Reactions of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one with aromatic amines

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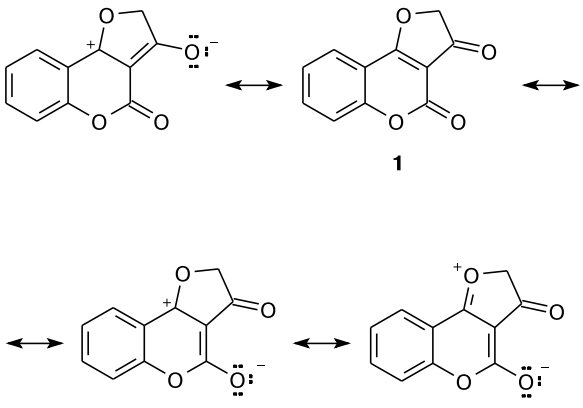
2,3-Dihydrofuro[3,2-*c*]coumarin-3-one reacts with aromatic amines in two pathways, depending on the solvent. The reactions in ethanol afford its enamines, while the use of acetic acid favors the formation of enamines of the 2,3-dihydrofuro[3,2-*c*]coumarin-3-one dimer. Electronic absorption spectroscopy in different solvents revealed that the enamines obtained can undergo tautomeric transformations. The product of a reaction of 2,3-dihydrofuro-[3,2-*c*]coumarin-3-one with 4-bromoaniline exists in the enamine form (X-ray diffraction data).

Key words: furocoumarinones, imines, enamines, tautomerism, dimerization, X-ray diffraction analysis, electronic absorption spectra.

Aromatic imines tend to undergo various transformations between different isomers. Some of them are tautomers, while others are geometric isomers about the C=N bond. These transformations can be initiated by various factors (solvent, temperature, or irradiation) and can be of interest for design of novel sensor structures.[1—3] An example of isomerization accompanied by considerable changes in fluorescence is the previously studied[4] *E*—*Z* isomerization of 8-[(9*H*-fluoren-2-ylimino)methyl]-7-hydroxy-4-methyl-2*H*-1-benzopyran-2-one in acetonitrile.

Scheme 1



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Literature data on tautomeric transformations of furocoumarinone imines and hydrazones are lacking. At the same time, such compounds are of interest because of intense fluorescence of many hydroxy- and amino-coumarins.[5,6] Earlier, we have studied condensation reactions of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one (**1**)[7] with aromatic aldehydes[8] and found that the condensation products exhibit pronounced fluorescence.

Interest in reactions of dihydrofurocoumarinone **1** is also due to its structural analogy with β-dicarbonyl compounds.[5,9] The resonance structures (Scheme 1) show a particular electron density distribution in its molecule, which determines the distinctive features of its reactivity.

Results and Discussion

In the present work, we studied reactions of ketone **1** with various aromatic amines. Prolonged heating of ketone **1** with an excess of an aromatic amine in ethanol afforded derivatives **2** (Scheme 2).

Ad_N-E reactions of ketone **1** with aromatic amines (N-nucleophiles) should give condensation products **2** in the imino form. However, the compounds obtained are not imines (^{1}H NMR data). The absence of signals at δ 5 is indicative of the absence of two protons at the C(4a) atom and, consequently, of aromatization of the dihydrofuran ring giving rise to enamines **2**.

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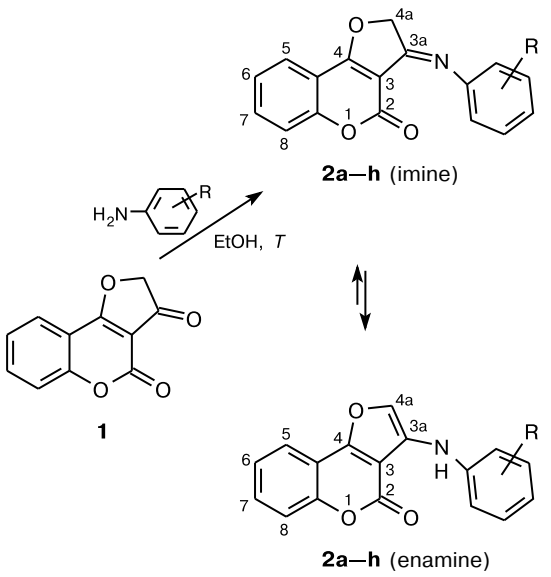
Scheme 2

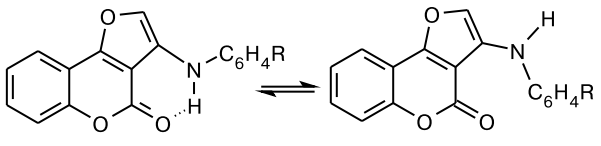


R = H (**a**), 4-OMe (**b**), 4-Br (**c**), 4-Me (**d**), 4-NO_2 (**e**), 2-OMe (**f**), 4-F (**g**), 3-NO_2 (**h**)

The formation of enamines **2** is also confirmed by other signals in the ^{1}H NMR spectrum. For instance, the presence of a narrow singlet at δ 8.08—8.40 is due to the C(4a)H proton of the furan ring; the strong downfield shift of this signal agrees with the aromaticity of the furan ring. The broadened singlet at δ 7.27—8.90 (depending on the structure of the starting aromatic amine) should be assigned to the amino group NH in the enamine form.

