Effect of intramolecular hydrogen bond on the azide-tetrazole equilibrium of 5-(2′-hydroxyphenyl)tetrazolo[1,5-*a*]pyrimidine, -tetrazolo[1,5-*c*]pyrimidine, -tetrazolo[1,5-*c*]quinazoline, and 7-(2′-hydroxyphenyl)tetrazolo[1,5-*c*]pyrimidine*

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The intramolecular hydrogen bond between the phenolic hydroxyl and the pyrimidine nitrogen atom in the title compounds exerts a destabilizing effect on the tetrazole ring and shifts the azide-tetrazole equilibrium toward the azide form, especially in the case of tetrazolo[*c*]pyrimidine and -[*c*]quinazoline. It has been found that the introduction of a methoxy group into the *ortho*-position of the phenyl fragment stabilizes the tetrazole tautomer more efficiently than introduction of this group into the *para*-position.

Key words: azidopyrimidines, azidoquinazolines, tetrazolopyrimidines, tetrazoloquinazolines, intramolecular hydrogen bond, azide-tetrazole tautomerism, ^{1}H NMR, ^{17}O NMR spectra.

Considerable interest in aromatic and heteroaromatic azides is caused by the diversity of their chemical and photochemical transformations and their wide application.[2,3] The chemical reactions and the practically significant properties of these compounds are based on the fact that an azide group can both participate in the transformations itself and generate highly reactive intermediates, nitrenes, in thermal or photochemical processes. The specific nature of azaaromatic compounds having an azide group in the α-position with respect to the nitrogen atom is manifested as azide-tetrazole tautomerism, which is also an essential factor that determines physical properties, biological activity, and reactivity of compounds during the synthesis, ring opening, and recyclization of heterocycles.[4–6]

Previously we have developed a convenient method for synthesizing 2- and 4-chloropyrimidines with *o*-hydroxyphenyl substituents[7] and prepared the corresponding azidopyrimidines on their base. There are very few data on compounds of this type in the series of azines and their benzo analogs. The simultaneous presence of an azide group and an *o*-phenol moiety in a pyrimidine molecule is certainly of scientific and practical interest, since the formation of a strong intramolecular hydrogen bond between the phenolic hydroxyl and the aza atom of the heteroaromatic ring has an effect on the reactivity[8–10] and spectral luminescent properties of these compounds.[11] Rapid intramolecular transfer of a proton in the excited state is the basis for high light-stabilizing efficiency of compounds with intramolecular H-bonds.[12]

In the present work we studied the effect of intramolecular H-bonds on azide-tetrazole equilibria of the title compounds and also the corresponding model compounds, incorporating no chelate H-rings, in solvents of various polarities. The proportions of tautomers in equilibrium mixtures were quantitatively evaluated and the effect of the mutual arrangement of *o*-hydroxyphenyl, the reaction center, and the azido group (or annelated tetrazole) in even positions of the pyrimidine ring and its benzo analog, quinazoline, on the relative stabilities of the tautomers was studied. The structures of the tautomers were confirmed by an analysis of characteristic parameters of the ^{1}H NMR spectra (see Ref. 13 and references therein) and the data of ^{17}O NMR, IR, and UV spectroscopy.

Results and Discussion

Tautomeric equilibrium of 4-azido-2-arylpyrimidines* (**1A—5A**) and of the benzo analog* of compound **1A**, *viz.*, 4-azido-2-phenylquinazoline (**6A**), can be presented by Scheme 1 (the annelated benzene ring in quinazoline **6** is shown by the dashed line).

* For preliminary communication, see Ref. 1.

* The numbering of atoms in Scheme 1 refers only to compounds **1—5**.

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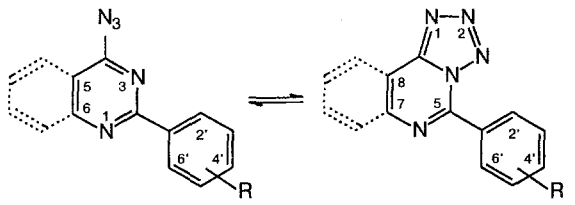
Scheme 1



