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NOVEL ASPECTS OF THE REACTION OF 3-(BENZIMIDAZOL-2-YL)-2-IMINO-COUMARINS WITH AROMATIC ALDEHYDES

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The reaction of 3-(benzimidazol-2-yl)-2-iminocoumarins with aromatic aldehydes has been studied. The condensation products 7-aryl-7H-benzo[4,5]imidazo[1,2-c]benzopyrano[3,2-e]pyrimidines or 3-(benzimidazol-2-yl)coumarins are formed depending on the nature of the substituent in the starting 2-iminocoumarin and aldehyde. In DMF medium, 7-aryl-7H-benzo[4,5]imidazo[1,2-c]benzopyrano-[3,2-e]pyrimidines isomerize to the corresponding 7-aryl-14H-benzo[4,5]imidazo[1,2-c]benzopyrano-[3,2-e]pyrimidines. The effect of the substituent on the isomerization process has been studied and the reaction mechanisms are discussed.

Keywords: 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidine, 7-aryl-14H-benzo[4,5]-imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidine, aromatic aldehyde, 3-(benzimidazol-2-yl)-2-imino-coumarin, 3-(benzimidazol-2-yl)coumarin, substituent effect, isomerization, proton transfer, equilibrium.

The considerable attention of investigators to 2-iminocoumarin derivatives is connected with their high reactivity, potentially reacting both with electrophilic and with nucleophilic substituents [1-4]. Special interest in this program has focused on reactions which form novel heterocyclic systems [5, 6].

In previous work [7] we reported the reaction of the 3-benzimidazol-2-yl-2-iminocoumarins **1a-c** with an excess of aromatic aldehydes **2b-f,k** in refluxing *n*-propanol or *n*-butanol in the presence of catalytic amounts of piperidine to give the 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidines **3a,i-k**.

In several cases the condensation product could not be separated due to a side reaction involving the hydrolysis of the 2-imino group to give 3-(benzimidazol-2-yl)coumarins [8, 9] (see Scheme 1).

With the aim of a detailed examination of the effect of the reaction conditions and nature of the substituent on the course of the studied reaction for the 3-(benzimidazol-2-yl)-2-iminocoumarins and the corresponding aromatic aldehydes in *n*-pentanol or *n*-butanol in the presence of pyridine, the 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidines **3a-m** were prepared (Table 1).

The effect of increasing the reaction temperature of the medium (exchanging *n*-butanol for *n*-pentanol) in the case of the difficultly soluble starting unsubstituted 3-(benzimidazol-2-yl)-2-iminocoumarin **1a** and the methoxy derivative **1b** was significant to decrease the time to carry out the reaction and to increase the yield, however in the case of the 7-dialkyl derivatives **1c,d** the use of *n*-butanol was optimal.

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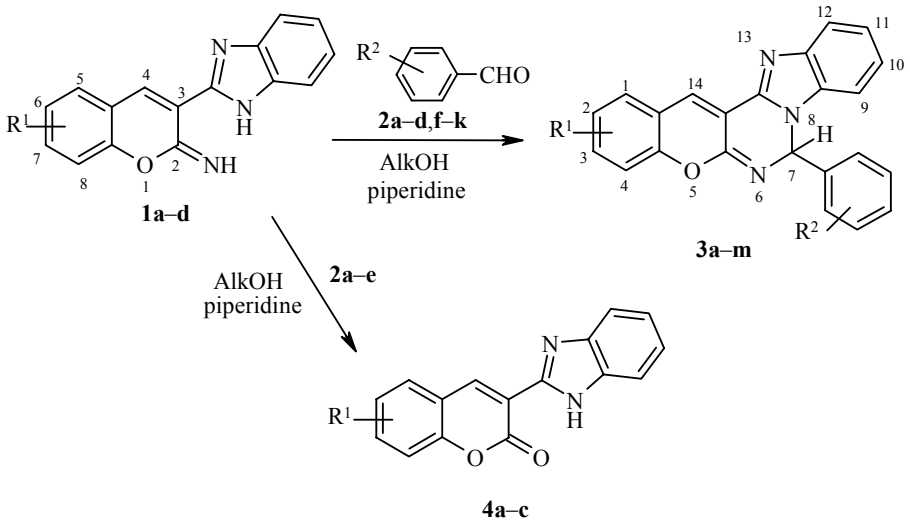
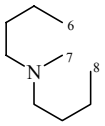
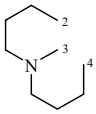
Scheme 1



