Structure and solvatochromic properties of the azo coupling products of 2,3-dihydrofuro[3,2-*c*]cumarin-3-one

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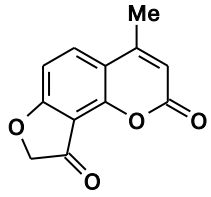
The azo coupling reaction of 2,3-dihydrofuro[3,2-*c*]-coumarin-3-one with the arenediazonium salts was studied. The dependence of the product composition on the structure of the diazo component was shown. The solvatochromic properties of the compounds obtained were studied.

Key words: furocoumarinones, hydrazones, azo coupling, tautomerism, azo enol, azo ketone, keto hydrazone, labeled nitrogen atom, solvatochromism, electronic absoprtion spectra.

Furocoumarins differ by the expressed photochemical activity and valuable spectral properties.[1—5] For example, many of these compounds are capable of considerable change in the fluorescence intensity upon intercalation into the DNA structures.[6] Such compounds are useful in investigation of the structures of proteins and nucleic acids. Using these compounds, the high-sensitivity and specific rapid methods for diagnostics of various diseases and pathologies inducing changes in the structures of nucleic acids may be developed.[2,7] The absorption and emission spectra of furocoumarin derivatives are also susceptible to other effects (complexation with metal ions, solvent effect and pH value), which may be of interest for design of sensing elements.

Earlier,[8,9] we have developed several new approaches to synthesis of furocoumarins and their derivatives and shown that dihydrofurocoumarins **1** and **2** are valuable



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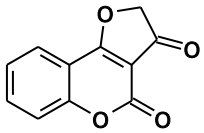

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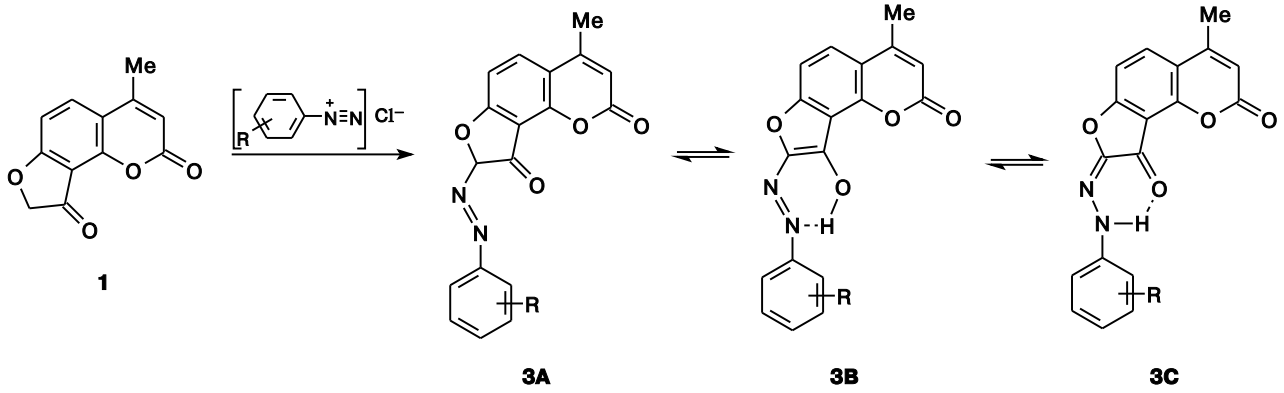
intermediates for preparation of both furocoumarins and their derivatives substituted at the furan ring. In particular, the azo coupling reaction, which allows elongation of the chaing length, affords compounds that *a priori* tend to tautomeric transformations, which allow expectation of interesting spectral properties.

For example, in the azo coupling reaction of 4-methyldihydro[2,3-*h*]coumarin-9-one (**1**) with the arenediazonium

Scheme 1



1 **3A** **3B** **3C**

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salts (Scheme 1), a mixture of tautomers, *viz.*, azo ketone **3A**, azo enol **3B**, and keto hydrazone **3C**, is produced. According to the spectral data, azo compounds **3A—C** exist in the form of keto hydrazones **3C** (see Refs 10, 11).

In the present work, we studied the azo coupling reaction of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one (**2**) with the arenediazonium salts and the properties of the compounds obtained. Dihydrocoumarin **2** is of great interest as starting compound, since, the products possessing intense fluorescence have earlier been synthesized by condensation of **2** with the heteroaromatic aldehydes and amines.[12,13]

Azo coupling of compound **2** with the diazo compounds obtained from substituted anilines in a dioxane—acetic acid mixture (1 : 1) in the presence of catalytic amounts of pyridine affords compounds **4a—k** (Scheme 2). The use of a mixture of dioxane and acetic acid is due to the low solubility of compound **2**.