The preferred formation of compounds **2a**—**h** as enamine tautomers was confirmed by quantum-chemical calculations. We calculated their enthalpies of formation making allowance for hydrogen bonding between the amino NH atom and the carbonyl O atom of the lactone fragment and without this bonding. According to the data obtained (Table 1), the enamine form is more stable than the imine form for most of compounds **2**, even in the absence of the above hydrogen bonding (Scheme 3).

Scheme 3



Reactions of ketone **1** with excesses of aromatic amines in acetic acid yield different products. With aniline and 4-nitroaniline as the amino components, the major products were enamines **2**. From other substituted anilines,

Table 1. PM3-calculated enthalpies of formation ($H°_f$) of the tautomeric (imine and enamine) forms of compounds **2a**—**h** in the presence (I) and in the absence of intramolecular hydrogen bonding (II)

Tautomer	$-H°_f$/kcal mol^{-1}		
	Imine	Enamine	
		I	II
2a	20.36	24.47	20.39
2b	58.11	61.37	58.04
2c	12.79	16.08	12.81
2d	29.87	33.84	33.09
2e	29.46	33.82	30.73
2f	56.11	61.33	58.00
2g	64.03	67.82	67.15
2h	29.81	34.20	30.73

the expected enamines **2** did not form. Instead, we obtained compounds **3**, which are amino derivatives of 2,3′-bi(2*H*-furo[3,2-*c*]chromene)-3,4,4′-trione, a dimer of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one (Scheme 4).

Earlier,[3] we have demonstrated that compound **1** tends to undergo self-condensation leading to dimer **4**. For this reason, one could assume that reactions of ketone **1** with some aromatic amines would proceed through the formation of intermediate 2,3′-bi(2*H*-furo[3,2-*c*]chromene)-3,4,4′-trione (**4**) followed by the same Ad_N-E reaction with an appropriate amine as that in the case of ketone **1** (Scheme 5, pathway *a*).

To verify this assumption, we dissolved prepared dimer **4** in a mixture of acetic acid and DMSO and refluxed the resulting solution with 4-bromoaniline for 4 h. However, after the reaction mixture was cooled, the expected 3-(4-bromophenylamino)-2,3′-bi(4*H*-furo[3,2-*c*]chromene)-4,4′-dione (**3c**) was not detected; instead, the starting reagents were recovered.

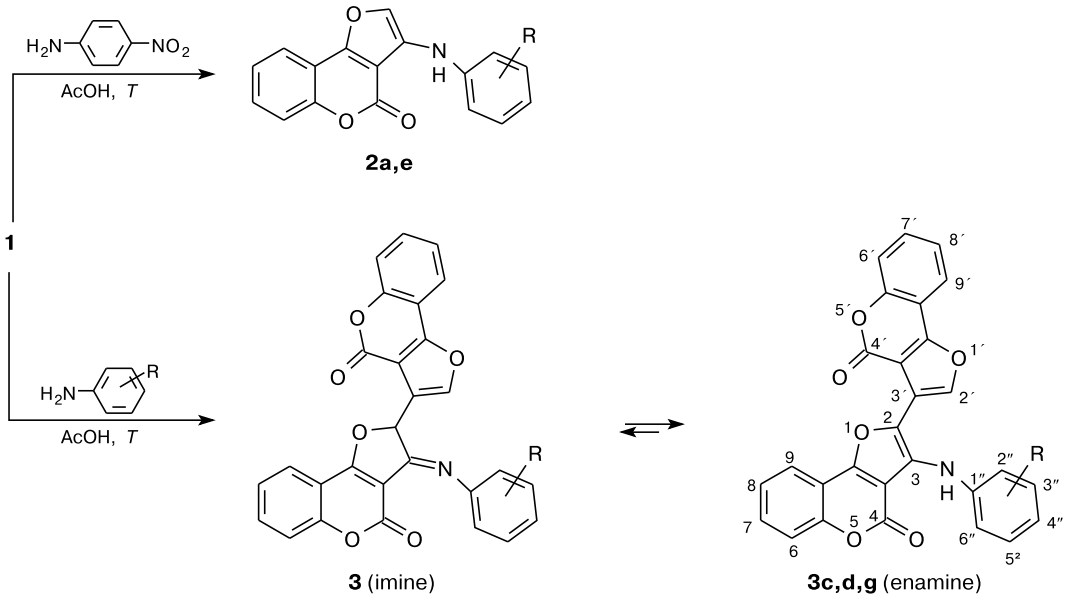
The formation of compounds **3** can follow an alternative reaction sequence involving the initial formation of an imino derivative of 2,3-dihydrofuro[3,2-*c*]coumarin-3-one **2** and its reaction in the enamine form with another molecule of compound **1** at position 4a (Scheme 5, pathway *b*).