1 a R^1 = H, **b** R^1 = 6-MeO, **c** R^1 = 7-NEt_2, **d** R^1 = 

2 a R^2 = H, **b** R^2 = 4-Cl, **c** R^2 = 4-Br, **d** R^2 = 4-OMe, **e** R^2 = 4-NO_2, **f** R^2 = 4-NMe_2, **g** R^2 = 4-OH, **h** R^2 = 2-OH, **i** R^2 = 4-OH-3-OMe, **j** R^2 = 2-OH-3-OMe, **k** R^2 = 2-OH-5-OMe; **3 a–e** R^1 = H, **a** R^2 = 4-NMe_2, **b** R^2 = 4-OH, **c** R^2 = 2-OH, **d** R^2 = 2-OH-3-OMe, **e** R^2 = 4-OH-3-OMe, **f**, **g** R^1 = 2-MeO, **f** R^2 = 2-OH, **g** R^2 = 2-OH-3-OMe, **h–k** R^1 = 3-NEt_2, **h** R^2 = H, **i** R^2 = 4-Cl, **j** R^2 = 4-OCH_3, **k** R^2 = 2-OH-5-OMe, **l**, **m** R^1 =  , **l** R^2 = H, **m** R^2 = 4-Br; **4 a** R^1 = H, **b** R^1 = 6-MeO, **c** R^1 = 7-NEt_2

The substituents in the starting 2-iminocoumarins **1a-d** and the aromatic aldehydes proved to have a significant effect on the reaction course. Hence in the case of the 2-iminocoumarins which contain a dialkylamino group in position 7 (compounds **1c,d**) the reaction occurs in good yield, even in *n*-butanol. For completion of the reaction 15-60 min is sufficient, moreover it is possible to obtain the condensation products with virtually all of the aromatic aldehydes **2a-d,k**. However, the reaction of the 2-iminocoumarin **1c** with *para*-nitrobenzaldehyde **2e** gave only the 3-benzimidazolylcoumarin **4c**.

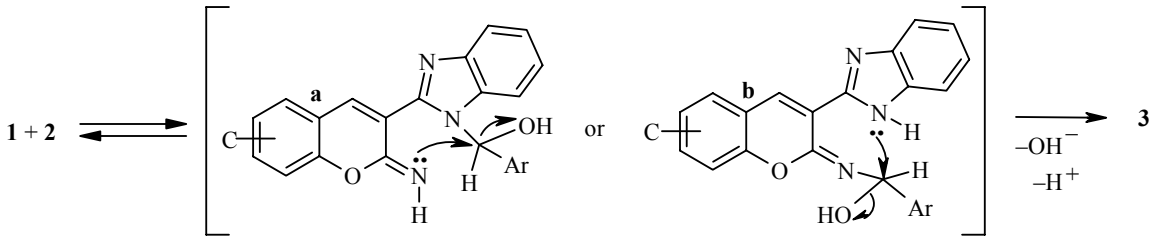
The reaction time increases to 2 h when using the unsubstituted 3-benzimidazol-2-yl-2-iminocoumarin **1a** and the 6-methoxy derivative **1b**. In these conditions, the condensation products (Table 1) are only formed when using the aromatic aldehydes **2f-j** with donor substituents in the aromatic ring. The presence of only one *para*-methoxy group in the benzaldehyde **2d** does not allow the condensation. The benzaldehydes **2a-e** give the 3-benzimidazolylcoumarins **4a,b** in almost quantitative yield.

In order to explain the effect reported above on the effect of the substituent one should bear in mind that a donor substituent in position 7 of the 2-iminocoumarin increases the electron density both at the nitrogen atoms of the benzimidazole and also on the 2-imino group nitrogen thus increasing the overall nucleophilicity of the heterocyclic system. This makes possible the condensation of the 7-dialkylamino derivatives **1c,d** with aromatic aldehydes containing a different kind of substituent. Not so evident are the reasons why aromatic aldehydes containing donor substituent take part in condensation with the 2-iminocoumarins **1a,b** and those not containing them don't.