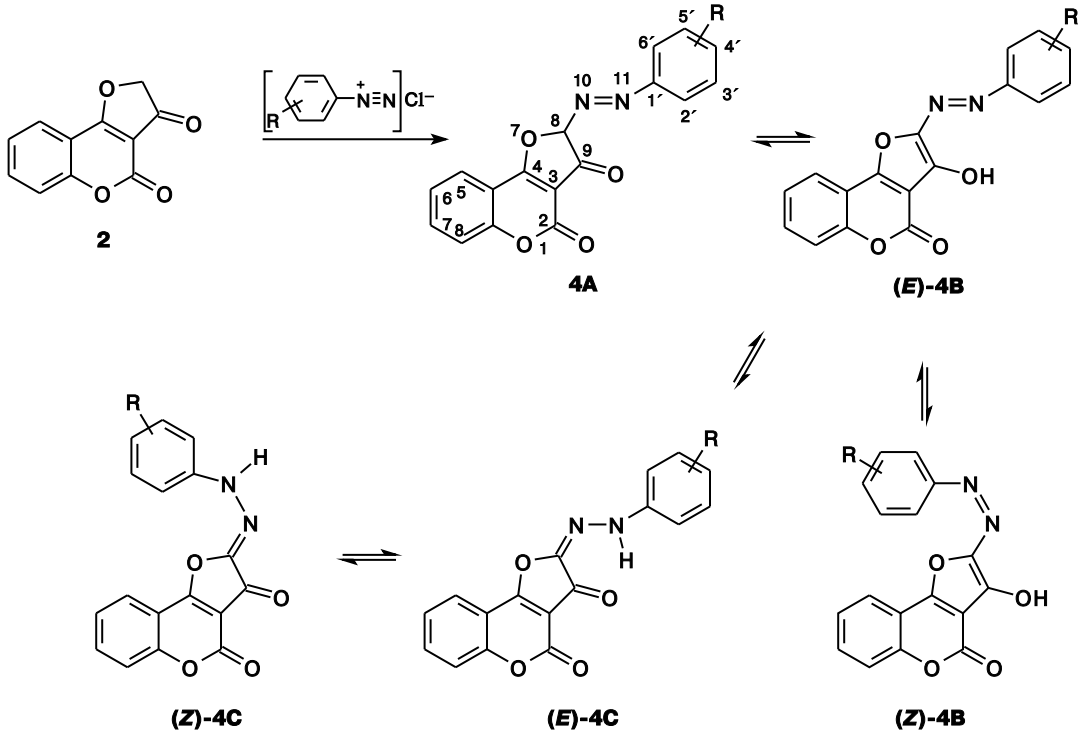
The structures and composition of the synthesized compounds **4a—k** were confirmed by the data from ^{1}H NMR, mass spectroscopy and elemental analysis. For example, the characteristic signals for the protons of coumarin fragment and aromatic ring of azo compound are observed in the ^{1}H NMR spectra in the region of 7.00—8.30. The signal for the proton H(5) of the coumarin fragment in the form of doublet of doublets (except for *p*-nitro derivative **4b**) is shifted downfield and a multiplet is observed in the upper field region, which corresponds to the signals for the protons H(6) and H(8).

By theory, the azo coupling products **4** can be in three forms: azo ketone **4A**, azo enol **4B** or keto hydrazone **4C** (see Scheme 2).

However, the ^{1}H NMR spectral data unambiguously suggest the absence of the azo ketone form **A**, which should be characterized by the signal for proton of furan ring in the region of δ 5. It is difficult to draw the unambiguous conclusion in favor of the azo enol form **B** or keto hydrazone form **C**. The ^{1}H NMR spectra of all compounds **4a—k** contains the downfield signal at δ about 11 and, for compounds **4g—k** having *ortho*-substituent in the benzene ring, a further downfield signal is observed in the region of δ ≈ 12. The ^{1}H NMR spectrum (DMSO-d_6) of compound **4a** in a freshly prepared solution contains, besides the signal at δ 11.2, a further broadened low-intensity signal at δ 11.87, which disappears after 1 day with the intensity of signal at δ 11.2 being increased.

The unambiguous assignment of the said signals to the protons of NH and OH groups was made based on the analysis of the ^{1}H NMR spectra of compounds **4** ^{15}N-labeled on the N(10) atom. The latters were prepared

Scheme 2



4: R = H (**a**), R = 4-NO_2 (**b**), R = 4-OMe (**c**), R = 4-Cl (**d**), R = 4-Br (**e**), R = 4-Me (**f**), R = 2-NO_2 (**g**), R = 2-OMe (**i**), R = 2-Cl (**h**), R = 2-Me (**k**)

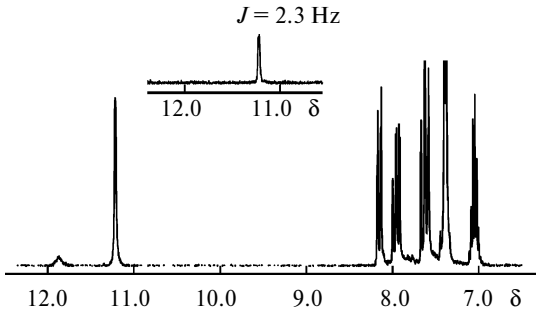


Fig. 1. The ^{1}H NMR spectrum of a freshly prepared solution of the ^{15}N-labeled compound **4a** in DMSO-d_6. Insert: the downfield spectrum region after 1 day of the sample preparation.

