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RECYCLIZATION OF 2-IMINOCOUMARINS USING NUCLEOPHILIC REAGENTS. 6*. REACTION OF 2-IMINOCOUMARIN-3-CARBOXAMIDES WITH 2-AMINOBENZOPHENONES

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It has been shown that the reaction of 2-iminocoumarin-3-carboxamides with substituted 2-aminobenzophenones occurs in accordance with recyclization mechanism to form substituted 3-(4-phenylquinazolin-2-yl)coumarins. The structure of the compounds obtained was confirmed by spectroscopic data and by X-ray analysis.

Keywords: 2-aminobenzophenones, 3-(4-arylquinazolin-2-yl)coumarins, 2-iminocoumarins, X-ray analysis, recyclization.

In previous reports we have shown that, depending on the conditions, the reaction of 2-imino-2H-1-benzopyran-3-carboxamides with N-nucleophilic reagents can take place both *via* formation of 2-N-substituted iminocoumarins (acid medium, 20°C) [2-7] and by recyclization mechanism to give 3-substituted coumarins (neutral medium, 120-200°C) [2, 7]. In certain examples the use of binucleophilic reagents (*o*-substituted anilines, arenecarboxylic acid hydrazides, thiosemicarbazides, anthranilic acid derivatives) gives 3-heterylcoumarins which are the products of their subsequent cyclization [1, 6-8]. In this study we continue to investigate the reaction of 2-imino-2H-1-benzopyran-3-carboxamides with nucleophilic reagents and to study the behavior of these compounds when reacting with substituted 2-aminobenzophenones.

The starting R^1-substituted 2-iminocoumarin-3-carboxamides **1** were prepared by known methods and introduced into the reaction with substituted 2-aminobenzophenones **2**. As shown by us, the recyclization products R^1-substituted 3-[6-R^2-4-(R^3-phenyl)quinazolin-2-yl]coumarins **7a-u** (see Scheme 1 and Table 1) rather than the expected 2-substituted coumarins **3** are formed in glacial acetic acid, even in the cold.

Analysis of the ^{1}H NMR spectra of the reaction products shows that the signals for the protons of the imino group (12-13 ppm) and the protons of the amide group (9.0-9.2, 7.7-7.9 ppm), which are characteristic of the spectra of the starting 2-iminocoumarin-3-carboxamides **1** [9], are lost in the course of the reaction. The presence in the ^{1}H NMR spectra of the overlapping signals for the aromatic protons of the coumarin and quinazoline fragments in the region of 6.54-8.70 ppm and the singlet signal for the H-4 proton of the coumarin ring (8.65-9.49 ppm) agree fully with the proposed structure (Table 2).

* For Communication 5 see [1].