TABLE 1. Characteristics of the Compounds **3b-h,l,m**

Com-pound	Empirical formula	Found N, % / Calculated N, %	mp, °C	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)	Yield, %
3b	$C_{23}H_{15}N_3O_2$	11.50 / 11.62	244-246	1452, 1520, 1560 (C=C); 1600, 1660 (C=N); 2830, 3008, 3060 (C–H); ~3400 (O–H)	6.7 (2H, d, *J* = 8.5, 3',5'-H); 7.1-7.3 (8H, m, 2,3,4,7,9,11,2',6'-H); 7.5 (1H, td, *J* = 7.9, *J* = 1.5, 10-H); 7.6-7.8 (2H, m, 1,12-H); 8.3 (1H, s, 14-H); 9.4 (1H, s, OH)	52
3c	$C_{23}H_{15}N_3O_2$	11.50 / 11.66	257-259	1456, 1508, 1524 (C=C); 1600, 1672 (C=N); 2860, 3036 (C–H); ~3450 (O–H)	6.7-6.8 (2H, m, 3',5'-H); 7.0-7.3 (7H, m, 2,3,4,9,11,2',6'-H); 7.4 (1H, s, 7-H); 7.5 (1H, td, *J* = 7.9, *J* = 1.5, 10-H); 7.6-7.8 (2H, m, 1,12-H); 8.3 (1H, s, 14-H); 9.7 (1H, s, OH)	71
3d	$C_{24}H_{17}N_3O_3$	10.63 / 10.79	247-248	1452, 1492, 1528 (C=C); 1600, 1680 (C=N); 2830, 2912, 3056 (C–H); ~3450 (O–H)	3.7 (3H, s, OMe); 6.7-6.8 (2H, m, 4'- or 6',5'-H); 6.9 (1H, dd, *J* = 7.6, *J* = 2.1, 4'- or 6'-H); 7.0-7.3 (5H, m, 2,3,4,9,11-H); 7.5 (1H, s, 7-H); 7.5 (1H, td, *J* = 7.9, *J* = 1.5, 10-H); 7.6-7.8 (2H, m, 1,12-H); 8.3 (1H, s, 14-H); 8.9 (1H, s, OH)	67
3e	$C_{24}H_{17}N_3O_3$	10.63 / 10.69	261-262	1540, 1560, 1576 (C=C); 1604,1676 (C=N);2932,3064 (C–H) ; ~3300 (O–H)	6.6-6.8 (2H, m, 5',6'-H); 7.0 (1H, d, *J* = 1.2, 2'-H); 7.0-7.3 (6H, m, 2,3,4,7,9,11-H); 7.5 (1H, td, *J* = 7.9, *J* = 1.5, 10-H); 7.6-7.8 (2H, m, 1,12-H); 8.3 (1H, s, 14-H); 9.0 (1H, s, OH)	71
3f	$C_{24}H_{17}N_3O_3$	10.63 / 10.50	272-273	1460, 1528, 1584 (C=C); 1604, 1672 (C=N); 2936, 2972, 3064 (C–H); ~3450 (O–H)	3.8 (3H, s, OMe); 6.7-6.8 (2H, m, 3',5'-H); 7.0-7.3 (7H, m, 3,4,9,10,11,4',6'-H); 7.3 (1H, d, *J* = 2.7, 1-H); 7.4 (1H, s, 7-H); 7.7 (1H, d, *J* = 7.9, 12-H); 8.2 (1H, s, 14-H); 9.7 (1H, s, OH)	58
3g	$C_{25}H_{19}N_3O_4$	9.88 / 10.06	289-290	1458, 1482, 1580 (C=C); 1623, 1667 (C=N); 2837, 2942, 2994, 3057 (C–H); ~3450 (O–H)	3.73 (3H, s, 3'-OMe); 3.79 (3H, s, 2-OMe); 6.6-6.8 (2H, m, 4'- or 6',5'-H); 6.9 (1H, dd, *J* = 7.6, *J* = 2.7, 4'- or 6'-H); 7.0–7.2 (5H, m, 3,4,9,10,11-H); 7.3 (1H, d, *J* = 2.7, 1-H); 7.4 (1H, s, 7-H); 7.7 (1H, d, *J* = 7.9, 12-H); 8.2 (1H, s, 14-H); 8.9 (1H, s, OH)	79
3h	$C_{27}H_{24}N_4O$	13.32 / 13.24	261-263	1512, 1532, 1549 (C=C); 1612, 1668 (C=N); 2896, 2928, 2972, 3052, 3080 (C–H)	1.1 (6H, t, *J* = 7.3, $N(CH_2\underline{CH_3})_2$); 3.4 (4H, q, *J* = 7.3, $N(\underline{CH_2}CH_3)_2$); 6.4 (1H, d, *J* = 2.4, 4-H); 6.6 (1H, dd, *J* = 8.9, *J* = 2.4, 2-H); 7.0-7.2 (3H, m, 9,10,11-H); 7.2–7.4 (6H, m, 7,2',3',4',5',6'-H); 7.5 (1H, d, *J* = 8.9, 1-H); 7.6 (1H, d, *J* = 7.9, 12-H); 8.1 (1H, s, 14-H)	66
3 l	$C_{27}H_{24}N_4O$	12.60 / 12.45	271-273	1542, 1564 (C=C); 1608, 1676 (C=N); 2932, 2952, 3004, 3024, 3044 (C–H)	1.9 (4H, q, *J* = 6.0, $N(CH_2\underline{CH_2}CH_2)_2$); 2.7 (4H, t, *J* = 6.0, $N(CH_2CH_2\underline{CH_2})_2$); 3.3 (4H, m, $N(\underline{CH_2}CH_2CH_2)_2$); 7.0-7.2 (4H, m, 1,9,10,11-H); 7.2–7.4 (5H, m, 2',3',4',5',6'-H); 7.3 (1H, s, 7-H); 7.2-7.4 (5H, m, 2',3',4',5',6'-H); 7.6 (1H, d, *J* = 7.9, 12-H); 8.0 (1H, s, 14-H)	72
3m	$C_{29}H_{23}BrN_4O$	10.70 / 10.63	>300	1452, 1528, 1568 (C=C); 1608, 1672 (C=N); 2848, 2892, 2932, 3048 (C–H)	1.8 (4H, q, *J* = 6.0, $N(CH_2\underline{CH_2}CH_2)_2$); 2.7 (4H, t, *J* = 6.0, $N(CH_2CH_2\underline{CH_2})_2$); 3.3 ($N(\underline{CH_2}CH_2CH_2)_2$); 6.9-6.2 (4H, m, 1,9,10,11-H); 7.2 (1H, s, 7-H); 7.3 (2H, d, *J* = 8.2, 2',6'-H); 7.5 (2H, d, *J* = 8.2, 3',5'-H); 7.6 (1H, d, *J* = 7.9, 12-H); 8.0 (1H, s, 14-H)	45