To verify the possibility of this pathway, we dissolved prepared 3-(4-bromophenylamino)-4*H*-furo[3,2-*c*]coumarin **2c** in acetic acid and slightly refluxed with an excess of ketone **1**. The reaction gave the expected 3-(4-bromophenylamino)-2,3′-bi(4*H*-furo[3,2-*c*]coumarin) **3c**.

Therefore, the formation of compound **3** proceeds through the formation of enamine **2** rather than dimer **4**. In a reaction with ketone **1**, enamine **2** acts as a stronger C-nucleophile than the enol (and very minor[8]) form of the starting ketone.

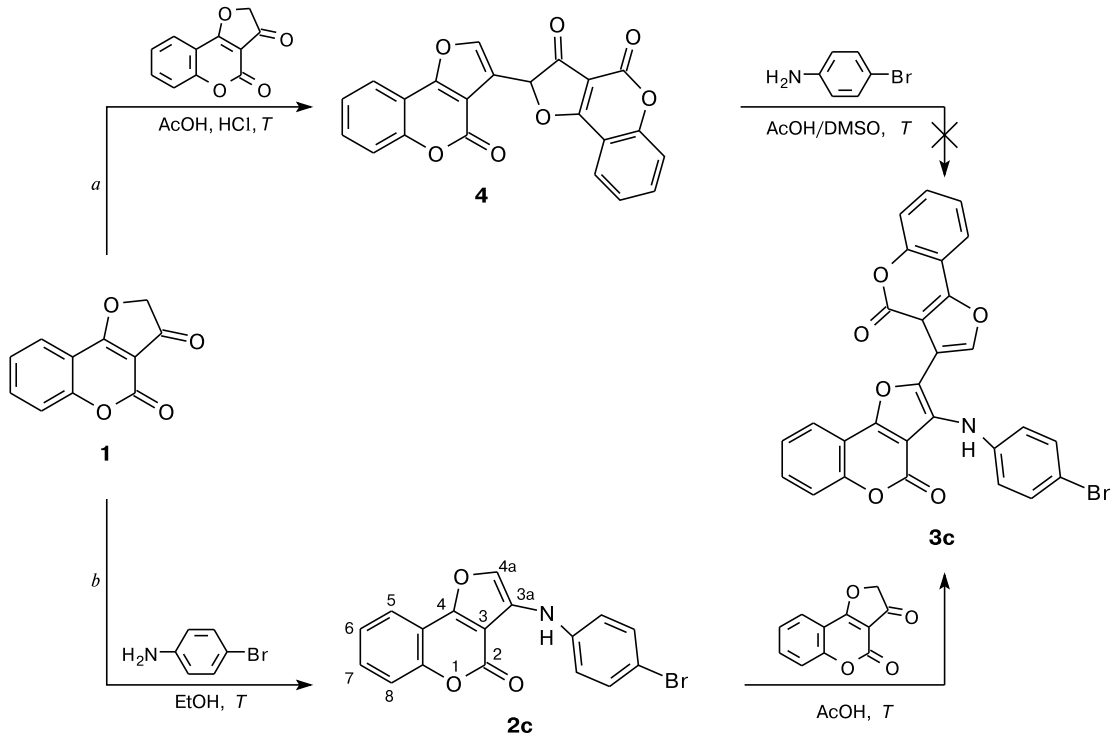
As noted above, the reactions of ketone **1** with aniline and 4-nitroaniline in acetic acid do not yield com-

Scheme 4



R = H (**a**), 4-Br (**c**), 4-Me (**d**), 4-NO_2 (**e**), 4-F (**g**)

Scheme 5



pounds **3**. The formation of product **3e** from compound **2e** is most likely precluded by its low solubility in acetic acid: compound **2e** precipitates during the course of the reaction, thus leaving the reaction zone. In the case of unsubstituted aniline, the absence of product **3a** is difficult to explain since compound **2a** is well soluble in acetic acid and was obtained in good yield when a great excess of the amine was used.