Table 1. The chemical shifts for the protons of the NH and OH groups in the ^{1}H NMR spectra (DMSO-d_6, δ) of compounds **4a—k** and the content of tautomeric forms*

Tautomer	δ	
	NH (keto hydrazone)	OH (azo enol)
4a	11.22 (90)	11.87 (10)
4b	11.69 (100)	—
4c	11.28 (100)	—
4d	11.37 (100)	—
4e	11.12 (100)	—
4f	11.12 (100)	—
4g	11.22 (45)	13.51 (55)
4h	10.06 (52)	12.12 (48)
4i	9.98 (60)	12.08 (40)
4k	10.13 (70)	12.01 (30)

* The percentages of tautomeric forms are given in parentheses.

by the reaction of **2** with the ^{15}N-labeled benzenediazonium salts, which, in turn, were synthesized by diazotation of aniline and *o*-chloroaniline with the ^{15}N-labeled sodium nitrite.

As is seen from the ^{1}H NMR spectra, there are two tautomeric forms in a freshly prepared solution of the ^{15}N-labeled solution of compound **4a**, but only one predominant form remains after 1 day (Fig. 1). The singlet at δ 11.22 is splitted into doublet through spin-spin coupling with the ^{15}N nucleus ($^2J_{^{15}N,NH}$ = 2.3 Hz). Thus, the abovementioned signal relates to the proton of hydrazone group of tautomer **C** of compound **4a** and the low-intensity signal at δ 11.87 observed in a freshly prepared solution should be assigned to the proton of hydroxyl group of the azo enol form **B**.

If the *ortho*-substituent is present in the benzene ring, the pattern of spectrum is not changed with time and the ratio and intensity of signals remain constant. For example, introduction of the ^{15}N isotope into the position N(10) of the *o*-chloro derivative **4h** leads to splitting of the signal at δ 10.06 into doublet ($^2J_{^{15}N,NH}$ = 1.85 Hz) and, consequently, this signal relates to the proton of the NH group of the keto hydrazone form **C**. At the same time, the singlet at δ 12.12 remains unchanged and we believe that it belongs to the OH group of the azo enol form **B** of compound **4h**.

The chemical shifts of the NH and OH protons, as well as the contents of tautomeric forms are given in Table 1. The contents of tautomers were determined from the ratio of integral intensities of the signals for the proton H(5) of the coumarin fragment of the azo enol and keto hydrazone forms, as well as of the signals for the NH proton of keto hydrazone **C** and OH proton of the corresponding azo enol **B**.

It should be noted that the signal for the OH group of the *o*-nitro derivative **4g** is downfield shifted by an

Table 2. The enthalpies of formation (H_f°) of keto hydrazone and azo enol tautomeric forms of compounds **4a—k** in the presence (I) and in the absence (II) of the intramolecular hydrogen bond according to the quantum chemical calculation by the PM3 method

Tautomer	$-H_f^\circ$/kcal mol^{-1}					
	E-azo enol		*Z*-azo enol	*E*-keto hydrazone		*Z*-keto hydrazone
	I	II		I	II	
4a	25.69	25.12	19.74	25.69	28.18	26.59
4b	33.43	32.95	27.37	33.43	36.88	35.30
4c	64.12	63.58	58.13	64.12	66.06	64.38
4d	32.22	31.65	26.24	32.22	34.71	33.13
4e	17.65	17.08	11.63	17.65	20.25	18.67
4f	35.24	34.68	29.32	35.24	37.63	36.05
4g	31.81	29.51	19.83	33.66	33.71	30.26
4h	31.60	29.72	25.18	31.60	34.01	32.80
4i	60.80	60.07	54.86	61.81	63.85	62.80
4k	33.50	32.31	27.17	33.51	36.05	34.79

average of 1.5 ppm compared to other *ortho*-substituted compounds **4d—f**. The signal for the NH group is also downfield shifted (see Table 1). The above-mentioned shifts of the signals for the OH and NH groups can be associated with the capability of nitro group to form intramolecular hydrogen bonds.[14]

Evidently, keto hydrazones **C** exist only as *E*-isomers. According to the quantum chemical calculations performed in two variants: taking into account the possibility of hydrogen bonding and in the absence of hydrogen bonds, the enthalpies of formation of the *E*-isomers are by 1—2 kcal mol^{-1} lower than those of the *Z*-isomers (Table 2). In addition, no doubling of the signals for protons in the ^{1}H NMR spectra was noted in any case. The same also relates to the azo enols. The enthalpies of formation of the *E*-isomers of azo enols **B** are by 6 kcal mol^{-1} lower than those of the *Z*-isomers. At the same time, the energy of formation of keto hydrazone **C** is by an average of 5 kcal mol^{-1} lower than that of the corresponding azo enol **B**. This agrees well with the fact that it is keto hydrazone, which is the predominant form according to the ^{1}H NMR spectral data (see Table 1).

