One-step synthesis of substituted 2-amino-4*H*-chromenes and 2-amino-4*H*-benzo[*f*]chromenes. Molecular and crystal structure of 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene

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Substituted 2-aminochromenes were synthesized by three-component condensation of aromatic aldehydes, derivatives of cyanoacetic acid, and phenols or naphthols. The molecular and crystal structure of 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene was established by X-ray diffraction analysis.

Key words: pyran, phenol, naphthol, chromene, benzochromene, X-ray diffraction analysis, molecular structure, crystal structure.

Considerable interest in fused 2-amino-4*H*-pyrans stems from the possibility of their use as drugs, pesticides, analogs of natural compounds, dyes, and other materials of practical importance.[1—7] Substituted 2-amino-4*H*-benzochromenes were proposed for the treatment of immune diseases and diabetic complications resulted from an increase in permeability of blood vessels and a change in blood pressure.[2] Some of these compounds exhibit activity preventing cell growth and multiplication by interfering with one of the phases of the cell cycle.[3] Chromen-4-one derivatives or their salts can be used as immunomodulators and for the prophylaxis and treatment of different diseases of connective tissues, diabetes, psoriasis, pernicious anemia, ulcerous colitis, and chronic hepatitis.[4] In addition, many compounds containing the enaminonitrile fragment are used as convenient synthons in the organic synthesis.[1,5—7]

Previously,[8—11] 2-amino-4*H*-chromenes (**1—3**, Scheme 1) have been synthesized in two steps. The first step consisted in preparing and isolating arylmethylenemalononitrile. The second step involved the reaction of this compound with the corresponding phenol or naphthol. However, the preliminary synthesis (and isolation of arylmethylenemalononitriles) is sometimes impossible.[12] In addition, this process is associated with a particular danger because the resulting compounds are strong lacrimators and are similar in toxicity to CS, which is a component of war gases.[7] When considering methods for the synthesis of substituted chromenes, we got interested in the study[13] in which 2-amino-4-aryl-3-cyano-4*H*-(benzo)chromenes were prepared by three-component condensation of aromatic aldehydes, malononitrile, and resorcinol or β-naphthol. In the cited study,[13] the product of the reaction of benzaldehyde, malononitrile, and resorcinol was assigned the structure of 2-amino-3-cyano-5-hydroxy-4-phenyl-4*H*-chromene without reporting the interpretation of the ^{1}H NMR spectra, and, hence, this assumption was not confirmed.

The present study had two main purposes. One goal was to examine the behavior of phenol and naphthol derivatives, which differ from those described earlier,[13] in three-component condensation. Another aim was to study the structures of the resulting products in detail.

Three-component condensation was carried out by adding a catalytic amount of triethylamine to an ethanolic solution of aromatic aldehyde **4**, malononitrile **5a** (or cyanoacetic ester **5b**), and the corresponding phenol **6** (or naphthalenediol **7—9**) taken in an equimolar ratio and bringing the reaction mixture to boiling. Under these conditions, the reaction proceeded regioselectively to give the final (benzo)chromenes **1—3** in high yields (see the Experimental section).

The use of naphthalenediols attracted our attention because the reactions of some of these compound with double amounts of aromatic aldehyde **4** and malononitrile **5a** can afford naphthopyrans **10** and **11**, which are of interest for further investigation.

An earlier attempt[9] to synthesize benzochromenes from 2,7-naphthalenediol and arylmethylenemalononitriles has failed. We succeeded in preparing 2-amino-