Table 2. Experimental parameters of the electronic absorption spectra of compounds **2a—h**

Compound	λ_{max}/nm (log ε)		
	CCl_4	EtOH	DMF
2a	357 (4.03)	354 (4.08)	353 (4.00)
2b	365 (4.09)	365 (4.37)	364 (3.94)
2c	358 (3.92)	352 (3.75)	353 (3.93)
2d	360 (4.06)	355 (3.92)	354 (3.93)
2e	370 (4.32)	367 (4.32)	381 (4.43)
2f	365 (3.92)	361 (3.89)	359 (3.92)
2g	357 (3.87)	355 (3.60)	354 (3.86)
2h	347 (4.14)	339 (4.11)	336 (4.10)

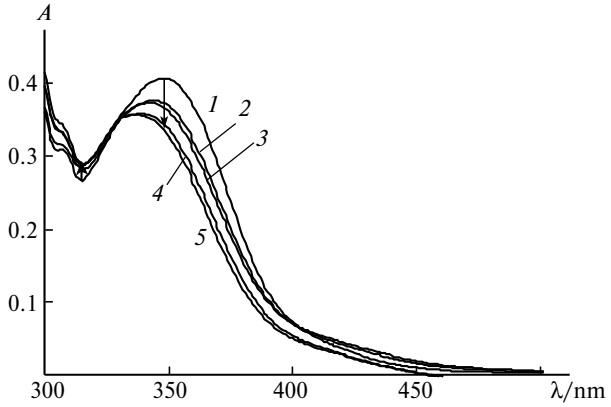


Fig. 1. Electronic absorption spectra of compound **2h** in (*1*) CCl_4, (*2*) CCl_4—DMF (3 : 1), (*3*) CCl_4—DMF (1 : 1), (*4*) CCl_4—DMF (1 : 3), and (*5*) DMF.

The electronic absorption spectra of compounds **2** in various solvents show that the peak wavelengths differ only slightly (Table 2). The bathochromic shift of the longer-wavelength absorption peak of compounds **2** when moving from DMF to CCl_4 is most likely due to an increased contribution from the enamine form to its structure, which can be stabilized in a nonpolar solvent by a hydrogen bond between the NH group of the enamine and the carbonyl O atom of the lactone fragment. The equilibrium between the imino and enamine forms is confirmed by an isosbestic point arising when moving from a polar solvent to a nonpolar one (see Fig. 1).

In conclusion, note that the enamine form of compounds **2** was confirmed by X-ray diffraction (Fig. 2). The

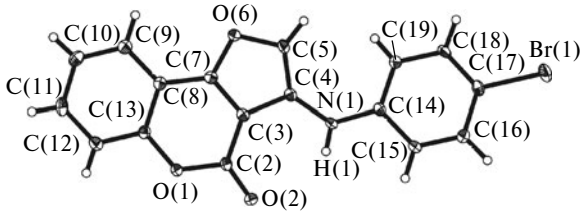


Fig. 2. Molecular structure **2c** with atomic numbering.

N atom in compound **2c** is sp^2-hybridized because of the conjugation of its lone electron pair with the π-systems of the phenyl and furan fragments. The C(4)—C(5) bond is shortened (1.357 Å). It can be seen in Table 3 that the C(4)—C(5) bond is even shorter than the double C(3)=C(7) bond (1.362(3) Å) in the lactone ring of coumarin. This provides unambiguous evidence for the aromatization of the five-membered ring in compounds **2**.

In the crystal structure of compound **2c**, one crystallographically independent molecule occupies the general position (see Fig. 2). The molecule is nearly planar: the largest deviation from the mean-square plane of all nonhydrogen atoms is 0.10 Å (O(2)). The deviation of the N(1) atom from the plane H(1)C(4)C(14) is 0.007 Å. The dihedral angle between the planes of the benzene ring C(14)C(15)...C(19) and the furochromene tricyclic system O(1)C(2)C(3)...C(13) is 3.6°.

In contrast to the (2*Z*)-2-[4′-(dimethylamino)benzylidene]-4*H*-furo[3,2-*c*]chromene-3,4(2*H*)-dione[8] structure characterized by regular stacks, the crystal structure of compound **2c** consists of layers of its molecules united

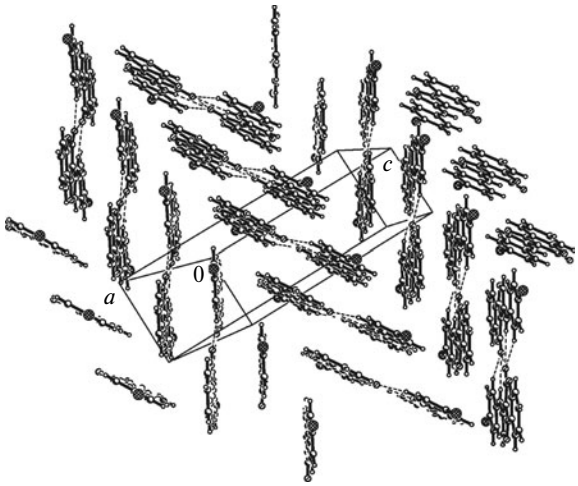


Fig. 3. Crystal structure **2c**.