The mass spectral data confirm the presence of the keto hydrazone (**C**) and azo enol (**B**) forms of the azo coupling products. The spectrum of each compound displays the characteristic peak of molecular ion corresponding to the value of molecular weight of the compound. The molecular ions of compound **4** undergo fragmentation under electron impact to form the species R—C_6H_4—NH—N=C. In addition, the characteristic peak with *m/z* 189 suggests formation of the fragment of the azo enol form through simultaneous cleavage of two bonds in the furan ring to eliminate the fragment R—C_6H_4—N=N—C. For compound **4a,g—k**, the characteristic peaks corresponding to the fragment R—C_6H_4—N=N are observed, which also suggests the presence of the azo enol form.

The existence of compounds **4** in different tautomeric forms was also confirmed by electronic absorption spectroscopy. To investigate solvatochromic properties of the compounds obtained, the electronic absoprtion spectra (EAS) in DMF—CCl_4 mixtures were recorded. On going from the polar solvent to non-polar one, the spectra of all compounds synthesized display isosbestic point, which unambiguously evidenced the tautomeric form (Fig. 2).

In the EAS of compounds **4** obtained with the use of the benzenediazonium salt and diazonium salts containing electron-releasing substituents in the benzene ring, a hypsochromic shift of the longest wavelength band is observed on going from CCl_4 to DMF. To elucidate the nature of the spectral changes observed, quantum chemical calculations of the absorption spectra of different tautomeric forms of compound **4** were performed by the Pariser—Parr—Pople method taking into account configuration interactions (PPP-CI). This method provides,

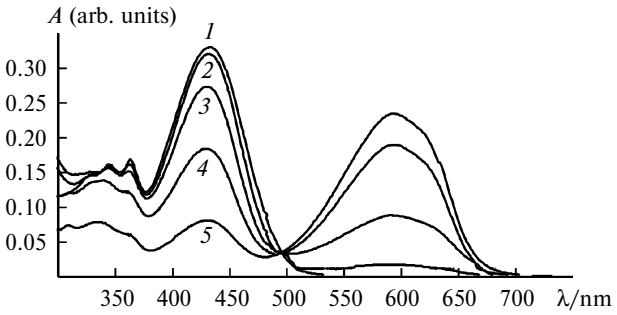
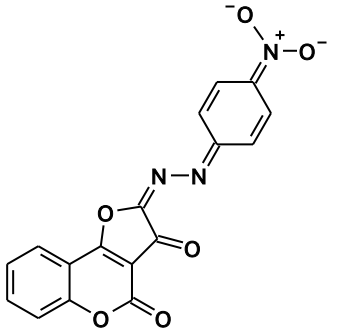


Fig. 2. The electronic absorption spectra of compound **4** recorded at different ratios of CCl_4 to DMF: *1* — CCl_4, *2—4* — CCl_4—DMF mixtures with the 3 : 1 (*2*), 1 : 1 (*3*), and 1 : 3 (*4*) ratios, *5* — DMF.

in general, a well description for the EAS of complex π-conjugated systems. At the same time, the calculation results often depend on the adequate choice of atomic and bond parameters. Earlier,[15] we have shown that the reliability of analysis of such systems is determined by the objectivity of taking account of intramolecular hydrogen bonding and molecule geometry.

For calculation of the EAS of compounds **4a—k**, the standard parameters taking into account intramolecular hydrogen bonding of carbonyl and hydroxyl groups were applied.[16] Scheme 2 shows a part of the most probable tautomeric forms and their geometric isomers that were calculated by the PPP-CI method. Table 3 presents experimental data and the results of calculations of the EAS of compounds **4** by the PPP-CI method.

The analysis of calculation data allows one to suggest that non-polar solvents displace equilibrium in favor of the keto hydrazone form **C** and polar solvents displace equilibrium in favor of the azo enol form **B**. The considerable differences as compared with compounds **4a,c,f** were observed in the EAS of the compounds obtained from the arenediazonium salts bearing electron-withdrawing substituents. In particular, in the absorption spectra of compound **4b** in DMF, a new absorption band appears in a considerably more long-wave region compared to the spectrum of this compound in CCl_4 (see Fig. 2). As shown by the



4b(D)

Table 3. Experimental* and calculated by the PPP-CI method parameters for the electronic absorption spectra of compounds **4a—k**

Tautomer	λ_{max}^{exp}/nm (log ε)		λ_{max}^{calc}/nm (*f*)**	
	CCl_4	DMF	*E*-keto hydrazone	*E*-azo enol
4a	451 (18.14)	434 (14.86)	477.13 (1.01)	417.60 (1.31)
4b	432 (12.06)	592 (8.96) 429 (3.33)	477.89 (1.17)	426.47 (1.40)
4c	452 (5.04)	434 (3.65)	494.48 (1.05)	423.97 (1.37)
4d	451 (18.9)	435 (13.36) 537 (2.8)	482.00 (1.02)	419.24 (1.33)
4e	438 (4.26)	438 (4.13) 525(3.96)	—	—
4f	466 (14)	446 (11.83)	—	—
4g	446 (17.4)	445 (10.6) 530 (3.56)	490.78 (0.79)	436.07 (1.09)
4h	447 (4.30)	432 (4.15) 534 (3,54)	482.59 (1.00)	419.87 (1.28)
4i	477 (7.76)	457 (5.9)	499.85 (0.98)	430.14 (1.21)
4k	469 (15.4)	442 (9.9)	—	—

* The observed values of λ_{max} are given. The difference in the experimental curves provides considerably better convergence of the calculated and experimental values. ** The values of oscillator strength *f* are given in parentheses.