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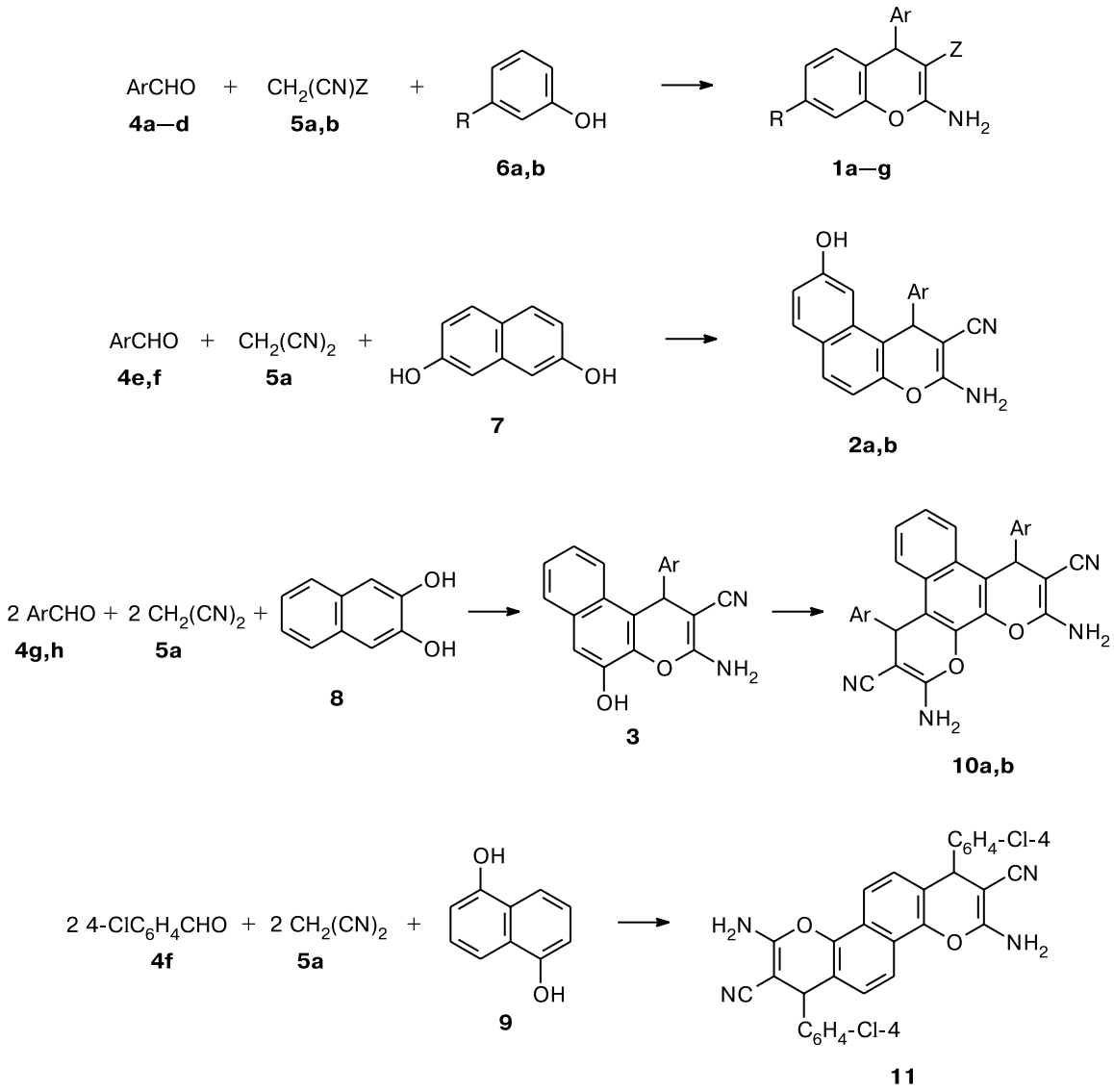
Scheme 1



Ar = 4-MeOCOC$_6$H$_4$ (**1a,e, 4a**), 2,4-F$_2$C$_6$H$_3$ (**1b,c,f, 4b**), 3-BrC$_6$H$_4$ (**1d, 4c**), 3-C$_5$H$_4$N (**1g, 4d**), Ph (**2a, 4e**), 4-ClC$_6$H$_4$ (**2b, 4f, 11**), 3-C$_4$H$_3$S (**3, 4g, 10a**), 4-FC$_6$H$_4$ (**4h, 10b**);
R = OH (**1a—c, 6a**), NH$_2$ (**1d—g, 6b**);
Z = CN (**1a,b,d—g, 5a**), COOEt (**1c, 5b**)

4-aryl-3-cyano-6-hydroxy-4*H*-benzo[*f*]chromenes **2a,b** (Ar = Ph or 4-ClC$_6$H$_4$) by three-component condensation. In addition, we found that the reaction of *p*-chlorobenzaldehyde, malononitrile, and 2,7-naphthalenediol afforded only benzochromene **2b** regardless of the reagent ratio (1 : 1 : 1 or 2 : 2 : 1), whereas three-component condensation with the use of 2,3-naphthalenediol gave benzochromene **3** and pyranobenzochromenes **10a,b**.