1A—6A **1T—6T**

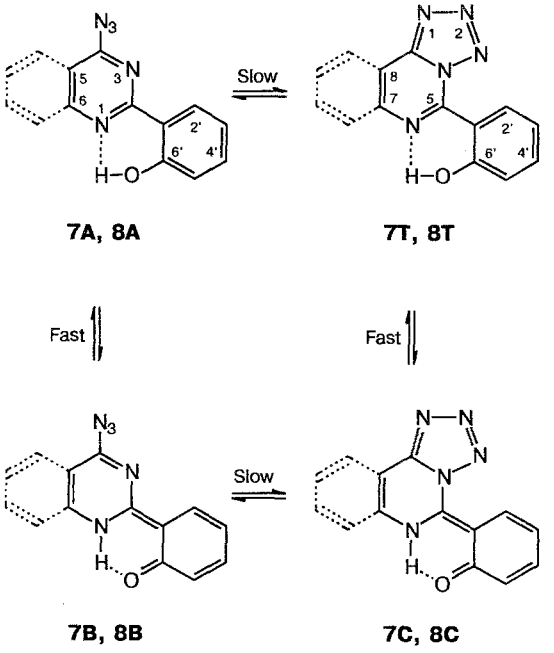
R = H (**1**), 4'-OH (**2**), 4'-OMe (**3**), 4'-Br (**4**), 2'-OMe (**5**)

The IR spectra of compounds **1—5** recorded in KBr, $CHCl_3$, or DMSO exhibit an adsorption band corresponding to the azide group in the 2100—2200 cm^{-1} region, whose intensity is noticeably lower in DMSO, which unambiguously indicates the presence of the azide form and points to the existence of the **1A—5A** $\rightleftharpoons$ **1T—5T** azide-tetrazole equilibrium in solutions. The latter is supported by the quantitative data on the equilibrium ratio between the azide and tetrazole forms obtained from the ^1H NMR spectra (Table 1). The decrease in the proportion of the azide form on going from $CDCl_3$ to DMSO-d_6 is in agreement with the literature data on the stabilization of the tetrazole tautomer by more polar solvents.[4—6] A characteristic feature that makes it possible to distinguish structures **1A—5A** and **1T—5T** is the magnitudes of the $^1H—^1H$ spin coupling constants, whose difference is caused by the increase in the degree of double bonding between the C(7) and C(8) atoms in the latter due to the change in the hybridization of the pyrimidine N(3) atom resulting from annelation of the tetrazole ring.

From the data on the ratio between the tautomers obtained (see Table 1), it follows that the introduction of an electron-withdrawing substituent (*p*-Br) in the phenyl fragment stabilizes the azide form, and, conversely, the introduction of an electron-releasing substituent (*p*-MeO, *p*-HO, *o*-MeO) stabilizes the tetrazole tautomer. Unexpectedly, the *o*-methoxyphenyl group considerably shifts the azide-tetrazole equilibrium toward tetrazole with respect to the corresponding *para*-isomer (*cf.* compounds **5** and **3**), which is probably associated with the disruption of the coplanarity of the pyrimidine and *o*-methoxyphenyl fragments. The IR spectrum of quinazoline **6** recorded by us for a $CHCl_3$ solution, unlike that of pyrimidine **1**, exhibits no absorption band of the azide group in the 2100—2200 cm^{-1} region, *i.e.*, this compound exists in the tetrazole form (**6T**). Previously the same structure has been ascribed to this compound in the crystalline state and in a benzene solution.[14]

Thus, benzoannelation of the pyrimidine ring favors thermodynamic stability of the tetrazole form to the extent that azide **6A**, unlike azide **1A**, is not observed even in low-polarity $CHCl_3$.

Scheme 2



7A, 8A **7T, 8T**

7B, 8B **7C, 8C**

In 4-azidopyrimidine (**7**) and 4-azidoquinazoline (**8**) (the dashed line in Scheme 2 marks the annelated benzene ring in quinazoline **8**) the *o*-phenolic hydroxyl forms a strong intramolecular H-bond of the O—H...N type with the aza atom of the pyrimidine ring, and, consequently, the stability of the tautomeric forms are governed not only by the electron-releasing effect of the OH group, as in the case of **2**, but also by the strengths of the intramolecular H-bond in the azide and tetrazole tautomers. In addition, in the presence of chelate H-rings in these compounds, in parallel with the slow azide-tetrazole tautomerism, rapid prototropic equilibria to give fragments with an *ortho*-quinoid structure are possible in the ground state. The position of a rapidly established equilibrium of the **A** $\rightleftharpoons$ **B** or **T** $\rightleftharpoons$ **C** type can be judged by the electronic absorption spectra and other spectral data, for example, the oxygen chemical shifts in the ^{17}O NMR spectra (see Ref. 15).