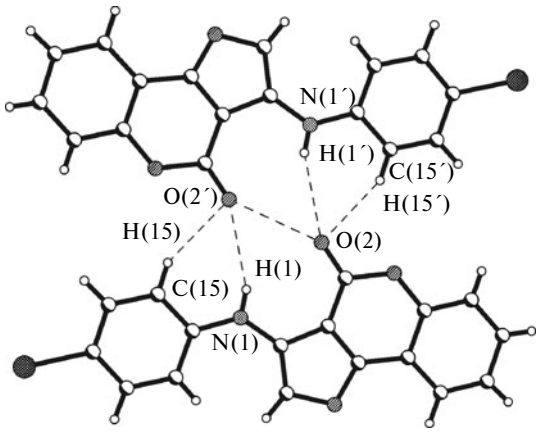


Fig. 4. Shortened intermolecular contacts in the dimeric associate $(\mathbf{2c})_2$.

into centrosymmetric dimers through shortened intermolecular contacts O...O and hydrogen bonds O...H—C and O...H—N: O(2)...O(2′), 2.850(3) Å; O(2)...H(1′), 2.55(3) Å; O(2)...H(15′), 2.45(2) Å (the sums of the van der Waals radii for these pairs of atoms are 3.04 (O...O) and 2.72 Å (O...H))[10] (Figs 3, 4). In adjacent layers, the molecules have different orientations making a dihedral angle of 63.4° between their mean-square planes.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200 MHz) in DMSO-d_6 and $CDCl_3$ with Me_4Si as the internal standard. Mass spectra were measured on a Finnigan MAT SSQ-710 mass spectrometer (EI, 70 eV). The course of the reactions was monitored, and the purity of the compounds obtained was checked, by TLC on Silufol UV-254 plates in the following solvent systems: (*A*) chloroform—acetone (16 : 1), (*B*) chloroform—acetone (5 : 1), and (*C*) hexane—acetone (2 : 1). Electronic absorption spectra were recorded on an APEL PD-303UV spectrometer. A cell with a solvent was used as a reference cell.

Quantum-chemical semiempirical PM3 calculations were performed with the Hyper Chem 6.0 program package. For preliminary geometry optimization, the molecular mechanics method (MM+ version) was employed.

A single crystal of compound **2c** was obtained by crystallization from ethanol.

Single-crystal X-ray diffraction was carried out on a Bruker SMART APEX2 CCD diffractometer (Mo-Kα radiation, graphite monochromator) at 200 K. The crystal structure was solved by the direct methods followed by difference Fourier syntheses with the SHELXS-97 program.[11] The structure was refined by the least-squares method in the anisotropic full-matrix approximation for all non-hydrogen atoms with the SHELXL-97 program.[12] An absorption correction was applied with the APEX2 program.[13] The coordinates of the hydrogen atoms were determined experimentally and refined isotropically.

Selected crystallographic parameters and the data collection statistics for compound **2c**: $C_{17}H_{10}BrNO_3$, M = 356.17, monoclinic crystals, space group $P2_1/c$, a = 17.442(2) Å, b = 5.570(2) Å, c = 15.511(2) Å, β = 115.634(1)°, V = 1358.6(5) Å^3, Z = 4, d_{calc} = 1.74 g cm^{-3}, μ = 3.038 mm^{-1}, $(2\theta)_{max}$ = 58.82°, the number of measured reflections 9401, the number of independent reflections 3399, the number of parameters refined 239, R = 0.041 for 2392 reflections with $F_0 > 4\sigma(F_0)$.

The bond lengths and bond angles are given in Table 3.

Table 3. Selected bond lengths (d) and bond angles (ω) in structure **2c** (X-ray diffraction data)

Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d/Å
O(2)—C(2)	1.209(3)	C(3)—C(4)	1.427(3)
N(1)—C(4)	1.382(3)	C(4)—C(5)	1.357(3)
N(1)—C(14)	1.383(3)	C(5)—O(6)	1.398(3)
N(1)—H(1)	0.80(3)	C(5)—H(5)	0.90(3)
C(2)—C(3)	1.434(3)	O(6)—C(7)	1.348(3)
C(3)—C(7)	1.362(3)	C(7)—C(8)	1.418(3)
Angle	ω/deg	Angle	ω/deg
C(4)—N(1)—C(14)	129.6(2)	N(1)—C(4)—C(3)	122.5(2)
C(4)—N(1)—H(1)	114(2)	C(4)—C(5)—O(6)	110.9(2)
C(14)—N(1)—H(1)	117(2)	N(1)—C(14)—C(15)	134(2)
O(2)—C(2)—O(1)	117.8(2)	C(4)—C(5)—H(5)	115(2)
O(2)—C(2)—C(3)	126.4(2)	O(6)—C(5)—H(5)	105.8(2)
O(1)—C(2)—C(3)	115.8(2)	C(7)—O(6)—C(5)	110.5(2)
C(7)—C(3)—C(4)	107.7(2)	O(6)—C(7)—C(3)	125.5(2)
C(7)—C(3)—C(2)	120.3(2)	O(6)—C(7)—C(8)	124.0(2)
C(4)—C(3)—C(2)	132.0(2)	C(3)—C(7)—C(8)	124.5(2)
C(5)—C(4)—N(1)	132.4(2)	N(1)—C(14)—C(19)	117.8(2)
C(5)—C(4)—C(3)	105.0(2)		