The addition of double amounts of 4-ClC$_6$H$_4$CHO and malononitrile to 1,5-naphthalenediol yielded chromenochromene **11**.

All the compounds were synthesized as stable colorless powders, which can be recrystallized from EtOH or MeCN. Their structures were confirmed by spectroscopic methods and elemental analysis (see the Experimental section).

In the ^{1}H NMR spectra of compounds **1a,b,d,e**, the signals for the H(5), H(6), and H(8) protons are well-resolved (δ, *J*/Hz): 6.59—6.78 (d, H(5) ^3J = 7.8—10.5); 6.27—6.48 (dd, H(6), ^3J = 7.8—10.5, ^4J = 0.6—1.4); 6.22—6.42 (d, H(8), ^4J = 0.6—1.1). In the spectra of compounds **1f,g**, the signals for the H(5) and H(6) pro-

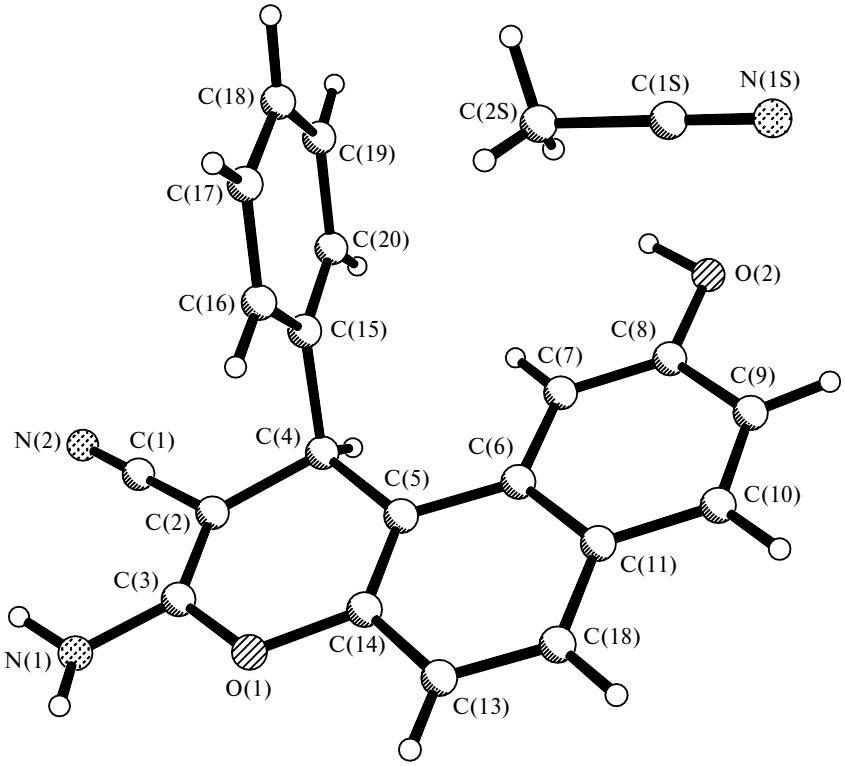


Fig. 1. Overall view of the 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene molecule (**2a**) and the acetonitrile molecule of solvation.

tons are observed as two doublets (δ 6.28—6.61, ^3J = 8.1—8.8 Hz) and the signals for the H(8) protons are observed as singlets (δ 6.24). The assignment of the signals was made based on the NMR spectroscopic data for substituted phenols,[14] which was allowable due to the nonaromaticity of the pyran ring. The results of our study provide evidence in favor of the 7-hydroxy- and 7-amino-4*H*-chromene structures rather than the 5-hydroxy- and 5-amino-4*H*-chromene structures, which have been erroneously proposed previously.[13]

The structure of 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene **2a** obtained as a solvate with acetonitrile was unambiguously established by X-ray diffraction analysis. Figure 1 shows the overall view of molecule **2a** and the acetonitrile molecule of solvation. The bond lengths and bond angles are given in Tables 1 and 2, respectively (the atomic numbering scheme used in the tables does not correspond to the IUPAC rules accepted in the text of the paper).