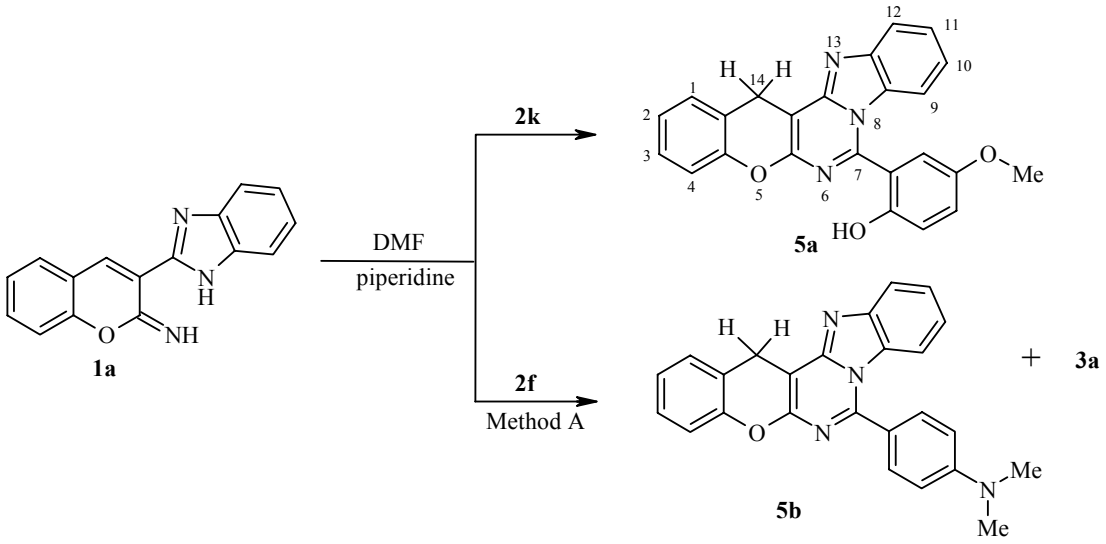
When considering a possible reaction mechanism it should be noted that, while not appearing possible to determine which of the nitrogen atoms (the nitrogen of the 2-imino group or one of the nitrogen atoms of the benzimidazole ring) undergoes initial attack by the electrophilic carbonyl group of the aromatic aldehyde, a necessary stage after the formation of the intermediate hemiaminal (**a** or **b**) is the fission of a molecule of water.



In both possible transition states for the second stage, the methine carbon atom is surrounded by three electron-acceptor atoms (the two nitrogen atoms and the oxygen atom) and must be markedly electron deficient. Electron-donor substituents in the aryl radical can partially compensate for the deficit of electron density for this atom, lowering the energy of the transition state for the irreversible terminal stage of the departure of a hydroxyl group (typical of substitution reactions occurring via an S_N1 mechanism).