The long-wave absorption maxima in the UV spectra of compounds **7** and **8** in $CHCl_3$ are located at 330 nm (ε 9200) and 345 nm (ε 9600), respectively, which confirms the existence of the O—H...N intramolecular H-bonds in these structures, and the absence of absorption bands of *o*-quinoid structures at $\lambda > 400$ nm both in $CHCl_3$ and in more polar DMSO indicates the stability of benzoid tautomers, **7A**, **8A** and **7T**, **8T**. The signal of the phenol oxygen in the ^{17}O NMR spectrum of compound **7** in a $CHCl_3$ solution is located at 96.9 ppm ($\Delta\nu_{1/2}$ = 670 Hz), which is in agreement with the data for *ortho*-substituted phenols containing a pyrimidine or 1,3,5-triazine fragment in the proton-withdrawing part of the chelate ring.[16] This means that the **7A** $\rightleftharpoons$ **7B** and/or **7T** $\rightleftharpoons$ **7C** prototropic equilibria are almost entirely shifted to the phenolic forms **7A** and/or **7T**.

The IR spectra of hydroxyphenylpyrimidine **7** recorded both in the crystalline state and in solutions in $CHCl_3$ or DMSO exhibit a strong absorption band corresponding to the azide group in the 2100—2200 cm^{-1}

Table 1. Parameters of the ^1H NMR spectra of 4-azido-2-arylpyrimidines **1A—5A**, **7A** and 5-aryltetrazolo[1,5-*c*]pyrimidines **1T—5T**, **7T** and the ratios between these compounds under equilibrium conditions