PPP-CI calculations, the emergence of a new long-wavelength maximum cannot be explained by hydrogen bonding and transitions between the *E*- and *Z*-isomers. Probably, the emergence of a new long-wavelength absorption band in the spectrum of compound **4b** in DMF is caused by ionization to form the corresponding quinoid form **D**.

In the spectrum of compound **4b**, the long-wavelength band with the maximum at 592 nm also observed in DMSO, which also has a basic character.[17,18] Formation of the ionized quinoid form **D** is also evindeced by the dependence of the absorption spectra of compounds **4** on the pH of solutions. For example, in the case of compound **4b**, addition of Et_3N increases the intensity of long-wavelength maximum, while addition of acetic acid inhibits deprotonation of compound **4b** (Fig. 3). Addition of Et_3N also causes the emergence of long-wavelength band with the maximum at 524 nm in the spectrum of compound **4a**.

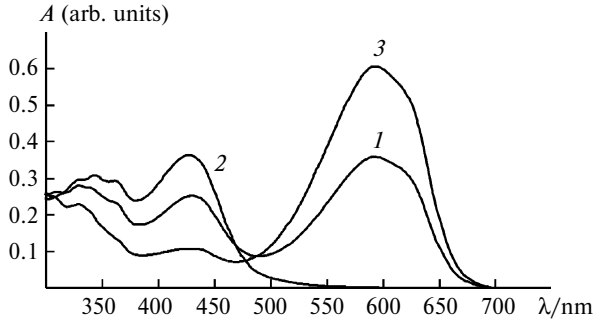


Fig. 3. The electronic absorption spectra of compound **4b** in DMF before (*1*) and after addition of acetic acid (*2*) and triethylamine (*3*) to the starting solution of **4b**.

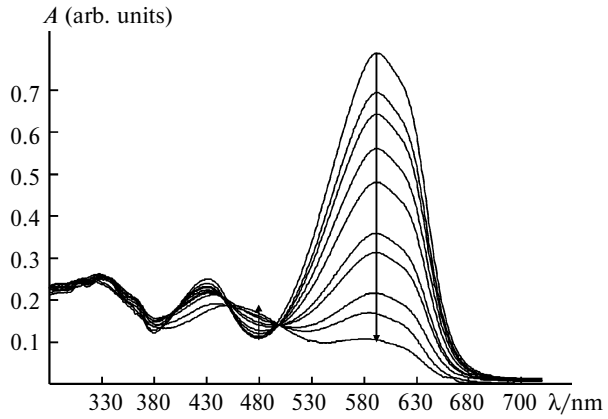


Fig. 4. The change in the electronic absorption spectrum of compound **4b** in DMF for 3 h.

Compounds **4** are stable upon storage in crystalline state and in solutions of the non-polar solvents (CCl_4, benzene). At the same time, discoloration of solutions of compounds **4** in the polar solvents (EtOH, DMF, DMSO) is observed. Fig. 4 shows changes in the absorption spectra of compound **4b** in solutions in DMF. We are studying at present the unusual behavior of compounds **4** in the above-mentioned solvents, the results of study will be presented in the next publications.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200-SY (200 MHz) spectrometer using Me_4Si as the internal standard. Mass spectra were recorded on a Kratos mass spectrometer (EI, 70 eV, direct injection). Electronic absorption spectra were

recorded on a APEL PD-303 UV spectrofotometer in DMF and DMF—CCl_4 mixtures of variable composition at the sample concentration of 10^{-4} mol L^{-1}. The course of reaction and the individuality of the compounds obtained were monitored by TLC on Sillufol UV 254 plates (the eluents were acetone, chloroform—acetone (1 : 1), hexane—acetone (2 : 1)).

The quantum chemical calculations of enthalpies of formation were performed by the semiempirical PM3 method in the HyperChem 6.0 program package. Preliminary geometry optimization was carried out using the molecular mechanics method in the MM^+ variant. The quantum chemical calculations of electronic absorption spectra were performed by the PPP-CI method in the π-approximation using the standard values of parameters taking into account intramolecular hydrogen bonding for the carbonyl, hydroxyl, and amino groups.[17]

Azo coupling of 2,3-dihydro[3,2-*c*]coumarin-3-one (2) with the arenediazonium salts (general procedure). 2,3-Dihydro-[3,2-*c*]coumarin-3-one (**2**) (2 g, 0.01 mol) was dissolved in glacial AcOH (20 mL) and pyridine (2 mL) was added. The solution obtained was mixed with a solution of the corresponding arenediazonium salt (0.01 mol) and stirred for 7 h at room temperature. The resulting solution was kept for 6 h. The precipitate formed was filtered off, washed with acetone, and recrystallized from an AcOH—DMSO mixture.