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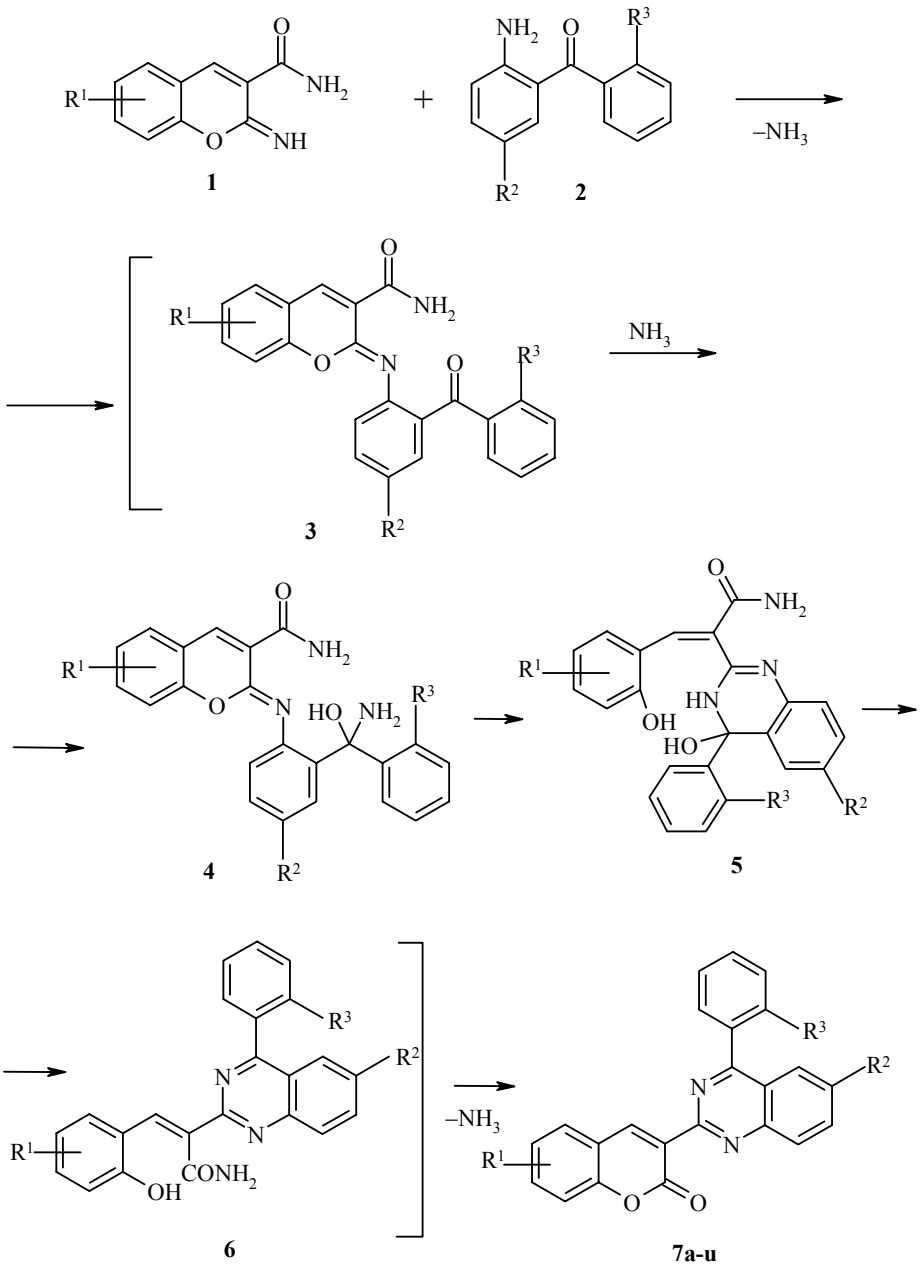
Scheme 1



7a $R^1 = R^3 = H$; **b** $R^1 = H$, $R^3 = Cl$; **c** R^1 = 7-OH, $R^3 = H$; **d** R^1 = 6-Br, $R^3 = H$; **e** R^1 = 6-Br, $R^3 = Cl$; **f** R^1 = 6-Br, $R^3 = H$; **g** R^1 = 6-Cl, $R^3 = H$; **h** R^1 = 6-Cl, $R^3 = Cl$; **i** R^1 = 6-OMe, $R^3 = H$; **j** R^1 = 6-OMe, $R^3 = H$; **k** R^1 = 7-OMe, $R^3 = H$; **l** R^1 = 7-OMe, $R^3 = Cl$; **m** R^1 = 7-OEt, $R^3 = H$; **n** R^1 = 7-NEt_2, $R^3 = H$; **o** R^1 = 8-OMe, $R^3 = H$; **p** R^1 = 8-OMe, $R^3 = Cl$; **q** R^1 = 8-OEt, $R^3 = H$; **r** R^1 = 8-OEt, $R^3 = Cl$; **s** R^1 = 8-$CH_2CH = CH_2$, $R^3 = H$; **t** R^1 = 5,6-benzo, $R^3 = H$; **u** R^1 = 6-*n*-C_6H_{13}-7-OH, $R^3 = H$; **a-e**,**g-u** $R^2 = Cl$, **f** $R^2 = Br$

The IR spectra of the compounds prepared show the absence of the N–H stretching vibrations of the imine and amide fragments (3400-3300 cm^{-1}) and those of the amide carbonyl group (1670-1690 cm^{-1}) seen in the starting 2-iminocoumarin-3-carboxamides **1** [9] but the appearance of a strong stretching vibration band for the lactone C=O (1713-1763 cm^{-1}) and a weak band for the C=N stretching vibrations (1632-1694 cm^{-1}) which,

in some examples, may be overlapped by the more intense aromatic C=C stretching vibration bands (Table 1). The existence of an intense molecular ion peak (*m/z* 414, *I* = 100%) and characteristic coumarin fragmentation ions (*m/z*: 414.9999 $[M]^+$, 379.3037 $[M-Cl]^+$. 190.1656, 177.2742 $[M-C_{14}H_8ClN_2]^+$, 127.1440) in the case of the molecule of 3-(6-chloro-4-phenylquinazolin-2-yl)-8-methoxycoumarin (**7o**) also confirms the correctness of the proposed structure.