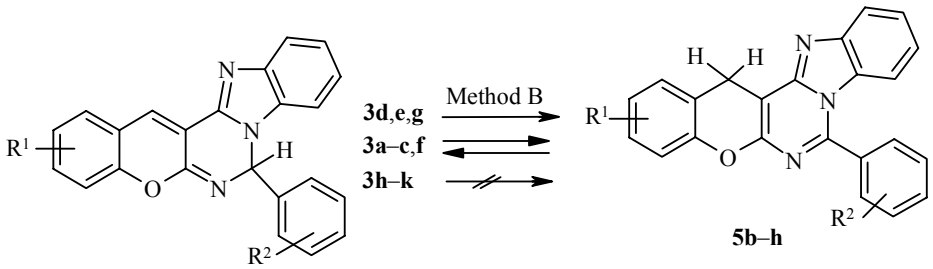
In the reactions with the aldehydes **2a-e** which give the 2-iminocoumarin hydrolysis products (the 3-benzimidazolylcoumarins **4a-c**) it can be stated with confidence that the aldehyde participates in the hydrolysis process. This is confirmed by the fact that a blank experiment (refluxing the 3-benzimidazolyl-2-iminocoumarin **1a** in *n*-pentanol in the presence of piperidine for 10 h) shows no production of the corresponding coumarin **4a**. Evidently the function of the aldehyde is to form an aldimine.

When using DMF as reaction medium the unsubstituted 2-iminocoumarin **1a** and 5-methoxysalicylaldehyde **2k** give the isomer 7-(2-hydroxy-5-methoxyphenyl)-14H-benzo[4,5]imidazo[1,2-*c*]-benzopyrano[3,2-*e*]pyrimidine (**5a**) but the *para*-dimethylaminobenzaldehyde **2f** leads to a mixture of the isomers **5b** and **3a** in the ratio 1:2 (method A).



These facts caused us to turn our investigation to the effect of solvent on the reaction course. It was found that the 7H-derivatives **3a-k** obtained in *n*-pentanol behaved differently, depending on the substituent, when heated in DMF in the presence of piperidine. If the aryl radical contains hydroxy and methoxy groups

together, as occurs in compounds **3d,e,g**, the isomerization occurs fully to give the 14H-isomers **5e,f,h** respectively (Table 2). Completion of this reaction needs about 2 h refluxing. If the aryl radical contains only one donor substituent (a hydroxy or dimethylamino group, compounds **3a-c,f**, method B) then after 2 h refluxing in DMF in the presence of piperidine a new product is found in the reaction medium (TLC analysis) which does not increase upon subsequent, prolonged reflux. Such behaviour points to the presence of an equilibrium between the two isomers of **3a-c,f** and **5b-d,g** respectively.



5 b–f R^1 = H, **b** R^2 = 4-NMe_2, **c** R^2 = 4-OH, **d** R^2 = 2-OH, **e** R^2 = 2-OH-3-OMe, **f** R^2 = 4-OH-3-OMe, **g**, **h** R^1 = 2-MeO, **g** R^2 = 2-OH, **h** R^2 = 2-OH-3-OMe

The ^{1}H NMR spectra of the precipitates formed upon cooling the mixtures also supported the presence of a mixture of the two isomers of **5b-d,g** and **3a-c,f** while in the case of the *para*-dimethylamino derivatives **5b** and **3a** a mixture of the same composition (1:2, method B) is formed as in the direct reaction of *para*-dimethylaminobenzaldehyde with 2-iminocoumarin **1a** in DMF (method A). The pure 14H-derivatives **5d,g** can be prepared in good yield by a double recrystallization of the equilibrium mixture from DMF (Table 2). In the case of the 3-diethylamino derivatives **3h-k** the isomerization is not observed.