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-phenylhydrazine (4a). The yield was 1.08 g (35.3%), amorphous orange-red powder, m.p. 293—295 °C. Found (%): C, 65.83; H, 3.26; N, 10.02. $C_{17}H_{10}N_2O_4$. Calculated (%): C, 66.67; H, 3.29; N, 9.15. ^{1}H NMR (DMSO-d_6), δ: 7.00—7.07 (m, 1 H, H(4′)); 7.36—7.47 (m, 4 H, H(2′), H(3′), H(5′), H(6′)); 7.57—7.65 (m, 2 H, H(6), H(8)); 7.91—7.99 (m, 1 H, H(7)); 8.13 (dd, 1 H, H(5), ^3J = 7.8 Hz, ^4J = 1.39 Hz); 11.22 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 306 $[M]^+$ (3), 189 $[M - PhN{=}N{-}C]^+$ (8), 118 $[PhNH{-}N{=}C]^+$ (22), 105 $[PhN{=}N]^+$ (5), 91 $[PhN]^+$ (100), 77 $[C_6H_5]^+$ (54).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(4-nitrophenyl)hydrazone (4b). The yield was 1.33 g (38%), amorphous brown-yellow powder, m.p. 316—318 °C. Found (%): C, 55.3; H, 2.44; N, 11.83. $C_{17}H_9N_3O_6$. Calculated (%): C, 53.13; H, 2.58; N, 11.96. ^{1}H NMR (DMSO-d_6), δ: 7.5 (d, 2 H, H(2′), H(6′), ^3J = 9.12 Hz); 7.55—7.70 (m, 2 H, H(6), H(8)); 7.94—8.02 (m, 1 H, H(7)); 8.11 (dd, 1 H, H(5), ^3J = 8.0 Hz, ^4J = 1.4 Hz); 8.25 (d, 2 H, H(3′), H(5′), ^3J = 9.12 Hz); 11.69 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 351 $[M]^+$ (20), 189 $[M - 4\text{-}NO_2C_6H_4N{=}N{-}C]^+$ (100), 163 $[4\text{-}NO_2C_6H_4NH{-}N{=}C]^+$ (15), 136 $[4\text{-}NO_2C_6H_4N]^+$ (18), 121 $[4\text{-}NO_2C_6H_4]^+$ (55), 92 $[C_6H_4O]^+$ (43), 76 $[C_6H_4]^+$ (13).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(4-chlorophenyl)hydrazone (4c). The yield was 1.26 g (37%), amorphous maroon powder, m.p. 274—275 °C. Found (%): C, 60; H, 2.65; N, 7.95; Cl, 10.03. $C_{17}H_9N_2O_4Cl$. Calculated (%): C, 59.93; H, 2.66; N, 8.22; Cl, 10.41. ^{1}H NMR (DMSO-d_6), δ: 7.34—7.45 (m, 4 H, Ar); 7.57—7.65 (t, 2 H, H(6), H(8), ^3J = 8.0 Hz, ^4J = 1.8 Hz); 7.9—8.0 (m, 1 H, H(7)); 8.11 (dd, 1 H, H(5), ^3J = 8.0 Hz, ^4J = 1.4 Hz); 11.28 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 340 [M] (28), 189 $[M - 4\text{-}ClC_6H_4N{=}N{-}C]$ (27), 152 $[4\text{-}ClC_6H_4NH{-}N{=}C]$ (20), 144 $[M - 4\text{-}ClC_6H_4N{=}N{=}C - 2\,CO - O]$ (7), 125 $[4\text{-}ClC_6H_4N]$ (70), 111 $[4\text{-}ClC_6H_4]^+$ (20), 99 $[4\text{-}ClC_5H_4]^+$ (54), 92 $[C_6H_4O]^+$ (73).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(4-bromophenyl)hydrazone (4d). The yield was 1.85 g (47.8%), amorphous canary-yellow powder, m.p. 294—295 °C. Found (%): C, 53.02; H, 2.47; N, 7.43; Br, 20.96. $C_{17}H_9N_2O_4Br$. Calculated (%): C, 53.01; H, 2.36; N, 7.27; Br, 20.75. ^{1}H NMR (DMSO-d_6), δ: 7.33 (d, 2 H, H(2′), H(6′), ^3J = 8.0 Hz); 7.51—7.60 (m, 4 H, H(6), H(8), H(3′), H(5′)); 7.93 (t, 1 H, H(7), ^3J = 8.0 Hz); 8.10 (dd, 1 H, H(5), ^3J =8.0 Hz, ^4J = 1.4 Hz); 11.37 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 386 $[Br^{79}M + 1]^{+\bullet}$ (20), 388 $[Br^{81}M + 1]^{+\bullet}$ (18), 196 $[4\text{-}BrC_6H_4N{=}N{=}C]$ (43), 189 $[M - 4\text{-}BrC_6H_4N{=}N{-}C]^+$ (90), 169 $[4\text{-}BrC_6H_4N]^+$ (100), 155 $[4\text{-}BrC_6H_4]^+$ (9), 145 $[M - 4\text{-}BrC_6H_4N{=}N{=}C - CO - O]^+$ (23), 121 $[M - 4\text{-}BrC_6H_4N{=}N{=}C - 2\,CO - C]^+$ (80), 92 $[C_6H_4O]^+$ (78), 76 $[C_6H_4]^+$ (33).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(4-methoxyphenyl)hydrazone (4e). The yield was 1.6 g (48%), amorphous brilliant orange powder, m.p. 279—281 °C. Found (%): C, 63.88; H, 4.62; N, 8.13. $C_{18}H_{12}N_2O_5$. Calculated (%): C, 64.77; H, 4.58; N, 7.95; O, 22.7. ^{1}H NMR (DMSO-d_6), δ: 3.76 (s, 3 H, 4′-OMe); 6.98 (d, 2 H, H(3′), H(5′), ^3J = 8.1 Hz); 7.34 (d, 2 H, H(2′), H(6′), ^3J = 9.8 Hz); 7.55—7.65 (m, 2 H, H(6), H(8)); 7.88—8.00 (m, 1 H, H(7)); 8.13 (dd, 1 H, H(5), ^3J = 8.0 Hz, ^4J = 1.4 Hz); 11.12 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 336 $[M]^+$ (7), 189 $[M - 4\text{-}OMeC_6H_4N{=}N{-}C]^+$ (6), 147 $[4\text{-}OMeC_6H_4N{=}N{=}C]^+$ (7), 133 $[M - 4\text{-}OMeC_6H_4N{=}N{=}C - 2\,CO]^+$ (12), 121 $[4\text{-}OMeC_6H_4N]^+$ (100), 106 $[4\text{-}OMeC_6H_4]^+$ (16), 92 $[C_6H_4O]^+$ (43).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(4-methylphenyl)hydrazone (4f). The yield was 1.35 g (42.2%), amorphous wine-colored powder, m.p. 285—286 °C. Found (%): C, 67.38; H, 3.73; N, 8.87. $C_{18}H_{12}N_2O_4$. Calculated (%): C, 67.5; H, 3.78; N, 8.75. ^{1}H NMR (DMSO-d_6), δ: 2.28 (s, 3 H, 4′-Me); 7.16—7.31 (m, 4 H, Ar); 7.56—7.65 (m, 2 H, H(6), H(8)); 7.89—7.98 (m, 1 H, H(7)); 8.13 (dd, 1 H, H(5), ^3J = 6.0 Hz, ^4J = 1.3 Hz); 11.17 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 320 $[M]^+$ (42), 189 $[M - 4\text{-}MeC_6H_4N{=}N{-}C]^+$ (22), 132 $[4\text{-}MeC_6H_4NH{-}N{=}C]^+$ (28), 121 $[M - 4\text{-}MeC_6H_4N{=}N{=}C - 2\,CO - C]^+$ (25), 105 $[4\text{-}MeC_6H_4N]^+$ (100), 92 $[C_6H_4O]^+$ (43), 77 $[C_6H_5]^+$ (75).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(2-nitrophenyl)hydrazone (4g(C)) and 3-hydroxy-2-[(*Z*)-2-nitrophenyldiazenyl]-4*H*-furo[3,2-*c*]chromen-4-one (4g(B)). The yield was 1.1 g (32%), amorphous brown-yellow powder, m.p. 284—286 °C. Found (%): C, 55.13; H, 2.60; N, 12.91. $C_{17}H_9N_3O_6$. Calculated (%): C, 53.13; H, 2.58; N, 11.96. ^{1}H NMR (DMSO-d_6), δ: 7.23 (t, 1 H, H(4′), J = 8.0 Hz); 7.53—7.67 (m, 2 H, H(3′), H(5′)); 7.79—8.00 (m, 3 H, H(6), H(8), H(6′)); 8.05—8.12 (m, 1 H, H(7)); 8.17 (dd, 0.42 H, H(5) azo enol, ^3J = 8.0 Hz, ^4J = 2.0 Hz); 8.24 (dd, 0.58 H, H(5) keto hydrazone, ^3J = 7.0 Hz, ^4J = 2.0 Hz); 11.22 (s, 0.34 H keto hydrazone, NH); 13.51 (s, 0.43 H azo enol, OH). MS, *m/z* (I_{rel} (%)): 351 $[M]^+$ (5), 189 $[M - 2\text{-}NO_2C_6H_4N{=}N{-}C]^+$ (100), 163 $[2\text{-}NO_2C_6H_4NH{-}N{=}C]^+$ (27), 150 $[2\text{-}NO_2PhN{=}N]^+$ (5), 136 $[2\text{-}NO_2C_6H_4N]^+$ (10), 121 $[2\text{-}NO_2C_6H_4]^+$ (75), 92 $[C_6H_4O]^+$ (95).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(2-chlorophenyl)hydrazone (4h(C)) and 3-hydroxy-2-[(*Z*)-2′-chlorophenyldiazenyl]-4*H*-furo[3,2-*c*]chromen-4-one (4h(B)). The yield was 1.43 g (42%), amorphous red-brown powder, m.p. 270—272 °C. Found (%): C, 59.69; H, 2.78; N, 8.50; Cl, 10.65. $C_{17}H_9N_2O_4Cl$. Calculated (%): C, 59.93; H, 2.66; N, 8.22; Cl, 10.41. ^{1}H NMR (DMSO-d_6), δ: 7.08—7.14 (m, 1 H, H(4′)); 7.38—7.66 (m, 5 H, H(6), H(8), H(3′), H(5′), H(6′)); 7.93—8.01 (td, 1 H, H(7), ^4J = 6.0 Hz, ^3J = 10.0 Hz); 8.13 (dd, 0.48 H, H(5) azo enol,