These facts have allowed us to propose that the given reaction occurs according to the recyclization mechanism [5] which includes the stage of forming intermediate 2-[(2-aroylaryl)imino]-2H-1-benzopyran-3-carboxamides **3** which could not be isolated. The instability of these structures is evidently connected with the activation of the carbonyl group of the benzophenone fragment under the action of ammonium ion liberated in the first stage and this leads to the formation of the novel intermediates – amino alcohols **4**. Further, as a result of the attack of the amino group on the carbon atom of the C=N bond of iminocoumarin the iminolactone ring is opened followed by a *cis-trans* isomerization of the intermediate **5** to **6** and then its cyclization to give R^1-substituted 3-[6-R^2-4-(R^3-phenyl)quinazolin-2-yl)coumarins **7a-u**.

TABLE 1. R^1-Substituted 3-[6-R^2-4-(R^3-Phenyl)quinazolin-2-yl]coumarins

Compound	Empirical formula	Found N, % / Calculated N, %	mp, °C	IR spectrum, ν, cm^{-1}			Yield, %
				C=O	C=N	C=C	
7a	$C_{23}H_{13}ClN_2O_2$	7.30 / 7.28	240-242	1751		1604	71
7b	$C_{23}H_{12}Cl_2N_2O_2$	6.67 / 6.68	194-196	1736		1603	68
7c	$C_{23}H_{13}ClN_2O_3$	6.96 / 6.99	301-303	1713	1694	1613	52
7d	$C_{23}H_{12}BrClN_2O_2$	6.07 / 6.04	223-225	1751	1632	1612	84
7e	$C_{23}H_{11}BrCl_2N_2O_2$	5.60 / 5.62	204-206	1739	1650	1605	87
7f	$C_{23}H_{12}Br_2N_2O_2$	5.50 / 5.51	242-244	1753	1640	1596	85
7g	$C_{23}H_{12}Cl_2N_2O_2$	6.68 / 6.68	235-237	1763	1651	1600	78
7h	$C_{23}H_{11}Cl_3N_2O_2$	6.20 / 6.17	237-239	1747		1600	71
7i	$C_{24}H_{15}ClN_2O_3$	6.77 / 6.75	238-240	1743	1680	1604	73
7j	$C_{24}H_{14}Cl_2N_2O_3$	6.20 / 6.23	230-232	1719	1687	1570	70
7k	$C_{24}H_{15}ClN_2O_3$	6.77 / 6.75	207-209	1727	1671	1615	66
7l	$C_{24}H_{14}Cl_2N_2O_3$	6.21 / 6.23	218-220	1743		1612	59
7m	$C_{25}H_{17}ClN_2O_3$	6.55 / 6.53	193-195	1739		1616	73
7n	$C_{27}H_{22}ClN_3O_2$	9.21 / 9.22	197-199	1715		1615	51
7o	$C_{24}H_{15}ClN_2O_3$	6.77 / 6.75	224-226	1738		1605	75
7p	$C_{24}H_{14}Cl_2N_2O_3$	6.20 / 6.23	235-237	1739		1603	77
7q	$C_{25}H_{17}ClN_2O_3$	6.55 / 6.53	206-208	1741		1602	78
7r	$C_{25}H_{16}Cl_2N_2O_3$	6.03 / 6.05	218-220	1724		1616	74
7s	$C_{26}H_{17}ClN_2O_2$	6.60 / 6.59	178-180	1746		1596	80
7t	$C_{27}H_{15}ClN_2O_2$	6.41 / 6.44	>300	1759	1671	1600	63
7u	$C_{29}H_{25}ClN_2O_3$	5.77 / 5.78	253-255	1720		1616	55

TABLE 2. ^{1}H NMR Spectral Characteristics of R^{1}-Substituted 3-[6-R^{2}-4-(R^{3}-Phenyl)quinazolin-2-yl]coumarins