Basic catalysis of the isomerization infers separation of a methine proton. In view of the absence of isomerization in alcohol medium it can be proposed that the anion is unstable under these conditions and can be rapidly protonated. On the other hand, in the aprotic dimethylformamide the anion is more stable and can exist for quite a long time thus bringing about a proton addition at position 14 and hence we were able to separate the thermodynamically more stable isomer or to observe the equilibrium. Based on such a mechanism we favored the proposal that acid may also serve as catalyst. In fact, in the protic *n*-butanol in the presence of sulfuric acid an equilibrium between the isomers of **5b** and **3a** is also observed but with a rather different ratio of isomers (3:4, method B). The position of the equilibrium depends on the relative thermodynamic stability of the isomers and the properties of the medium, hence the nature of the substituent in the coumarin and aryl fragments determines the ability of the 7H-derivatives **3a-k** to undergo isomerization. The presence in the 7H-derivatives of a donor substituent in position 3 (compounds **3h-k**) evidently stabilizes the 7H-isomer due to conjugation of the dimethylamino group with the acceptor benzimidazole and iminolactone heterocyclic system fragments hence these derivatives do not isomerize. On the other hand, donor substituents in the aryl radical stabilize the 14H-isomer thanks to their conjugation with the acceptor pyrimidine ring.

The ^{1}H NMR spectra of the synthesized compounds fully agree with the structure proposed (see Tables 1 and 2 and also [7]). The singlet for the methine proton at position 7 in the 7H-derivatives **3a-m** appears in the aromatic proton resonance region (7.0-7.5 ppm) but, none the less, its chemical shift can be identified in the majority of cases. To a significant extent the position of this signal depends on the nature of the substituent in the coumarin and aryl fragments of the molecules (see Table 1). The chemical shift of the singlet for the proton at position 14 depends only on the nature of the substituent R^1. This signal is subsequently shifted to high field with an increase in the donor strength of the substituent R^1 when going from the compounds unsubstituted in the coumarin fragment of the compounds **3b-e** to the julolidine derivatives **3l,m**. The multiplet for the ABCD spin system of the four benzimidazole protons is seen at 7.0-7.8 ppm. In several cases the signals for the protons in positions 10 and 12 appear, respectively, as a triplet of doublets at 7.5 and a doublet at 7.6-7.7 ppm with the

TABLE 2. Characteristics of the Compounds **5a,d-h**

Compound	Empirical formula	Found N, % / Calculated N, %	mp, °C	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm. (*J*, Hz)	Yield, %
5a	$C_{24}H_{17}N_3O_3$	10.63 / 10.75	281-283	1456, 1500, 1572 (C=C); 1636, 1667 (C=N); 2837, 2960, 3004, 3040 (C–H); ~3400 (O–H)	3.8 (3H, s, OMe); 4.3 (2H, s, CH_2); 6.7 (1H, d, *J* = 7.9, 9-H); 7.0-7.3 (6H, m, 1,2,4,10,3',6'-H); 7.3 (1H, m, 3-H); 7.4-7.5 (2H, m, 11,4'-H); 7.8 (1H, d, *J* = 7.9, 12-H); 9.5 (1H, s, OH)	48
5d	$C_{23}H_{15}N_3O_2$	11.50 / 11.38	291-293	1454, 1560, 1584 (C=C); 1598, 1630 (C=N); 2848, 2910, 3018, 3050 (C–H); ~3450 (O–H)	4.3 (2H, s, CH_2); 6.7 (1H, d, *J* = 7.9, 9-H); 6.9-7.7 (10H, m, 1,2,3,4,10,11,3',4',5',6'-H); 7.8 (1H, d, *J* = 7.9, 12-H); 10.1 (1H, s, OH)	63
5e	$C_{24}H_{17}N_3O_3$	10.63 / 10.65	269-271	1455, 1488, 1560 (C=C); 1622, 1648 (C=N); 2832, 2925, 2950 (C–H); ~3550 (O–H)	3.9 (3H, s, OMe); 4.3 (2H, s, CH_2); 6.6 (1H, d, *J* = 7.9, 9-H); 7.0-7.3 (5H, m, 2,4,10,5',4'- or 6'-H); 7.2-7.4 (2H, m, 3, 4'- or 6'-H); 7.4-7.5 (2H, m, 1,11-H); 7.8 (1H, d, *J* = 7.9, 12-H); 9.3 (1H, s, OH)	55
5f	$C_{24}H_{17}N_3O_3$	10.63 / 10.48	300-302	1491, 1573, 1590 (C=C); 1602, 1632 (C=N); 2828, 2890, 2955 (C–H); ~3450 (O–H)	3.8 (3H, s, OMe); 4.2 (2H, s, CH_2); 6.8 (1H, d, *J* = 7.9, 9-H); 6.7-7.5 (9H, m, 1,2,3,4,10,11,2',5',6'-H); 7.7 (1H, d, *J* = 7.9, 12-H); 9.7 (1H, s, OH)	70
5g	$C_{24}H_{17}N_3O_3$	10.63 / 10.54	288-290	1490, 1570, 1590 (C=C); 1604, 1642 (C=N); 2832, 2929, 3006 (C–H); ~3450 (O–H)	3.8 (3H, s, OMe); 4.3 (2H, s, CH_2); 6.6 (1H, d, *J* = 7.9, 9-H); 6.8 (1H, dd, *J* = 8.9, *J* = 2.7, 3-H); 6.9-7.2 (5H, m, 1,4,10,3',5'-H); 7.4 (1H, t, *J* = 7.9, 11-H); 7.5-7.6 (2H, m, 4',6'-H); 7.8 (1H, d, *J* = 7.9, 12-H); 10.0 (1H, s, OH)	60
5h	$C_{25}H_{19}N_3O_4$	9.88 / 9.95	299-302	1455, 1487, 1582 (C=C); 1628, 1640 (C=N); 2828, 2890, 2930, 2982 (C–H); ~3450 (O–H)	3.8 (3H, s, 2-OMe); 3.9 (3H, s, 3'-OMe); 4.3 (2H, s, CH_2); 6.6 (1H, d, *J* = 7.9, 9-H); 6.9 (1H, dd, *J* = 8.9, *J* = 2.7, 3-H); 7.0-7.2 (5H, m, 1,4,10,4'- or 6',5'-H); 7.3 (1H, dd, *J* = 6.4, *J* = 3.1, 4'- or 6'-H); 7.4 (1H, t, *J* = 7.9, 11-H); 7.8 (1H, d, *J* = 7.9, 12-H); 9.3 (1H, s, OH)	45