Unlike substituted 4*H*-pyrans studied previously,[8,15,16] including 2-amino-3-ethoxycarbonyl-4-(2-fluorophenyl)-4*H*-benzo[*f*]chromene,[8] which have a flattened boat conformation of the heterocycle, the pyran ring in molecule **2a** has a sofa conformation with the C(4) atom deviating from the plane through the remaining five atoms of the ring (coplanar to within ±0.014 Å) by 0.129 Å (the O(1) atom is strictly in the plane). The folding angles along the O(1)...C(4) and C(3)...C(5) lines are rather small (6.4 and 8.4°, respectively). The dihedral angle between the naphthalene bicycle and the planar fragment of the heterocycle is 2.3°, which indicates that the tricyclic moiety of the molecule is flattened. The pseudoaxial phenyl substituent is virtually perpendicular to the planar fragment of the pyran ring (the dihedral angle be-

Table 1. Bond lengths (*d*) in 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene (**2a**)

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(2)	1.356(2)	C(7)—C(8)	1.370(3)
O(1)—C(14)	1.398(2)	C(8)—C(9)	1.400(3)
O(2)—C(8)	1.365(3)	C(9)—C(10)	1.359(3)
N(1)—C(2)	1.350(3)	C(10)—C(11)	1.418(3)
N(2)—C(1)	1.146(3)	C(11)—C(12)	1.416(3)
N(1S)—C(1S)	1.129(4)	C(12)—C(13)	1.358(3)
C(1)—C(3)	1.420(3)	C(13)—C(14)	1.406(3)
C(2)—C(3)	1.356(3)	C(15)—C(16)	1.398(3)
C(3)—C(4)	1.518(3)	C(15)—C(20)	1.388(3)
C(4)—C(5)	1.521(3)	C(16)—C(17)	1.386(3)
C(4)—C(15)	1.535(3)	C(17)—C(18)	1.381(3)
C(5)—C(14)	1.369(3)	C(18)—C(20)	1.384(4)
C(5)—C(6)	1.436(3)	C(19)—C(20)	1.393(3)
C(6)—C(7)	1.411(3)	C(1S)—C(2S)	1.453(5)
C(6)—C(11)	1.432(3)		

Table 2. Bond angles (ω) in 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene (**2a**)

Angle	ω/deg	Angle	ω/deg
C(2)—O(1)—C(14)	118.5(2)	C(7)—C(8)—C(9)	120.8(2)
N(2)—C(1)—C(3)	179.3(2)	C(10)—C(9)—C(8)	120.0(2)
N(1)—C(2)—O(1)	109.9(2)	C(9)—C(10)—C(11)	121.1(2)
N(1)—C(2)—C(3)	127.2(2)	C(12)—C(11)—C(10)	121.6(2)
C(3)—C(2)—O(1)	122.8(2)	C(12)—C(11)—C(6)	119.5(2)
C(2)—C(3)—C(1)	118.0(2)	C(10)—C(11)—C(6)	119.0(2)
C(2)—C(3)—C(4)	123.5(2)	C(13)—C(12)—C(11)	120.5(2)
C(1)—C(3)—C(4)	118.3(2)	C(12)—C(13)—C(14)	119.5(2)
C(3)—C(4)—C(5)	109.4(2)	C(5)—C(14)—O(1)	123.3(2)
C(3)—C(4)—C(15)	110.3(2)	C(5)—C(14)—C(13)	123.6(2)
C(5)—C(4)—C(15)	111.7(1)	O(1)—C(14)—C(13)	113.0(2)
C(14)—C(5)—C(4)	121.6(2)	C(20)—C(15)—C(16)	119.3(2)
C(14)—C(5)—C(6)	117.5(2)	C(20)—C(15)—C(4)	121.7(2)
C(6)—C(5)—C(4)	120.9(2)	C(16)—C(15)—C(4)	119.0(2)
C(7)—C(6)—C(5)	122.6(2)	C(17)—C(16)—C(15)	119.9(2)
C(11)—C(6)—C(5)	119.4(2)	C(18)—C(17)—C(16)	120.7(2)
C(7)—C(6)—C(11)	118.0(2)	C(17)—C(18)—C(19)	119.7(2)
C(8)—C(7)—C(6)	121.0(2)	C(18)—C(19)—C(20)	120.1(2)
O(2)—C(8)—C(7)	122.9(2)	C(15)—C(20)—C(19)	120.3(2)
O(2)—C(8)—C(9)	116.3(2)	N(1S)—C(1S)—C(2S)	179.0(4)

tween these planes is 88.1°). Apparently, this orientation of the substituent is determined by forced intramolecular nonbonded contacts (C(3)...C(16), 3.086(3) Å; C(5)...C(16), 3.057(3) Å; and C(7)...C(20), 3.383(3) Å), which are shorter than twice the van der Waals radius of the carbon atom.[17]

In the planar N(1)—C(2)=C(3)—C(1)≡N(2) fragment, the bond lengths are essentially redistributed as compared to the standard values[18] due to conjugation of the NH_2 and CN groups with the C(2)=C(3) double bond.