Compound	Chemical shifts, δ, ppm (SSCC, *J*, Hz)			
	Aromatic protons			Other protons
	Coumarin ring	Quinazoline ring	Benzene ring	
1	2	3	4	5
7a	7.32-7.38 (2H, m, H-6, H-8); 7.76 (1H, d, J = 8, H-5); 8.80 (1H, s, H-4)	7.91 (1H, dd, J_1 = 8, J_2 = 1, H-7); 8.15 (1H, d, H-8); 8.18 (1H, s, H-5)	7.62 (3H, m); 7.84 (2H, m)	
7b	6.80 (2H, m, H-6, H-8); 7.64 (1H, m, H-7); 7.90 (1H, m, H-5); 8.78 (1H, s, H-4)	8.11 (3H, m)	7.52-7.90 (4H, m)	
7c	6.80 (2H, m, H-6, H-8); 8.03 (1H, m, H-5); 8.71 (1H, s, H-4)	8.02 (3H, m)	7.62-7.97 (5H, m)	10.80 (1H, s, OH)
7d	7.40 (1H, d, J = 10, H-8); 7.54 (1H, m, H-7); 7.73 (1H, d, J = 8, H-5); 8.76 (1H, s, H-4)	7.96 (1H, m, H-7); 8.09 (1H, m, H-5); 8.18 (1H, m, H-8)	7.54 (3H, m); 7.90 (2H, m)	
7e	7.43 (1H, d, J = 9, H-8); 7.57 (1H, m, H-7); 7.86 (1H, dd, J_1 = 10, J_2 = 1, H-5); 8.77 (1H, s, H-4)	8.09 (1H, dd, J_1 = 9, J_2 = 1, H-5); 8.20 (2H, m, H-7, H-8)	7.62-7.70 (4H. m)	
7f	7.38 (1H, d, J = 10, H-8); 7.43 (1H, m, H-7); 7.74 (1H, dd, J_1 = 8, J_2 = 1, H-5); 8.73 (1H, s, H-4)	8.08 (2H, m, H-5, H-7); 8.24 (1H, s, H-8)	7.43-8.08 (5H, m)	
7g	7.47 (1H, d, J = 9, H-8); 7.65 (1H, m, H-7); 7.58 (1H, m, H-5); 8.75 (1H, s, H-4)	7.65 (1H, dd, J_1 = 7, J_2 = 1, H-7); 8.09 (1H, m, H-5); 8.14 (1H, d, J = 7, H-8)	7.65-8.05 (5H, m)	
7h	7.47 (1H, d, J = 9, H-8); 7.58 (1H, m, H-7); 7.70 (1H, m, H-5); 8.77 (1H, s, H-4)	8.08 (2H, dd, J_1 = 10, J_2 = 1, H-5, H-7); 8.20 (1H, d, J = 10, H-8),	7.58-7.70 (4H, m)	
7i	7.28 (1H, dd, J_1 = 10, J_2 = 1, H-8); 7.62 (1H, m, H-7); 7.87 (1H, m, H-5); 8.80 (1H, s, H-4)	8.06-8.12 (3H, m, H-5, H-7, H-8)	7.43-7.52 (4H, m); 7.87 (1H, m)	3.81 (3H, s, OCH_3)
7j	7.26 (1H, dd, J_1 = 10, J_2 = 1, H-8); 7.40 (1H, d, J = 9, H-7); 7.50 (1H, d, J = 5, H-5); 8.77 (1H, s, H-4)	7.70 (1H, m, H-7); 8.17 (1H, dd, J_1 = 9, J_2 = 1, H-5); 8.40 (1H, d, J = 9, H-8)	7.50-7.70 (4H, m)	3.77 (3H, s, OCH_3)

TABLE 2 (continued)