Synthesis of 3-arylimino-2,3-dihydrofuro[3,2-*c*]coumarins 2a—h (general procedure). 2,3-Dihydrofuro[3,2-*c*]coumarin-3-one[7] (0.3 g, 1.5 mmol) was dissolved in boiling ethanol (35 mL). Then a solution of an appropriate aromatic amine (1.65 mmol) in ethanol (5 mL) was added. The resulting solution turned orange. The course of the reaction was monitored by TLC. The heating time was varied from 2 to 2.5 h, depending on the amine structure. On cooling, the precipitate that formed was filtered off, washed with ethanol, dried, and recrystallized from 96% ethanol or glacial acetic acid.

3-Phenylamino-4*H*-furo[3,2-*c*]coumarin (2a). Yield 0.18 g (43.4%), yellow needles, m.p. 193—194 °C. ^{1}H NMR (DMSO-d_6), δ: 6.86—6.88 (m, 1 H, H(4′)); 7.12 (d, 2 H, H(2′), H(6′), $J_{2',6'}$ = 6 Hz); 7.26—7.39 (m, 2 H, H(3′), H(5′)); 7.40—7.60 (m, 2 H, H(6), H(8)); 7.49 (s, 1 H, NH); 7.64—7.66 (m, 1 H, H(7)); 7.95 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.22 (s, 1 H, CH). MS, m/z (I_{rel} (%)): 278 $[M + 1]^+$ (100), 277 $[M]^+$ (80), 276 $[M - 1]^+$ (88). Found (%): C, 73.61; H, 4.02; N, 5.25. $C_{17}H_{11}NO_3$. Calculated (%): C, 73.64; H, 4.00; N, 5.05.

3-(4-Methoxyphenylamino)-4*H*-furo[3,2-*c*]coumarin (2b). Yield 0.2 g (43.8%), gray needles, m.p. 184—186 °C. ^{1}H NMR (DMSO-d_6), δ: 3.72 (s, 3 H, OMe); 6.88 (d, 2 H, H(3′), H(5′), $J_{3',2'}$ = 8 Hz); 7.12 (d, 2 H, H(2′), H(6′), $J_{2',3'}$ = 8 Hz); 7.27 (s, 1 H, NH); 7.40—7.60 (m, 3 H, H(6), H(7), H(8)); 7.63—7.65 (m, 1 H, H(7)); 7.94 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.08 (s, 1 H, CH). MS, m/z (I_{rel} (%)): 308 $[M + 1]^{+\bullet}$ (100). Found (%): C, 71.00; H, 3.90; N, 4.60. $C_{18}H_{13}NO_4$. Calculated (%): C, 70.35; H, 4.26; N, 4.56.

3-(4-Bromophenylamino)-4*H*-furo[3,2-*c*]coumarin (2c). Yield 0.26 g (48%), yellow needles, m.p. 237—238 °C. ^{1}H NMR (DMSO-d_6), δ: 7.12 (d, 2 H, H(3′), H(5′), $J_{3',2'}$ = 10 Hz); 7.38 (d, 2 H, H(2′), H(6′), $J_{2',3'}$ = 8 Hz); 7.40—7.70 (m, 3 H, H(6), H(7), H(8)); 7.74 (s, 1 H, NH); 7.92 (d, 1 H, H(5), $J_{5,6}$ = 6 Hz); 8.20 (s, 1 H, CH). MS, m/z (I_{rel} (%)): 358 $[^{81}Br\ M + 1]^{+\bullet}$ (100), 356 $[^{79}Br\ M + 1]^{+\bullet}$ (98). Found (%): C, 56.92; H, 2.80; N, 3.80. $C_{17}H_{10}BrNO_3$. Calculated (%): C, 57.33; H, 2.83; N, 3.93.

3-(*p*-Toluidino)-4*H*-furo[3,2-*c*]coumarin (2d). Yield 0.18 g (42%), orange needles, m.p. 167—168 °C. ^{1}H NMR (DMSO-d_6), δ: 2.24 (s, 3 H, Me); 7.03 (d, 2 H, H(3′), H(5′), $J_{3',2'}$ = 8 Hz); 7.10 (d, 2 H, H(2′), H(4′), $J_{2',3'}$ = 8 Hz); 7.34 (s, 1 H, NH); 7.40—7.58 (m, 2 H, H(6), H(8)); 7.64—7.67 (m, 1 H, H(7)); 7.95 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.16 (s, 1 H, CH). MS, m/z (I_{rel} (%)): 292 $[M + 1]^{+\bullet}$ (100). Found (%): C, 74.01; H, 4.40; N, 4.83. $C_{18}H_{13}NO_3$. Calculated (%): C, 74.22; H, 4.50; N, 4.81.