^3J = 8.0 Hz, ^4J = 1.4 Hz); 8.27 (dd, 0.52 H, H(5) keto hydrazone, ^3J = 6.0 Hz, ^4J = 1.4 Hz); 10.06 (s, 0.52 H, NH); 12.12 (s, 0.48 H, azo enol, OH). MS, *m/z* (I_{rel} (%)): 340 $[M]^+$ (42), 189 $[M - 2\text{-}ClC_6H_4N{=}N{-}C]^+$ (46), 152 $[2\text{-}ClC_6H_4N{=}N{=}C]^+$ (43), 140 $[2\text{-}ClPhN{=}N]^+$ (5), 125 $[2\text{-}ClC_6H_4N]^+$ (100), 111 $[2\text{-}ClC_6H_4]^+$ (13), 99 $[2\text{-}ClC_5H_4]^+$ (33), 92 $[C_6H_4O]^+$ (47).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(2-methoxyphenyl)hydrazone (4i(C)) and 3-hydroxy-2-[(*Z*)2-methoxyphenyldiazenyl]-4*H*-furo[3,2-*c*]chromen-4-one (4i(B)). The yield was 1.37 g (40.8%), amorphous maroon powder, m.p. 254—255 °C. Found (%): C, 64.55; H, 4.60; N, 9.27. $C_{18}H_{12}N_2O_5$. Calculated (%): C, 64.77; H, 4.58; N, 7.95. ^{1}H NMR (DMSO-d_6), δ: 3.94 (s, 3 H, 4´-OMe); 6.96—7.14 (m, 3 H, H(3´), H(4´), H(5´)); 7.43—7.62 (m, 3 H, H(6), H(8), H(6´)); 7.90—7.97 (m, 1 H, H(7)); 8.10 (dd, 0.45 H, H(5) azo enol, ^3J = 6.0 Hz, ^4J = 1.3 Hz); 8.30 (dd, 0.5 H, H(5) keto hydrazone, ^3J = 6.0 Hz, ^4J = 1.3 Hz); 9.98 (s, 0.53 H, keto hydrazone, NH); 12.08 (s, 0.37 H, azo enol, OH). MS, *m/z* (I_{rel} (%)): 336 $[M]^+$ (80), 189 $[M - 2\text{-}OMeC_6H_4N{=}N{-}C]^+$ (43), 148 $[2\text{-}OMeC_6H_4NH{-}N{=}C]^+$ (22), 135 $[2\text{-}OMePhN{=}N]^+$ (5), 133 $[M - 2\text{-}OMeC_6H_4\text{-}N{=}N{=}C - 2\ CO]^+$ (17), 120 $[2\text{-}OMeC_6H_3N]^+$ (100), 106 $[2\text{-}OMeC_6H_4]^+$ (41), 92 $[C_6H_4O]^+$ (83).