1	2	3	4	5
7k	7.00 (1H, dd, J_1 = 9, J_2 = 1, H-6); 7.07 (1H, d, J = 5, H-8); 7.87 (1H, m, H-5); 8.80 (1H, s, H-4)	8.04-8.14 (3H, m, H-5, H-7, H-8)	7.66 (3H, m); 7.87 (2H, m)	3.90 (3H, s, OCH_3)
7l	6.96 (1H, dd, J_1 = 9, J_2 = 1, H-6); 7.02 (1H, d, J = 5, H-8); 7.80 (1H, d, J = 9, H-5); 8.72 (1H, s, H-4)	7.61 (1H, m, H-7); 8.02 (1H, dd, J_1 = 9, J_2 = 1, H-5); 8.14 (1H, d, J = 9, H-8)	7.52-7.70 (4H, m)	3.86 (3H, s, OCH_3)
7m	6.92 (1H, dd, J_1 = 9, J_2 = 1, H-6); 7.00 (1H, d, J = 5, H-8); 7.64 (1H, m, H-5); 8.74 (1H, s, H-4)	8.00-8.12 (3H, m, H-5, H-7, H-8)	7.64-7.85 (5H, m)	1.34 (6H, t, J = 7, $2CH_2C\underline{H}_3$); 4.11 (2H, q, J = 7, $2C\underline{H}_2CH_3$)
7n	6.54 (1H, d, J = 5, H-8); 6.71 (1H, dd, J_1 = 8, J_2 = 1, H-6); 7.58 (1H, m, H-5); 8.65 (1H, s, H-4)	7.94 (1H, d, J = 8, H-7); 7.98 (1H, d, J = 9, H-5); 8.06 (1H, dd, J_1 = 9, J_2 = 1, H-8)	7.58-7.86 (5H, m)	1.15 (6H, t, J = 7, $2CH_2C\underline{H}_3$); 3.45 (4H, q, J = 7, $2C\underline{H}_2CH_3$)
7o	7.26 (1H, t, J = 7, H-6); 7.81 (2H, m, H-5, H-7); 8.70 (1H, s, H-4)	7.92 (1H, d, J = 9, H-7); 8.10 (1H, s, H-5); 8.25 (1H, d, J = 9, H-8)	7.36 (2H, m); 7.65 (2H, m); 7.81 (1H, m)	4.02 (3H, s, OCH_3)
7p	7.32 (1H, t, J = 8, H-6); 7.65 (2H, m, H-5, H-7); 8.75 (1H, s, H-4)	8.03 (1H, d, J = 6, H-5); 8.18 (1H, d, J = 5, H-8)	7.55-7.74 (4H, m)	3.91 (3H, s, OCH_3)
7q	7.28 (1H, t, J = 8, H-6); 7.46 (1H, dd, J_1 = 8, J_2 = 1, H-5); 7.65 (1H, m, H-7); 8.80 (1H, s, H-4)	8.06-8.17 (3H, m, H-5, H-7, H-8)	7.30 (1H, m); 7.65 (2H, m); 7.88 (2H, m)	1.42 (3H, t, J = 7, $CH_2C\underline{H}_3$); 4.20 (2H, q, J = 7, $C\underline{H}_2CH_3$)
7r	7.34 (1H, d, J = 6, H-6); 7.58 (1H, d, J = 6, H-7); 7.64 (1H, m, H-5); 8.78 (1H, s, H-4)	7.72 (1H, d, J = 5, H-7), 8.10 (1H, dd, J_1 = 7, J_2 = 1, H-5); 8.24 (1H, d, J = 5, H-8)	7.32 (2H, m); 7.64-7.72 (2H, m)	1.42 (3H, t, J = 7, $CH_2C\underline{H}_3$); 4.20 (2H, q, J = 7, $C\underline{H}_2CH_3$)
7s	7.31 (1H, t, J = 8, H-6); 7.62 (1H, m, H-7); 7.74 (1H, d, J = 8, H-5); 8.71 (1H, s, H-4)	8.00-8.12 (3H, m, H-5, H-7, H-8)	7.50 (1H, d); 7.64 (2H, m); 7.86 (2H, m)	3.57 (2H, d, J = 9, $C\underline{H}_2CH{=}CH_2$); 5.07 (2H, dd, J_1 = 18, J_2 = 7, $CH_2CH{=}C\underline{H}_2$); 6.02 (1H, m, $CH_2C\underline{H}{=}CH_2$)
7t	7.65-8.06 (6H, m); 9.49 (1H, s, H-4)	8.20 (1H, m, H-7); 8.26 (1H, m, H-5); 8.56 (1H, d, J = 8, H-8)	7.63-7.90 (5H, m)	
7u	7.55 (1H, s, H-8); 7.77 (1H, m, H-5); 8.70 (1H, s, H-4)	8.00-8.10 (3H, m, H-5, H-7, H-8)	7.62 (3H, m); 7.85 (2H, m)	0.88 (3H, m); 1.29 (6H, s, $(CH_2)_2(C\underline{H}_2)_3CH_3$); 1.53 (2H, s, $C\underline{H}_2(CH_2)_4CH_3$); 2.50 (2H, s, $CH_2C\underline{H}_2(CH_2)_3CH_3$); 3.20 (1H, s, OH)

With the object of confirming the structure of the final products we have carried out an X-ray investigation of 3-(6-chloro-4-phenylquinazolin-2-yl)-7-hydroxycoumarin **7c**. The assignment of crystal of this compound to hexagonal syngony proved quite unexpected, but as the verification of the presence of twinning in the polarizing microscope proved negative, the refinement was carried out in the hexagonal cell by a direct method with subsequent electron density synthesis. It was found that the structure of compound **7c** was made up of triads of the molecules formed through O–H···O hydrogen bonding. The atomic coordinates can be obtained from the authors; the bond lengths and bond angles in the structure are given in Tables 3 and 4. Figure 1 shows the numbering scheme for the atoms in the basic molecular structures.