3-(4-Nitrophenylamino)-4*H*-furo[3,2-*c*]coumarin (2e). Yield 0.2 g (42%), orange needles, m.p. 310—312 °C. ^{1}H NMR (DMSO-d_6), δ: 7.10 (d, 2 H, H(2′), H(6′), $J_{2',3'}$ = 10 Hz);

7.40—7.60 (m, 3 H, H(6), H(8)); 7.66—7.67 (m, 1 H, H(7)); 7.99 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.08 (d, 2 H, H(3′), H(5′), $J_{3',2'}$ = 10 Hz); 8.39 (s, 1 H, CH); 8.87 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 323 $[M + 1]^{+\bullet}$ (100). Found (%): C, 63.01; H, 3.00; N, 8.72. $C_{17}H_{10}N_2O_5$. Calculated (%): C, 63.36; H, 3.13; N, 8.69.

3-(2-Methoxyphenylamino)-4*H*-furo[3,2-*c*]coumarin (2f). Yield 0.19 g (41%), white crystals, m.p. 243—244 °C. ^{1}H NMR (DMSO-d_6), δ: 6.84—7.15 (m, 4 H, H(3′), H(4′), H(5′), H(6′)); 7.40—7.70 (m, 3 H, H(6), H(7), H(8)); 7.60 (s, 1 H, NH); 7.97 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.36 (s, 1 H, CH). MS, *m/z* (I_{rel} (%)): 308 $[M + 1]^{+\bullet}$ (100). Found (%): C, 70.94; H, 4.34; N, 4.42. $C_{18}H_{13}NO_4$. Calculated (%): C, 70.35; H, 4.26; N, 4.56.

3-(4-Fluorophenylamino)-4*H*-furo[3,2-*c*]coumarin (2g). Yield 0.2 g (46%), bright green needles, m.p. 200—201 °C. ^{1}H NMR (DMSO-d_6), δ: 7.00—7.22 (m, 4 H, H(2′), H(3′), H(5′), H(6′)); 7.40—7.60 (m, 2 H, H(6), H(8)); 7.52 (s, 1 H, NH); 7.63—7.65 (m, 1 H, H(7)); 7.94 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.15 (s, 1 H, CH). MS, *m/z* (I_{rel} (%)): 296 $[M + 1]^{+\bullet}$ (100). Found (%): C, 69.36; H, 3.52; N, 4.73. $C_{17}H_{10}FNO_3$. Calculated (%): C, 69.15; H, 3.41; N, 4.74.

3-(3-Nitrophenylamino)-4*H*-furo[3,2-*c*]coumarin (2h). Yield 0.21 g (43%), yellow needles, m.p. 249—250 °C. ^{1}H NMR (DMSO-d_6), δ: 7.42—7.72 (m, 6 H, H(4′), H(5′), H(6′), H(6), H(7), H(8)); 7.88 (s, 1 H, H(2′)); 7.98 (d, 1 H, H(5), $J_{5,6}$ = 8 Hz); 8.34 (s, 1 H, CH); 8.36 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 323 $[M + 1]^{+\bullet}$ (100). Found (%): C, 63.45; H, 2.98; N, 8.54 $C_{17}H_{10}N_2O_5$. Calculated (%): C, 63.36; H, 3.13; N, 8.69.

Synthesis of 3-arylamino-4*H*-furo[3,2-*c*]coumarins 2a,e in acetic acid. A solution of an appropriate aromatic amine (1.64 mmol) in acetic acid (2 mL) was added to a hot solution of ketone **1** (1.5 mmol) in glacial acetic acid (3 mL). The reaction mixture was slightly refluxed for ~1 h. The solution turned dark claret. The course of the reaction was monitored by TLC. On cooling, the precipitate that formed was filtered off, washed with acetic acid, dried, and recrystallized from acetic acid or 96% ethanol.

3-Phenylamino-4*H*-furo[3,2-*c*]coumarin (2a). Yield 0.19 g (45%), pale yellow needles, m.p. 193—194 °C.

3-(4-Nitrophenylamino)-4*H*-furo[3,2-*c*]coumarin (2e). Yield 0.2 g (42%), orange needles, m.p. 310—312 °C.

Synthesis of 3-arylamino-2,3′-bi(4*H*-furo[3,2-*c*]chromene)-4,4′-diones 3c, 3d, and 3g in acetic acid. Reactions of ketone **1** with 4-bromoaniline, *p*-toluidine, and 4-fluoroaniline in acetic acid were carried out as described for the synthesis of compounds **2c,d,g**.