In the crystal, molecules **2a** and the solvent molecules are linked *via* the rather strong intermolecular O(2)—H(1)...N(1S) hydrogen bonds (2 − *x*, 0.5 + *y*, 1.5 − *z*) (O(2)...N(1S), 2.812(4) Å; O(2)—H(1), 0.99(4) Å; H(1)...N(1S), 1.83(4) Å; O(2)—H(1)...N(1S), 171(3)°). The H atoms of the amino group are also involved in weak intermolecular hydrogen bonds N(1)—H(1A)...N(2) (−*x*, 1 − *y*, 1 − *z*) (N(1)...N(2), 3.110(4) Å; N(1)—H(1A), 0.90(4) Å; H(1A)...N(2), 2.30(4) Å; N(1)—H(1A)...N(2), 150(3)°) and N(1)—H(1B)...O(1) (−*x*, − *y*, 1 − *z*) (N(1)...O(1), 3.403(4) Å; N(1)—H(1B), 0.87(4) Å; H(1b)...O(1), 2.58(4) Å; N(1)—H(1B)...O(1), 159(3)°) *via* which molecules **2a** are linked in infinite ribbons.

To summarize, the study of the behavior of substituted phenols and naphthols in three-component condensation with aldehydes and derivatives of cyanoacetic acid demonstrated the following facts. First, resorcinol and 3-aminophenol react under the above-described conditions at position 6 rather than at position 2 and further cyclization affords 7-hydroxy- or 7-aminochromenes **1** rather than 5-hydroxychromenes.[13] Second, 2,7-dihydroxynaphthalene reacts at position 1, which was confirmed by the results of X-ray diffraction analysis.

Experimental

The melting points were determined on a Kofler stage. The IR spectra were measured on a Perkin—Elmer 577 instrument in KBr pellets (1/200). The ^{1}H NMR spectra were measured on a Bruker AC-300 spectrometer (300 MHz) in DMSO-d_6; the chemical shifts are given in the δ scale relative to Me_4Si.

2-Amino-4-aryl-3-cyano(ethoxycarbonyl)-4*H*-(benzo[*f*])chromenes (1—3). Triethylamine (0.5 mL) was added to a solution of aromatic aldehyde **4** (10 mmol), malononitrile (or cyanoacetic ester) **5** (10 mmol), and phenol **6** (or naphthol **7—9**) (10 mmol) in EtOH (25 mL). The reaction mixture was refluxed for 10 min. The precipitate that formed was filtered off, washed with EtOH and hexane, and crystallized from EtOH. Compound **2a** was crystallized from MeCN.

For the synthesis of chromenes **10** and **11**, double amounts of aldehyde and malononitrile were required.

2-Amino-3-cyano-7-hydroxy-4-(4-methoxycarbonylphenyl)-4*H*-chromene (1a). The yield was 78%, m.p. 233 °C (decomp.). Found (%): C, 66.95; H, 4.34; N, 8.77. $C_{18}H_{14}N_2O_4$. Calculated (%): C, 67.08; H, 4.38; N, 8.69. IR, ν/cm^{-1}: 3480 (O—H); 3408, 3336 (N—H); 2192 (CN); 1702 (C=O); 1656 (NH_2 bending). ^{1}H NMR, δ: 3.83 (s, 3 H, Me); 4.74 (s, 1 H, H(4)); 6.42 (d, 1 H, H(8), *J* = 1.1 Hz); 6.48 (dd, 1 H, H(6), *J* = 1.1 Hz, *J* = 10.0 Hz); 6.78 (d, 1 H, H(5), *J* = 10.0 Hz); 6.84 (s, 2 H, NH_2); 7.31 and 7.89 (both d, 2 H each, C_6H_4, *J* = 9.4 Hz); 9.64 (s, 1 H, OH).