Three molecules of the compound make up the independent cell unit. In each molecule the coumarin and benzimidazole fragments lie in virtually one plane. Differences are observed in torsional angles between the planes of the phenyl substituent and the quinazoline fragment. As a result of the geometrical requirements in the least-squares refinement and the existence of pseudosymmetry it can be proposed that the standard deviations of the obtained geometrical parameters of the molecules (Tables 3 and 4) are reduced when compared with the actually observed scatter in the bond lengths and bond angles.

TABLE 3. Bond Lengths (*d*) in the Triad of Basic Molecules of Compound **7c**

Bond	*d*, Å		
	C	A	B
Cl(1)–C(19)	1.784(4)	1.787(4)	1.784(4)
O(1)–C(10)	1.401(4)	1.414(4)	1.403(4)
O(1)–C(2)	1.415(4)	1.414(5)	1.408(5)
C(2)–O(11)	1.198(5)	1.194(5)	1.192(5)
C(2)–C(3)	1.377(5)	1.382(5)	1.375(5)
C(3)–C(4)	1.331(5)	1.329(5)	1.333(5)
C(3)–C(14)	1.467(2)	1.471(2)	1.471(2)
C(4)–C(5)	1.501(4)	1.521(4)	1.511(4)
C(5)–C(6)	1.367(4)	1.384(4)	1.374(4)
C(5)–C(10)	1.375(4)	1.382(4)	1.378(4)
C(6)–C(7)	1.378(4)	1.375(4)	1.376(4)
C(7)–C(8)	1.381(3)	1.378(4)	1.385(4)
C(8)–C(9)	1.382(3)	1.380(3)	1.381(3)
C(8)–O(12)	1.426(4)	1.431(4)	1.434(4)
C(9)–C(10)	1.381(3)	1.381(3)	1.384(3)
N(13)–C(22)	1.321(2)	1.322(2)	1.321(2)
N(13)–C(14)	1.350(2)	1.352(2)	1.350(2)
C(14)–N(15)	1.313(2)	1.310(2)	1.310(2)
N(15)–C(16)	1.344(2)	1.347(2)	1.345(2)
C(16)–C(17)	1.496(5)	1.507(5)	1.497(5)
C(16)–C(23)	1.527(4)	1.532(4)	1.524(4)
C(17)–C(18)	1.373(3)	1.380(3)	1.382(3)
C(17)–C(22)	1.390(3)	1.383(3)	1.390(3)
C(18)–C(19)	1.374(4)	1.378(4)	1.381(4)
C(19)–C(20)	1.379(4)	1.382(4)	1.379(4)
C(20)–C(21)	1.377(3)	1.378(3)	1.378(3)
C(21)–C(22)	1.378(4)	1.378(4)	1.381(3)
C(23)–C(24)	1.3953(19)	1.3956(15)	1.3941(19)
C(23)–C(28)	1.3967(19)	1.3946(18)	1.3959(19)
C(24)–C(25)	1.3973(19)	1.3957(18)	1.3948(19)
C(25)–C(26)	1.397(2)	1.3977(19)	1.3955(15)
C(26)–C(27)	1.3962(19)	1.3946(19)	1.3954(19)
C(27)–C(28)	1.3953(19)	1.3949(15)	1.3960(19)

