SYNTHESIS OF SOME AZOLYLQUINAZOLINES

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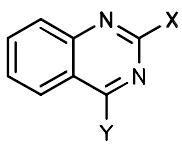
The azole rings combined with carbonyl group via methylene bridge or with imidoyl group directly are frequent structural units of organic compounds possessing phytoefectorical and mainly pesticidal activities[1,2]. In this connection we realized to prepare a series of pyrimidine ring substituted azolylquinazolines *I – IV*. The title compounds were prepared by reaction of 2,4-dichloroquinazoline[3,4] with the corresponding azoles.



I – IV

In formulae *I – IV* :

Ia,	X = Cl, Y = imidazol-1-yl
Ib,	X = Cl, Y = benzimidazol-1-yl
IIa,	X = Y = imidazol-1-yl
IIb,	X = Y = benzimidazol-1-yl
IIc,	X = Y = 1,2,4-triazol-1-yl
IId,	X = Y = benztriazol-1-yl
IIIa,	X = imidazol-1-yl, Y = morpholinyl
IIIb,	X = benzimidazol-1-yl, Y = morpholinyl
IVa,	X = morpholinyl, Y = imidazol-1-yl
IVb,	X = morpholinyl, Y = benzimidazol-1-yl

EXPERIMENTAL

^{1}H NMR spectra of hexadeuteriodimethyl sulfoxide solution were recorded on a Tesla BS 487C (80 MHz) spectrometer using tetramethylsilane as internal standard. The IR spectra of compounds in KBr pellets were measured with a Philips PU 9800 FTIR. Ultraviolet spectra of methanolic solution ($\approx 10^{-4}$ mol l^{-1} concentration in a 0.2 cm cell) were taken with a Specord M 40 (Zeiss, Jena).

2-Chloro-4-(azol-1-yl)quinazolines *Ia – Ib*

The mixture of 2,4-dichloroquinazoline (0.005 mol) and corresponding azole (0.005 mol) in absolute ethanol (20 ml) was stirred for 6 h. The separated product was filtered off and crystallized from acetonitrile. Characterization of compounds is given in Tables I, II and III.

2,4-Bis(azol-1-yl)quinazolines *IIa – IId*

The mixture, prepared from 2,4-dichloroquinazoline (0.005 mol) dissolved in acetonitrile (30 ml) and sodium salt of corresponding azole (0.01 mol) was stirred and refluxed for 5 – 8 h. The formed precipitate (NaCl) was removed by filtration; the filtrate was left to crystallize. Characterization of compounds is given in Tables I, II and III.

TABLE I
Characteristic data of prepared compounds

Compound	M.p., °C Yield, %	Formula (M.w.)	Calculated/Found		
			% C	% H	% N
Ia	260 – 265 42	$C_{11}H_7N_4Cl$ (230.6)	57.28 57.13	3.06 3.01	24.29 24.13
Ib	229 – 230 61.5	$C_{15}H_9N_4Cl$ (280.2)	64.18 64.04	3.23 3.16	19.96 19.78
IIa	130 – 135 40	$C_{14}H_{10}N_6$ (262.3)	64.11 64.02	3.84 3.79	32.06 31.90
IIb	140 – 143 56	$C_{22}H_{14}N_6$ (362.4)	72.92 72.84	3.89 3.83	23.19 23.09
IIc	125 – 130 51	$C_{12}H_8N_8$ (264.5)	54.54 54.32	3.05 3.00	42.40 42.18
IId	170 – 173 73	$C_{20}H_{12}N_8$ (364.4)	65.93 65.81	3.32 3.29	30.75 30.68
IIIa	150 – 152 72	$C_{15}H_{15}N_5O$ (281.2)	64.04 63.98	5.37 5.33	24.89 24.76
IIIb	95 – 97 38	$C_{19}H_{17}N_5O$ (331.4)	68.87 68.80	5.17 5.13	21.13 21.03
IVa	>300 56	$C_{15}H_{15}N_5O$ (281.2)	64.04 63.97	5.37 5.34	24.89 24.71
IVb	164 – 165 85	$C_{19}H_{17}N_5O$ (331.4)	68.87 68.73	5.17 5.09	21.13 21.07

2-(Azol-1-yl)-4-morpholinoquinazolines *IIIa – IIIb*

To the solution of 2-chloro-4-morpholinoquinazoline[5] (0.004 mol) in acetonitrile (20 ml), sodium salt of corresponding azole (0.04 mol) was added. The reaction mixture was then stirred and refluxed for 6 h, filtered and left to crystallize. Characterization of compounds is given in Tables I, II and III.