(2*E*)-4*H*-Furo[3,2-*c*]chromene-2,3,4-trione 2-(2-methylphenyl)hydrazone (4k(C)) and 3-hydroxy-2-[(*Z*)2-methylphenyldiazenyl]-4*H*-furo[3,2-*c*]chromen-4-one (4k(B)). The yield was 1.05 g (33%), amorphous brilliant orange powder, m.p. 249—251 °C. Found (%): C, 66.98; H, 3.89; N, 8.6. $C_{18}H_{12}N_2O_4$. Calculated (%): C, 67.5; H, 3.78; N, 8.75. ^{1}H NMR (DMSO-d_6), δ: 2.31 (s, 1 H, azo enol, 4´-Me); 2.42 (s, 2 H, keto hydrazone, 4´-Me); 6.96—7.06 (m, 1 H, H(4´)); 7.17—7.28 (m, 2 H, H(3´), H(5´)); 7.38—7.67 (m, 3 H, H(6), H(8), H(6´)); 7.90—7.99 (td, 1 H, H(7), ^3J = 6.0 Hz, ^4J = 2.0 Hz); 8.21 (dd, 1 H, H(5), ^3J = 6.0 Hz, ^4J = 1.3 Hz); 10.13 (s, 0.7 H, keto hydrazone, NH); 12.01 (s, 0.3 H, azo enol, OH). MS, *m/z* (I_{rel} (%)): 320 $[M]^+$ (20), 189 $[M - 2\text{-}MeC_6H_4N{=}N{-}C]^+$ (30), 131 $[2\text{-}MeC_6H_4N{=}N{-}C]^+$ (32), 121 $[M - 2\text{-}MeC_6H_4N{=}N{=}C - 2\ CO - C]^+$ (47), 119 $[2\text{-}MePhN{=}N]^+$ (5), 105 $[2\text{-}MeC_6H_4N]^+$ (100), 92 $[C_6H_4O]^+$ (43), 77 $[C_6H_5]^+$ (75).

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