TABLE 4. Bond Angles (ω) in The Triad of Basic Molecules of Compound **7c**

Angle	ω, deg		
	C	A	B
C(10)–O(1)–C(2)	120.7(4)	122.7(4)	124.3(4)
O(11)–C(2)–C(3)	132.4(3)	133.5(4)	133.8(4)
O(11)–C(2)–O(1)	106.1(3)	107.1(3)	107.2(3)
C(3)–C(2)–O(1)	121.4(4)	119.4(4)	118.5(4)
C(4)–C(3)–C(2)	118.8(3)	119.2(3)	118.9(3)
C(4)–C(3)–C(14)	118.0(3)	118.2(3)	117.7(3)
C(2)–C(3)–C(14)	123.2(3)	122.7(3)	123.0(3)
C(3)–C(4)–C(5)	122.3(4)	124.0(4)	124.6(4)
C(6)–C(5)–C(10)	117.0(3)	115.5(4)	113.5(3)
C(6)–C(5)–C(4)	125.4(4)	128.6(4)	131.1(4)
C(10)–C(5)–C(4)	117.3(3)	115.0(3)	115.0(3)
C(5)–C(6)–C(7)	123.4(4)	124.3(4)	126.4(4)
C(6)–C(7)–C(8)	116.5(3)	115.9(4)	113.9(4)
C(7)–C(8)–C(9)	122.8(3)	123.7(4)	125.7(3)
C(7)–C(8)–O(12)	111.6(3)	111.7(3)	110.8(3)
C(9)–C(8)–O(12)	124.3(3)	124.5(3)	123.4(3)
C(10)–C(9)–C(8)	116.3(3)	116.4(4)	113.7(4)
C(5)–C(10)–C(9)	123.2(3)	123.5(4)	126.1(3)
C(5)–C(10)–O(1)	119.3(3)	119.1(3)	118.6(3)
C(9)–C(10)–O(1)	117.4(3)	117.0(3)	115.1(3)
C(22)–N(13)–C(14)	116.2(3)	116.6(3)	116.0(3)
N(15)–C(14)–N(13)	130.2(3)	129.8(3)	130.5(3)
N(15)–C(14)–C(3)	109.8(3)	110.9(3)	109.5(3)
N(13)–C(14)–C(3)	120.0(3)	119.4(3)	119.6(3)
C(14)–N(15)–C(16)	112.9(3)	113.0(3)	113.0(3)
N(15)–C(16)–C(17)	123.4(3)	122.3(3)	123.8(3)
N(15)–C(16)–C(23)	116.2(3)	116.0(4)	116.3(4)
C(17)–C(16)–C(23)	119.8(3)	117.7(3)	119.8(3)
C(18)–C(17)–C(22)	121.1(3)	121.9(3)	122.3(3)
C(18)–C(17)–C(16)	125.6(3)	124.1(3)	124.9(3)
C(22)–C(17)–C(16)	113.1(2)	113.1(2)	112.7(2)
C(17)–C(18)–C(19)	113.9(4)	113.3(4)	113.3(4)
C(18)–C(19)–C(20)	128.6(4)	129.3(4)	128.9(4)
C(18)–C(19)–Cl(1)	115.7(3)	115.1(3)	115.3(3)
C(20)–C(19)–Cl(1)	114.8(3)	115.1(3)	115.7(3)
C(21)–C(20)–C(19)	114.0(4)	113.1(4)	113.0(4)
C(20)–C(21)–C(22)	121.0(3)	122.2(3)	122.8(4)
N(13)–C(22)–C(21)	115.3(3)	116.6(3)	116.9(3)
N(13)–C(22)–C(17)	123.6(3)	123.4(3)	123.8(3)
C(21)–C(22)–C(17)	120.9(3)	120.0(3)	119.0(3)
C(24)–C(23)–C(28)	119.94(12)	120.01(11)	120.01(12)
C(24)–C(23)–C(16)	120.7(4)	127.1(4)	122.2(4)
C(28)–C(23)–C(16)	119.2(4)	112.7(4)	117.8(4)
C(23)–C(24)–C(25)	119.84(13)	119.86(12)	120.01(12)
C(24)–C(25)–C(26)	119.41(15)	119.68(13)	119.99(12)
C(27)–C(26)–C(25)	119.56(15)	119.82(12)	119.85(13)
C(28)–C(27)–C(26)	119.90(13)	120.05(12)	119.85(13)
C(27)–C(28)–C(23)	119.93(12)	119.91(12)	119.90(12)