TABLE II
IR and UV data of prepared compounds

Compound	IR spectrum, cm^{-1}			UV spectrum					
	ν(CH)	ν(C=N)	ν(C=C)	λ_{max}, nm/log ε					
Ia	3 061	1 614	1 527	229	333	350	401		
	3 032			3.30	2.48	2.36	2.38		
Ib	3 092	1 616	1 560	200	223	235	286	333	
	3 063		1 552	3.71	3.39	3.55	2.57	2.84	
IIa	3 107	1 616	1 557	201	209	225	299	333	
	3 069			3.46	3.39	3.59	2.51	2.69	
	3 030								
IIb	3 128	1 622	1 576	201	213	228	297	333	
	3 053			3.42	3.32	3.58	2.52	2.70	
IIc	3 119	1 611	1 583	201	211	231	299	333	
			1 561	3.38	3.28	3.52	2.49	2.72	
IId	3 107	1 614	1 562	200	219	232	296	339	
	3 082			3.79	3.55	3.64	2.89	3.03	
IIIa	3 113	1 616	1 574	203	211	242	315	333	
			1 556	3.28	3.22	3.35	2.75	2.83	
IIIb	3 067	1 612	1 566	216	224	228	266	296	308
	3 020			3.63	3.40	3.42	2.77	2.99	2.87
IVa	3 055	1 616	1 581	217	263	311			
				3.83	2.55	2.74			
IVb	3 069	1 618	1 576	203	225	248	338	382	
	3 001		1 550	3.58	3.04	3.52	1.80	2.49	

2-Morpholino-4-(azol-1-yl)quinazolines *IVa – IVb*

The mixture of 2-chloro-4-(azol-1-yl)quinazoline (0.004 mol) and morpholine (0.005 mol) in acetonitrile (40 ml) was refluxed 5 – 6 h. After cooling during 48 h the precipitate of the product was formed. Characterization of products is given in Tables I, II and III.

TABLE III
^{1}H NMR data of prepared compounds (δ, ppm)

Compound	Azole	Quinazoline	Morpholine
Ia	9.15 s, 1 H; 8.49 – 8.72 m, 2 H	8.03 – 7.62 m, 4 H	
Ib	8.87 s, 1 H; 7.97 – 7.37 m, 4 H	8.28 – 8.15 m, 4 H	
IIa	8.46 s, 1 H; 7.30 s, 1 H; 7.95 – 7.79 m, 4 H	8.32 – 8.11 m, 4 H	
IIb	8.74 s, 1 H; 8.71 s, 1 H; 7.40 – 7.34 m, 8 H	8.67 – 7.87 m, 4 H	
IIc	10.07 – 9.91 d, 1 H; 9.36 – 8.62 m,1 H; 9.61 s, 1 H; 8.59 s, 1 H	8.40 – 7.76 m, 4 H	
IId	9.24 – 8.78 m, 4 H; 7.99 – 7.54 m, 4 H	8.67 – 8.08 m, 4 H	
IIIa	8.63 s, 1 H; 8.00 – 7.98 m, 2 H	7.81 – 7.47 m, 4 H	3.97 – 3.85 m, 8 H
IIIb	8.05 s, 1 H; 7.53 – 7.46 m, 4 H	7.94 – 7.70 m, 4 H	3.78 – 3.65 m, 8 H
IVa	8.61 s, 1 H; 8.03 – 7.89 m, 2 H	7.95 – 7.19 m, 4 H	3.76 – 3.72 m, 8 H
IVb	8.75 s, 1 H; 7.37 – 7.26 m, 4 H	7.78 – 7.46 m, 4 H	3.75 – 3.71 m, 8 H

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