. $C_{17}H_{10}Cl_2N_2O_3$. Calculated (%): C, 56.53; H, 2.79; N, 7.76.

(3*E*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-dione 3-[(2′,4′-dichlorophenyl)hydrazone] (2e). The yield was 0.37 g (68%), m.p. 246—248 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 5.54 (s, 2 H, CH_2); 6.96 (dd, 1 H, H(5′), $J_{5',6'}$ = 8.6 Hz, $J_{5',3'}$ = 2.5 Hz); 7.05—7.40 (m, 2 H, H(6), H(8)); 7.40—7.65 (m, 2 H, H(7), H(9)); 7.75—8.00 (m, 2 H, H(5), H(6′)); 11.06 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 360 $[M]^+$ (68). Found (%): C, 56.51; H, 2.89; N, 7.70. $C_{17}H_{10}Cl_2N_2O_3$. Calculated (%): C, 56.53; H, 2.79; N, 7.76.

(3*E*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-dione 3-[(4′-methylphenyl)hydrazone] (2f). Coumarinone **1** (0.4 g, 2 mol) was dissolved in ethanol. A solution of *p*-methylphenylhydrazine hydrochloride (2.2 mmol) and triethylamine (0.15 g, 2.2 mmol) in ethanol (3 mL) was prepared separately. Then a mixture of *p*-methylphenylhydrazine with triethylamine was added dropwise to the boiling solution of dihydrofurocoumarinone. The reaction mixture was refluxed until a precipitate stopped to form. After the reaction mixture was cooled down, hydrazone was filtered off and recrystallized from EtOH. The yield was 0.3 g (50%), m.p. 185—187 °C (from EtOH). ^{1}H NMR (DMSO-d_6), δ: 2.22 (s, 3 H, Me); 5.49 (s, 2 H, CH_2); 7.03 (s, 4 H, H(2′), H(3′), H(5′), H(6′)); 7.40—7.53 (m, 2 H, H(6), H(8)); 7.71—7.85 (m, 2 H, H(5), H(7)); 9.03 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 306 $[M]^+$ (43), 201 $[M - NHC_6H_4Me + 1]^+$ (10), 187 $[M - NNHC_6H_4Me + 1]^+$ (40), 121 $[NNHC_6H_4Me + 1]^+$ (50), 106 $[NHC_6H_4Me]^+$ (100), 91 $[C_6H_4Me]^+$ (95). Found (%): C, 71.01; H, 4.62; N, 9.35. $C_{18}H_{14}N_2O_3$. Calculated (%): C, 70.58; H, 4.61; N, 9.15.

Reaction of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one with nitrophenylhydrazines. A solution of nitrophenylhydrazine (2 mmol) in 3 mL of acetic acid (or in 5 mL of toluene). The precipitate that formed was filtered off. Recrystallization was carried out from acetic acid or dioxide.

(3*E*)-4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-dione 3-[(4′-nitrophenyl)hydrazone] (2g). The yield was 0.48 g (94.5%), m.p. 281—283 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 5.58 (s, 2 H, CH_2); 7.23 (d, 2 H, H(2′), H(6′), *J* = 8.80 Hz); 7.4—7.6 (m, 2 H, H(6), H(8)); 7.75—7.95 (m, 2 H, H(5), H(7)); 8.14 (d, 2 H, H(3′), H(5′)); 10.15 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 337 $[M + 1]^+$ (90), 336 $[M - 1]^+$ (20). Found (%): C, 60.03; H, 3.32; N, 12.50. $C_{17}H_{11}N_3O_5$. Calculated (%): C, 60.54; H, 3.29; N, 12.46.

4*H*-Furo[3,2-*c*]chromene-3,4(2*H*)-dione 3-[(2,4-dinitrophenyl)hydrazone] (2h). The yield was 0.26 g (46%), m.p. 284—286 °C (from DMF). The ^{1}H NMR spectrum was not detected because of the very low solubility of the substance. MS, *m/z* (I_{rel} (%)): 383 $[M + 1]^+$ (100), 384 $[M + 2]^+$ (20). Found (%): C, 52.99; H, 2.60; N, 14.71. $C_{17}H_{10}N_4O_7$. Calculated (%): C, 53.41; H, 2.64; N, 14.66.