2-Amino-3-cyano-4-(2,4-difluorophenyl)-7-hydroxy-4*H*-chromene (1b). The yield was 87%, m.p. 221 °C. Found (%): C, 63.90; H, 3.47; N, 9.22. $C_{16}H_{10}F_2N_2O_2$. Calculated (%): C, 64.00; H, 3.36; N, 9.33. IR, ν/cm^{-1}: 3480 (O—H); 3408, 3344, 3256 (N—H); 2196 (CN); 1644 (NH_2 bending). ^{1}H NMR, δ: 4.89 (s, 1 H, H(4)); 6.41 (d, 1 H, H(8), *J* = 0.6 Hz); 6.47 (dd, 1 H, H(6), *J* = 0.6 Hz, *J* = 10.5 Hz); 6.57 (br.s, 2 H, NH_2); 6.75 (d, 1 H, H(5), *J* = 10.5 Hz); 6.96 (m, 2 H, C_6H_3); 7.18 (m, 1 H, C_6H_3); 9.39 (s, 1 H, OH).

2-Amino-3-ethoxycarbonyl-4-(2,4-difluorophenyl)-7-hydroxy-4*H*-chromene (1c). The yield was 69%, m.p. 205 °C. Found (%): C, 62.33; H, 4.30; N, 3.91. $C_{18}H_{15}F_2NO_4$. Calculated (%): C, 62.25; H, 4.35; N, 4.03. IR, ν/cm^{-1}: 3424 (O—H); 3308 (N—H); 1666 (C=O); 1615 (NH_2 bending). ^{1}H NMR, δ: 1.07 (t, 3 H, Me, *J* = 8.9 Hz); 3.95 (κ, 2 H, OCH_2, *J* = 8.9 Hz); 5.11 (s, 1 H, H(4)); 6.43 (m, 2 H, H(8), H(6)); 6.83 (m, 3 H, H(5), C_6H_3); 7.13 (m, 1 H, C_6H_3); 7.44 (br.s, 2 H, NH_2); 9.24 (s, 1 H, OH).

2,7-Diamino-4-(3-bromophenyl)-3-cyano-4*H*-chromene (1d). The yield was 60%, m.p. 232 °C. Found (%): C, 56.19; H, 3.63; N, 12.19. $C_{16}H_{12}BrN_3O$. Calculated (%): C, 56.16; H, 3.54; N, 12.28. IR, ν/cm^{-1}: 3456, 3380, 3336 (N—H); 2194 (CN); 1640 (NH_2 bending). ^{1}H NMR, δ: 4.57 (s, 1 H, H(4)); 5.21 (br.s, 2 H, C(7)NH_2); 6.24 (d, 1 H, H(8), *J* = 1.4 Hz); 6.29 (dd, 1 H, H(6), *J* = 1.4 Hz, *J* = 7.8 Hz); 6.65 (d, 1 H, H(5), *J* = 7.8 Hz); 6.76 (br.s, 2 H, C(2)NH_2); 7.16 (d, 1 H, H(4′), *J* = 7.1 Hz); 7.26 (t, 1 H, H(5′), *J* = 7.1 Hz); 7.29 (s, 1 H, H(2′)); 7.39 (d, 1 H, H(6′), *J* = 7.1 Hz).

2,7-Diamino-3-cyano-4-(4-methoxycarbonylphenyl)-4*H*-chromene (1e). The yield was 89%, m.p. 232 °C. Found (%): C, 67.37; H, 4.69; N, 13.10. $C_{18}H_{15}N_3O_3$. Calculated (%): C, 67.28; H, 4.71; N, 13.08. IR, ν/cm^{-1}: 3448, 3392, 3340 (N—H); 2182 (CN); 1728 (C=O); 1646 (NH_2 bending). ^{1}H NMR, δ: 3.83 (s, 3 H, OMe); 4.63 (s, 1 H, H(4)); 5.23 (br.s, 2 H, C(7)NH_2); 6.22 (s, 1 H, H(8), J = 0.6 Hz); 6.27 (dd, 1 H, H(6), J = 0.6 Hz, J = 10.0 Hz); 6.59 (d, 1 H, H(5), J = 10.0 Hz); 6.79 (br.s, 2 H, C(2)NH_2); 7.29 and 7.89 (both d, 2 H each, C_6H_4, J = 9.4 Hz).