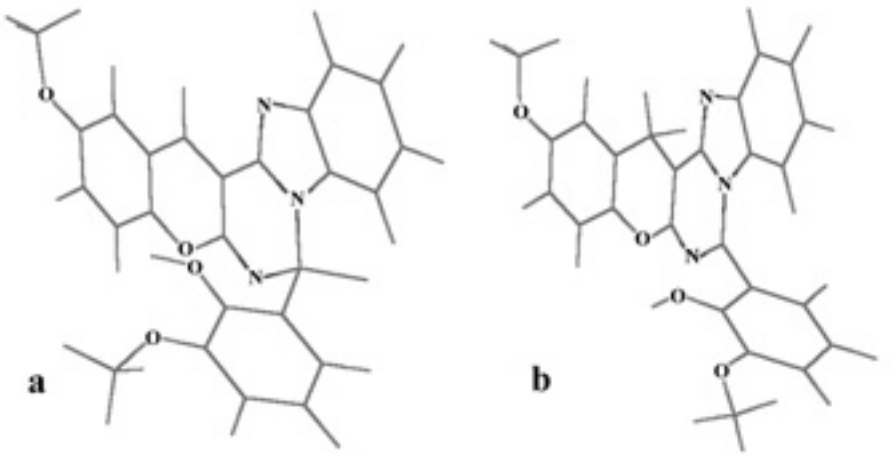


Fig. 1. Resulting calculated structures for compounds **3g** (**a**) and **5h** (**b**) using the method of molecular mechanics (MM+).

single large spin-spin coupling of J = 7.9 Hz. The signal for the methylene group closest to the nitrogen in the julolidine derivatives **3l,m** is partially (for compound **3l**) or fully (for **3m**) obscured by the signal for the water in the DMSO-d_6.

In the ^{1}H NMR spectra of the 14H-derivatives **5a-h** a singlet is observed in the region 4.2-4.3 ppm for the two protons of the methylene group. Additionally, the characteristic signal for the proton at position 14 in the range 8.2-8.3 ppm is not observed. For a precise and proven assignment of the aromatic proton signals in the spectrum of the derivative **5h** we have used the COSY 2D ^{1}H NMR spectroscopic method. The presence of three cross peaks for the doublet at 6.6 ppm shows that this signal lies at an anomalously high field position for a benzimidazole [10], none the less it is assigned to position 9. Such a shift is attributable to the magnetic anisotropy of the aryl radical in position 7. The fact that this proton is found over the plane of the aryl radical in position 7 in the molecule **5h** (in contrast to the isomer **3g**) is confirmed by structural calculations made by molecular mechanics (Figure 1).

Strong bands for a C=N bond are observed in IR spectra of the 7H-derivatives **3b-h,l,m** in the region 1600-1680 cm^{-1}. The spectra of the 14H-isomers **5a,d-h** show two C=N vibrations at 1598-1667 cm^{-1}. In both series of isomers bands of varying intensity for the C=C bonds in the aromatic and heterocyclic rings are found in the range 1452-1590 cm^{-1}. C–H Alkyl bond bands are seen at 2828-2972 cm^{-1} and weak bands for the aromatic and heterocyclic C–H vibrations appear in characteristic regions of the spectrum at 2994-3080 cm^{-1} (see Tables 1 and 2).