3-(4-Bromophenylamino)-2,3′-bi(4*H*-furo[3,2-*c*]chromene)-4,4′-dione (3c). Yield 0.11 g (26.5%), white crystals, m.p. 234—235 °C. ^{1}H NMR (DMSO-d_6), δ: 6.72 (d, 2 H, H(3″), H(5″), $J_{3'',2''}$ = 8 Hz); 7.22 (d, 2 H, H(2″), H(6″), $J_{2'',3''}$ = 8 Hz); 7.45—7.62 (m, 4 H, H(6), H(8), H(6′), H(8′)); 7.63—7.67 (m, 2 H, H(7), H(7′)); 8.00 (d, 2 H, H(5), H(5′), $J_{5,6}$ = 8 Hz); 8.06 (s, 1 H, CH); 8.45 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 542 $[^{81}Br\ M + 1]^{+\bullet}$ (100), 540 $[^{79}Br\ M + 1]^{+\bullet}$ (95). Found (%): C, 62.15; H, 5.32; N, 2.50. $C_{28}H_{14}BrNO_6$. Calculated (%): C, 62.24; H, 2.61; N, 2.59.

3-(4-Toluidino)-2,3′-bi(4*H*-furo[3,2-*c*]chromene)-4,4′-dione (3d). Yield 0.07 g (18.6%), yellow crystals, m.p. 248—249 °C. ^{1}H NMR (DMSO-d_6), δ: 2.12 (s, 3 H, Me); 6.67 (d, 2 H, H(3″), H(5″), $J_{3'',2''}$ = 8 Hz); 6.89 (d, 2 H, H(2″), H(4″), $J_{2'',3''}$ = 8 Hz); 7.42—7.60 (m, 4 H, H(6), H(8), H(6′), H(8′)); 7.66—7.70 (m, 2 H, H(7), H(7′)); 7.75 (s, 1 H, NH); 8.02 (d, 2 H, H(5), H(5′), $J_{5,6}$ = 6 Hz); 8.34 (s, 1 H, CH). MS, *m/z* (I_{rel} (%)): 476 $[M + 1]^{+\bullet}$ (100). Found (%): C, 73.35; H, 3.64; N, 2.82. $C_{29}H_{17}NO_6$. Calculated (%): C, 73.26; H, 3.60; N, 2.95.

3-(4-Fluorophenyl)-2,3′-bi(4*H*-furo[3,2-*c*]chromene)-4,4′-dione (3g). Yield 0.07 g (19%), light brown crystals, m.p. 232—233 °C. ^{1}H NMR (DMSO-d_6), δ: 6.70—6.96 (m, 4 H, H(2″), H(3″), H(5″), H(6″)); 7.40—7.60 (m, 6 H, H(6), H(8), H(6′), H(8′)); 7.64—7.68 (m, 2 H, H(7), H(7′)); 7.83 (s, 1 H, NH); 7.99 (s, 2 H, H(5), H(5′), $J_{5,6}$ = 8 Hz); 8.38 (s, 1 H, CH). MS, *m/z* (I_{rel} (%)): 480 $[M + 1]^{+\bullet}$ (100). Found (%): C, 70.25; H, 3.02; N, 2.90. $C_{28}H_{14}FNO_6$. Calculated (%): C, 70.15; H, 2.94; N, 2.92.

Synthesis of 2,3′-bi(2*H*-furo[3,2-*c*]chromene)-3,4,4′-trione 4. Ketone **1** (0.93 g, 4.6 mmol) was refluxed in glacial acetic acid (12 mL) in the presence of conc. HCl (6 mL) for 3 h. The dimer obtained was filtered off, washed with hot acetone, and recrystallized from DMSO. The yield was 0.71 g (80%), dark claret crystals, m.p. 310 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 6.50 (s, 1 H, H(2)); 7.30—7.60 (m, 4 H, H(8), H(6), H(8′), H(6′)); 7.70—8.20 (m, 4 H, H(9), H(7), H(9′), H(7′)); 8.52 (s, 1 H, H(2′)). MS, *m/z* (I_{rel} (%)): 387 $[M + 1]^{+\bullet}$ (100). Found (%): C, 67.77; H, 2.60. $C_{22}H_{10}O_7$. Calculated (%): C, 68.40; H, 2.61.

Synthesis of compound 3c from 3-(4-bromophenylamino)-4*H*-furo[3,2-*c*]coumarin 2c. Compound **2c** (0.36 g, 1.00 mmol) was dissolved in boiling acetic acid. Then ketone **1** (0.2 g, 1.00 mmol) was added and the reaction mixture was refluxed for 2 h. On cooling, the precipitate that formed was filtered off, washed with acetic acid, dried, and recrystallized from acetic acid or 96% ethanol. Yield 0.21 g (40%), white crystals, m.p. 234—235 °C.

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