2,7-Diamino-3-cyano-4-(2,4-difluorophenyl)-4*H*-chromene (1f). The yield was 64%, m.p. 208 °C. Found (%): C, 64.08; H, 3.77; N, 13.97. $C_{16}H_{11}F_2N_3O$. Calculated (%): C, 64.21; H, 3.71; N, 14.04. IR, ν/cm^{-1}: 3456, 3388, 3328 (N—H); 2190 (CN); 1632 (NH_2 bending). ^{1}H NMR, δ: 4.82 (s, 1 H, H(4)); 4.96 (br.s, 2 H, C(7)NH_2); 6.24 (s, 1 H, H(8)); 6.28 and 6.59 (both d, 1 H each, H(6), H(5), J = 8.8 Hz); 6.48 (br.s, 2 H, C(2)NH_2); 6.93 (m, 2 H, C_6H_3); 7.16 (m, 1 H, C_6H_3).

2,7-Diamino-3-cyano-4-(3-pyridyl)-4*H*-chromene (1g). The yield was 68%, m.p. 213 °C. Found (%): C, 68.22; H, 4.52; N, 21.16. $C_{15}H_{12}N_4O$. Calculated (%): C, 68.17; H, 4.58; N, 21.20. IR, ν/cm^{-1}: 3408, 3312, 3152 (N—H); 2196 (CN); 1656 (NH_2 bending). ^{1}H NMR, δ: 4.61 (s, 1 H, H(4)); 5.20 (br.s, 2 H, C(7)NH_2); 6.24 (s, 1 H, H(8)); 6.28 and 6.61 (both d, 1 H each, H(5), H(6), J = 8.1 Hz); 6.76 (br.s, 2 H, C(2)NH_2); 7.30 (m, 1 H, H(5′)); 7.48 (m, 1 H, H(4′)); 8.40 (m, 2 H, H(2′), H(6′)).

2-Amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene (2a). The yield was 60%, m.p. 249—251 °C (decomp.). Found (%): C, 74.42; H, 4.95; N, 11.84. $C_{20}H_{14}N_2O_2 \cdot CH_3CN$. Calculated (%): C, 74.35; H, 4.82; N, 11.82. IR, ν/cm^{-1}: 3520 (O—H); 3400, 3258, 3210 (N—H); 2196 (CN); 1652 (NH_2 bending). ^{1}H NMR, δ: 5.01 (s, 1 H, H(4)); 6.68 (br.s, 2 H, NH_2); 7.12 (m, 8 H, C_6H_5, H(5), H(9), H(10)); 7.75 (m, 2 H, H(7), H(8)); 9.63 (br.s, 1 H, OH).

2-Amino-4-(4-chlorophenyl)-3-cyano-6-hydroxy-4*H*-benzo[*f*]chromene (2b). The yield was 74%, m.p. 263—267 °C (decomp.). Found (%): C, 68.79; H, 3.73; N, 10.26. $C_{20}H_{13}ClN_2O_2$. Calculated (%): C, 68.87; H, 3.76; N, 10.16. IR, ν/cm^{-1}: 3490 (O—H); 3380, 3256, 3190 (N—H); 2196 (CN); 1656 (NH_2 bending). ^{1}H NMR, δ: 5.00 (s, 1 H, H(4)); 6.70 (br.s, 2 H, NH_2); 6.90 (s, 1 H, H(5)); 6.91 and 7.03 (both d, 1 H each, H(9), H(10), J = 10.0 Hz); 7.15 and 7.26 (both d, 2 H each, C_6H_4, J = 8.9 Hz); 7.66 and 7.72 (both d, 2 H each, H(7), C(8)H, J = 8.2 Hz); 9.59 (br.s, 1 H, OH).

2-Amino-3-cyano-10-hydroxy-4-(3-thienyl)-4*H*-benzo[*f*]chromene (3). The yield was 69%, m.p. 258—263 °C (decomp.). Found (%): C, 67.52; H, 3.72; N, 8.85. $C_{18}H_{12}N_2O_2S$. Calculated (%): C, 67.48; H, 3.78; N, 8.74. IR, ν/cm^{-1}: 3523 (O—H); 3376, 3256 (N—H); 2192 (CN); 1656 (NH_2 bending). ^{1}H NMR, δ: 5.38 (s, 1 H, H(4)); 6.78 (d, 1 H, H(4) of thiophene, J = 5.7 Hz); 6.91 (br.s, 2 H, NH_2); 7.31 (m, 5 H, H(5), H(6), H(7), H(8), H(9)); 7.68 and 7.85 (both m, 1 H each, H(2) of thiophene, H(5) of thiophene); 10.22 (br.s, 1 H, OH).