Hence the reactivity of 3-(benzimidazol-2-yl)-2-iminocoumarins with aromatic aldehydes is controlled by the nature of the substituent and the conditions for carrying out the reaction.

The 7H-derivatives **3h-j,l,m** contain a dialkylamino group at position 3 and are high efficiency fluorophores. As was shown in our work [11], they can be used as laser dyes, the generation energy parameters of which exceed the corresponding value for the structurally similar laser dye coumarin 7 (compound **4c**).

EXPERIMENTAL

IR spectra were measured for KBr tables on a Specord M82 spectrophotometer in the range 400 to 4000 cm^{-1} and ^{1}H NMR spectra on a Varian Mercury 200 (200 MHz) instrument using DMSO-d_6 solvent and TMS internal standard. The purity of all of the products was monitored by TLC using Silufol UV-254 plates and with ethyl acetate as eluent.

7-Aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidine (3a-m) (General Method). A mixture of the 3-(benzimidazol-2-yl)-2-iminocoumarin **1a-d** (3.5 mmol) and the aromatic aldehyde **2a-k** (5 mmol) in *n*-pentanol (10-15 ml) (or the same volume of *n*-butanol for the 7-dialkylamino derivatives **1c,d**) was heated to reflux, piperidine (3-4 drops) was added, and the product was refluxed for 2 h, cooled, and left overnight. The precipitated solid was filtered off, washed with ethanol, and recrystallized from *n*-butanol or a mixture of *n*-butanol and DMF (see Table 1).

7-(Hydroxy-5-methoxyphenyl)-14H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidine (5a). A mixture of the 3-(benzimidazol-2-yl)-2-iminocoumarin **1a** (2 mmol) and 5-methoxysalicylaldehyde **2k** (3 mmol) in DMF (3 ml) was heated to reflux, piperidine (4 drops) added, refluxed for 3 h, cooled, and left overnight. The precipitated solid was filtered off, washed with ethanol, and recrystallized from DMF (Table 2).

Equilibrium Mixture of 7-(4-Dimethylaminophenyl)-14H-benzo[4,5]imidazo[1,2-*c*]benzopyrano-[3,2-*e*]-pyrimidine (5b) and 7-(4-Dimethylaminophenyl)-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]-pyrimidine (3a). A. A mixture of 3-(benzimidazol-2-yl)-2-coumarin **1a** (2 mmol) and *para*-dimethylaminobenzaldehyde **2f** (3 mmol) in DMF (3 ml) was heated to reflux, piperidine (4 drops) added, refluxed for 2 h, cooled, and left overnight. The precipitated solid was filtered off and washed with ethanol. According to ^{1}H NMR data the mixture contains the products **5b** and **3a** in the ratio of about 1:2. The equilibrium mixture for **5c** and **3b** was obtained similarly (about 3:5). Recrystallization from DMF and/or AcOH did not lead to the separation of a single product.

B. Piperidine (4 drops) was added to 7-(4-dimethylamino)-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano-[3,2-*e*]pyrimidine **3a** (2 mmol) in DMF (3 ml) and the product was refluxed for 2 h, cooled, and left overnight. The precipitated solid was filtered off and washed with ethanol. According to the ^{1}H NMR data the mixture contains the products **5b** and **3a** in the ratio of about 1:2.

C. Freshly prepared H_2SO_4 solution in *n*-butanol (5%, 4 drops) was added to 7-(4-dimethylamino)-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidine **3a** (2 mmol) in *n*-butanol (8 ml), and the product was refluxed for 2 h, cooled, and left overnight. The precipitated solid was filtered off and washed with ethanol. According to the ^{1}H NMR data the mixture contains the products **5b** and **3a** in the ratio of about 3: 4.

7-Aryl-14H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidine (5d-h) (General Method). Piperidine (4 drops) was added to the 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]-pyrimidine **3c-g** (2 mmol) in DMF (3 ml) and the product was refluxed for 2 h, cooled, and left overnight. The precipitated solid was filtered off, washed with ethanol, and recrystallized from a mixture of *n*-butanol and DMF. In the case of the *ortho*-hydroxy derivatives **3c** and **3f** the initially formed precipitate is a mixture of the isomers **5d** and **3c** or **5g** and **3f** respectively. A double recrystallization of these precipitates from DMF led to separation of the products **5d** and **5g** respectively (see Table 2).

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