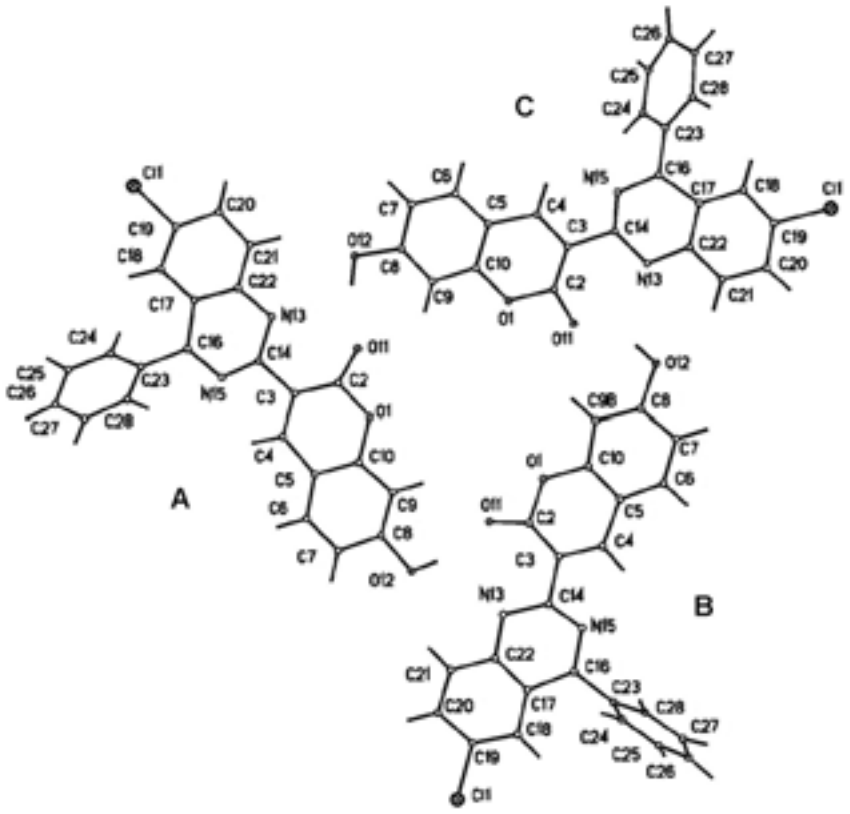


Fig. 1. Atom numbering in the triad of the basic molecules of 3-(6-chloro-4-phenylquinazolin-2-yl)-7-hydroxycoumarin (**7c**).

Hence the reaction of 2-iminocoumarin-3-carboxamides with substituted 2-aminobenzophenones in glacial acetic acid in the cold occurs in accordance with recyclization mechanism to give substituted 3-(4-arylquinazolin-2-yl)coumarins and is a convenient method for the synthesis of this series of 3-heterylcoumarins.

EXPERIMENTAL

IR spectra for the synthesized compounds were recorded on a Specord M-80 spectrophotometer for KBr tablets. ^{1}H NMR spectra were recorded on a Varian WXR-400 (200 MHz) instrument using DMSO-d_6 and TMS as internal standard. Electron impact mass spectra were obtained on a Finnigan MAT 4615B instrument with ionization energy of 70 eV and with ballistic heating of the sample. X-ray analysis was carried out on a Siemens P3/PC four-circle, automatic diffractometer.

R^1-Substituted 2-Iminocoumarin-3-carboxamides 1 were prepared by the method in [9].

3-(4-Arylquinazolin-2-yl)coumarins 7a-u (General Method). The corresponding 2-amino-benzophenone **2** (2 mmol) was dissolved with heating in glacial acetic acid (10 ml). 2-Iminocoumarin-3-carboxamide **1** (2 mmol) was added to the warm solution (30-40°C) and it was refluxed using a reflux condenser for 20-30 min. A heavy precipitate was formed upon cooling the reaction mixture. This was filtered off, washed with water and with ethanol, and recrystallized from mixture of ethanol–water (compounds **7c,d,g,s-u**) or from ethanol–DMF (compounds **7a,b,e,f,t**).

X-ray Analysis of 3-(6-Chloro-4-phenylquinazolin-2-yl)-7-hydroxycoumarin (7c). Measurement of the intensities was carried out by the 2θ/θ scanning method in the range of angles 4<2θ<50° at a rate of from 2 to 30 deg./min to give 2724 nonzero, nonequivalent reflections, of which 1954 were observed with $I > 2\sigma(I)$. The crystals are hexagonal with space group $P6_1$; M_r = 400.80; T = 293(2) K; $C_{23}H_{13}ClN_2O_3$; a = 20.520(6), c = 22.915 (10) Å; V = 8356(5) Å^3; Z = 18; d_{calc} = 1.434 g/cm^3; F_{000} = 3708; μ(MoKα) = 0.234 mm^{-1}. The structure was refined by full-matrix, least-squares analysis using the SHELX-97 computer program. Due to the presence of pseudosymmetry in the molecular packing (the presence of a third order pseudoaxis led to a strong correlation of the refined parameters) in the refinement of the structure there are additional geometrical requirements superimposed, e.g. all of the aromatic rings are constrained to be given as planar, identical bonds in the different molecules equal to one another, etc. The overall number of such geometrical restraints was 945. The hydrogen atoms were brought into the refinement on geometrical grounds and specifically attached to the corresponding non-hydrogen atom. The final confidence coefficients were R_1 = 0.0430, wR_2 = 0.1098 for those observed and R_1 = 0.0471, wR_2 = 0.1114 for all reflections S = 0.975.

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