Reaction of coumarinone 1 with phenylhydrazine and *p*-methylphenylhydrazine. A solution of the corresponding phenylhydrazine (7.5 mmol) in toluene (3 mL) was added dropwise to a boiling solution of coumarinone **1** (0.5 g, 2.5 mmol) in toluene (30 mL). The reaction mixture was refluxed for 15 min. After cooling of the reaction mixture, the precipitate was filtered off and recrystallized from acetic acid or toluene.

(*Z*)-3-[2-Imino-1-(2-phenylhydrazinyl)ethylidene]chromane-2,4-dione (3a). The yield was 0.38 g (50%), m.p. 299—301 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 6.95—6.99 (m, 1 H, H(4′)); 7.26—7.35 (m, 6 H, H(6), H(8), H(2′), H(3′), H(5′), H(6′)); 7.62—7.69 (m, 1 H, H(7)); 7.97 (d, 1 H, H(5) $J_{5,6}$ = 8 Hz); 8.88 (s, 1 H, CH); 9.47 (s, 1 H, =NH); 11.52 (s, 1 H, —NH); 11.80 (s, 1 H, N<u>H</u>—Ph). MS, *m/z* (I_{rel} (%)): 308 $[M + 1]^+$ (100), 307 $[M]^+$ (90), 279 $[M - CH{=}NH]^+$ (20), 216 $[M - Ph{-}NH]^+$ (22). Found (%): C, 66.50; H, 4.35; N, 13.70. $C_{17}H_{13}N_3O_3$. Calculated (%): C, 66.40; H, 4.26; N, 13.67.

(*Z*)-3-[2-Imino-1-(2-phenylhydrazinyl)ethylidene]chromane-2,4-dione (3a-^{15}N). ^{1}H NMR (DMSO-d_6), δ: 6.95—6.99 (m, 1 H, H(4′)); 7.26—7.35 (m, 6 H, H(6), H(8), H(2′), H(3′), H(5′), H(6′)); 7.62—7.69 (m, 1 H, H(7)); 7.97 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.87 (s, 1 H, CH); 9.47 (dd, 1 H, =NH, $^1J_{^{15}N-H}$ = 89.7 Hz, $^4J_{^{15}N-H} \approx$ 4.6 Hz); 11.52 (dd, 1 H, —NH, $^1J_{^{15}N-H}$ = 93.4 Hz, $^4J_{^{15}N-H} \approx$ 4.6 Hz); 11.81 (s, 1 H, N<u>H</u>—Ph).

MS, m/z (I_{rel} (%)): 309 $[M]^+$ (15), 201 $[M - {}^{15}NHNHPh]^+$ (90), 92 $[NHPh]^+$ (100).

(*Z*)-3-[2-Imino-1-(2-*p*-tolylhydrazinyl)ethylidene]chromane-2,4-dione (3b). The yield was 0.12 g (25%), m.p. 260—261 °C (from acetic acid). ^{1}H NMR (DMSO-d_6), δ: 2.25 (s, 1 H, Me); 6.95—6.99 (m, 1 H, H(4′)); 7.26—7.35 (m, 6 H, H(6), H(8), H(2′), H(3′), H(5′), H(6′)); 7.62—7.69 (m, 1 H, H(7)); 7.97 (д, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.85 (s, 1 H, CH); 9.43 (s, 1 H, =NH); 11.49 (s, 1 H, —NH); 11.76 (s, 1 H, NH—Ph). MS, m/z (I_{rel} (%)): 321 $[M]^+$ (5), 320 $[M - 1]^+$ (15), 201 $[M - NHNHPhMe - 1]^+$ (67), 121 $[NHNHPhMe]^+$ (50), 107 $[NHPhMe - 1]^+$ (67), 91 $[PhMe]^+$ (100). Found (%): C, 67.25; H, 4.80; N, 13.18. $C_{18}H_{15}N_3O_3$. Calculated (%): C, 67.28; H, 4.71; N, 13.08.

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