2,11-Diamino-3,10-dicyano-4,9-di(3-thienyl)-4*H*,9*H*-pyrano[3,2-*h*]benzo[*f*]chromene (10a). The yield was 83%, m.p. > 350 °C. Found (%): C, 64.87; H, 3.31; N, 11.53. $C_{26}H_{16}N_4O_2S_2$. Calculated (%): C, 64.98; H, 3.36; N, 11.66. IR, ν/cm^{-1}: 3400—3200 (N—H); 2186 (CN); 1646 (NH_2 bending). ^{1}H NMR, δ: 5.49 (s, 2 H, H(4), H(9)); 6.68 and 6.79 (both br.s, 2 H each, 2 NH_2); 6.86, 7.33, and 7.96 (all m, 2 H, 6 H, 2 H, 2 H(4′), 2 H(2′), H(5), H(6), H(7), H(8), 2 H(5′)).

2,11-Diamino-3,10-dicyano-4,9-di(4-fluorophenyl)-4*H*,9*H*-pyrano[3,2-*h*]benzo[*f*]chromene (10b). The yield was 72%, m.p. 241 °C (decomp.). Found (%): C, 71.30; H, 3.66; N, 11.20. $C_{30}H_{18}F_2N_4O_2$. Calculated (%): C, 71.42; H, 3.60; N, 11.11. IR, ν/cm^{-1}: 3400—3200 (N—H); 2192 (CN); 1660 (NH_2 bending). ^{1}H NMR, δ: 5.42 (s, 2 H, H(4), H(9)); 6.74 and 6.85 (both br.s, 2 H each, 2 NH_2); 7.10, 7.30, and 7.83 (all m, 4 H, 6 H, 2 H, 2 C_6H_4, H(5), H(6), H(7), H(8)).

2,8-Diamino-4,10-di(4-chlorophenyl)-3,9-dicyano-4*H*,10*H*-chromeno[8,7-*h*]chromene (11). The yield was 82%, m.p. 320—321 °C (decomp.). Found (%): C, 67.13; H, 3.49; N, 10.27. $C_{30}H_{18}Cl_2N_4O_2$. Calculated (%): C, 67.05; H, 3.38; N, 10.43. IR, ν/cm^{-1}: 3424, 3324, 3196 (N—H); 2200 (CN); 1666 (NH_2 bending). ^{1}H NMR, δ: 4.96 (s, 2 H, H(4), H(10)); 7.09 (br.s, 4 H, 2NH_2); 7.25 and 7.38 (both m, 6 H, 4 H, 2 C_6H_4, H(6), H(12)); 7.91 (d, 2 H, H(5), H(11), J = 9.4 Hz).

X-ray diffraction analysis of compound 2a. Single crystals of the solvate of 2-amino-3-cyano-6-hydroxy-4-phenyl-4*H*-benzo[*f*]chromene (**2a**) ($C_{20}H_{14}N_2O_2 \cdot CH_3CN$) were prepared by crystallization of **2a** from MeCN. The colorless crystals are monoclinic, at −80 °C, a = 8.643 (4), b = 9.723 (4), c = 21.475 (13) Å, β = 101.55 (4)°, V = 1768 (2) Å^3, d_{calc} = 1.335 g cm^{-3}, Z = 4, space group $P2_1/c$.

The unit cell parameters and intensities of 4324 reflections were measured on an automated four-circle Syntex $P2_1$ diffractometer (λ(Mo-Kα), graphite monochromator, θ/2θ scan technique, θ_{max} = 28°). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The acetonitrile molecule was revealed from a difference Fourier synthesis. The H atoms were located from a difference Fourier synthesis and refined isotropically. The final reliability factors were as follows: R_1 = 0.056 using 2558 independent reflections, wR_2 = 0.150 using 3997 reflections. All calculations were carried out with the use of the SHELXL-97 program package.[19] The atomic coordinates and isotropic equivalent (isotropic for H atoms) thermal parameters were deposited with the Cambridge Structural Database.

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