Compound	Solvent	Percentages of the tautomers, A:T	δ, *J*/Hz					
			Tautomer **A**			Tautomer **T**		
			H(5) ($J_{5,6}$)	H(6) ($J_{6,5}$)	Phenyl ring protons	H(7) ($J_{7,8}$)	H(8) ($J_{8,7}$)	Phenyl ring protons
1	$CDCl_3$	85:15	6.67 (5.3)	8.60 (5.3)	8.44* (m, 2 H, H(2'), H(6')); 7.48 (m, 3 H, H(3'), H(4'), H(5'))	8.44*	7.88 (6.1)	8.70 (m, 2 H, H(2'), H(6')); 7.65 (m, 3 H, H(3'), H(4'), H(5'))
	Acetone-d_6	72:28	6.89 (5.5)	8.76 (5.5)	8.50 (m, 2 H, H(2'), H(6')); 7.55 (m, 3 H, H(3'), H(4'), H(5'))	8.59 (6.2)	8.12 (6.2)	8.70 (m, 2 H, H(2'), H(6')); 7.72 (m, 3 H, H(3'), H(4'), H(5'))
	DMSO-d_6	40:60	7.03 (5.5)	8.77 (5.5)	8.37 (m, 2 H, H(2'), H(6')); 7.54 (m, 3 H, H(3'), H(4'), H(5'))	8.58 (6.2)	8.26 (6.2)	8.51 (m, 2 H, H(2'), H(6')); 7.70 (m, 3 H, H(3'), H(4'), H(5'))
2	$CDCl_3$	72:28	6.61 (5.6)	8.55 (5.6)	8.36 (d, 2 H, H(2'), H(6'), J = 8.8); 6.91 (d, 2 H, H(3'), H(5'), J = 8.8)	8.39 (6.2)	7.82 (6.2)	8.73 (d, 2 H, H(2'), H(6'), J = 8.8); 6.91 (d, 2 H, H(3'), H(5'), J = 8.8)
	Acetone-d_6	50:50	6.97 (5.5)	8.66 (5.5)	8.37 (d, 2 H, H(2'), H(6'), J = 9.0); 6.97 (d, 2 H, H(3'), H(5'), J = 9.0); 8.89 (s, 1 H, H(4')O)	8.50 (6.2)	7.99 (6.2)	8.70 (d, 2 H, H(2'), H(6'), J = 9.0); 7.14 (d, 2 H, H(3'), H(5'), J = 9.0); 9.37 (s, 1 H, H(4')O)
	DMSO-d_6	22:78	6.90 (5.5)	8.68 (5.5)	8.23 (d, 2 H, H(2'), H(6'), J = 8.8); 6.90 (d, 2 H, H(3'), H(5'), J = 8.8); 10.06 (br.s, 1 H, H(4')O)	8.50 (6.2)	8.12 (6.2)	8.52 (d, 2 H, H(2'), H(6'), J = 8.8); 7.04 (d, 2 H, H(3'), H(5'), J = 8.8); 10.52 (br.s, 1 H, H(4')O)
3	$CDCl_3$	69:31	6.59 (5.5)	8.54 (5.5)	8.38* (d, 2 H, H(2'), H(6'), J = 8.6); 6.97 (d, 2 H, H(3'), H(5'), J = 8.6); 3.86 (s, 3 H, 4'-MeO)	8.38*	7.79 (6.2)	8.76 (d, 2 H, H(2'), H(6'), J = 9.2); 7.09 (d, 2 H, H(3'), H(5'), J = 9.2); 3.93 (s, 3 H, 4'-MeO)
	Acetone-d_6	57:43	6.79 (5.4)	8.65 (5.4)	8.41 (d, 2 H, H(2'), H(6'), J = 9.0); 7.05 (d, 2 H, H(3'), H(5'), J = 9.0); 3.88 (s, 3 H, 4'-MeO)	8.50 (6.2)	8.00 (6.2)	8.73 (d, 2 H, H(2'), H(6'), J = 9.2); 7.22 (d, 2 H, H(3'), H(5'), J = 9.2); 3.96 (s, 3 H, 4'-MeO)
	DMSO-d_6	28:72	6.93 (5.5)	8.71 (5.5)	8.32 (d, 2 H, H(2'), H(6'), J = 9.0); 7.08 (d, 2 H, H(3'), H(5'), J = 9.0); 3.84(s, 3 H, 4'-MeO)	8.52 (6.2)	8.15 (6.2)	8.59 (d, 2 H, H(2'), H(6'), J = 9.1); 7.24 (d, 2 H, H(3'), H(5'), J = 9.1); 3.91(s, 3 H, 4'-MeO)
4	$CDCl_3$	91:9	6.62 (5.5)	8.53 (5.5)	8.25 (d, 2 H, H(2'), H(6'), J = 8.6); 7.54 (d, 2 H, H(3'), H(5'), J = 8.6)	8.35 (6.2)	7.84 (6.2)	8.58 (d, 2 H, H(2'), H(6'), J = 9.0); 7.70 (d, 2 H, H(3'), H(5'), J = 9.0)
	Acetone-d_6	83:17	6.91 (5.5)	8.73 (5.5)	8.38 (d, 2 H, H(2'), H(6'), J = 9.0); 7.71 (d, 2 H, H(3'), H(5'), J = 9.0)	8.57 (6.2)	8.13 (6.2)	8.63 (d, 2 H, H(2'), H(6'), J = 9.0); 7.90 (d, 2 H, H(3'), H(5'), J = 9.0)
	DMSO-d_6	56:44	7.01 (5.5)	8.73 (5.5)	8.24 (d, 2 H, H(2'), H(6'), J = 8.6); 7.70 (d, 2 H, H(3'), H(5'), J = 8.6)	8.56 (6.2)	8.26 (6.2)	8.45 (d, 2 H, H(2'), H(6'), J = 8.8); 7.89 (d, 2 H, H(3'), H(5'), J = 8.8)
5	$CDCl_3$	15:85	6.64 (5.4)	8.60 (5.4)	3.83 (s, 3 H, 2'-MeO); 7.10 (m, 1 H, H(3')); 7.37 (td, 1 H, H(4')); 7.02 (t, 1 H, H(5'); 7.74 (d, 1 H, H(6'))	8.37 (6.3)	7.87 (6.3)	3.75 (s, 3 H, 2'-MeO); 7.10 (m, 2 H, H(3'), H(5')); 7.58 (m, 1 H, H(4'); 7.60 (d, 1 H, H(6'))
	Acetone-d_6	5:95	6.87 (5.6)	8.71 (5.6)	3.81 (s, 3 H, 2'-MeO); 7.15 (d, 1 H, H(3')); 7.46 (td, 1 H, H(4')); 7.06 (td, 1 H, H(5')); 7.72 (dd, 1 H, H(6'))	8.52 (6.3)	8.11 (6.3)	3.85 (s, 3 H, 2'-MeO); 7.30 (dd, 1 H, H(3'), J = 9.0, J = 1.0); 7.67 (td, 1 H, H(4')); 7.20 (td, 1 H, H(5')); 7.69 (d, 1 H, H(6'), J = 7.5)
	DMSO-d_6	<2:98	7.01 (5.4)	8.75 (5.4)	3.79 (s, 3 H, 2'-MeO)	8.57 (6.3)	8.30 (6.3)	3.75 (s, 3 H, 2'-MeO); 7.32 (d, 1 H, H(3')); 7.70 (m, 1 H, H(4')); 7.20 (td, 1 H, H(5')); 7.68 (d, 1 H, H(6'))

Table 1. (*Continued*)

Com- pound	Solvent	Percentages of the tautomers, A:T	δ, *J*/Hz					
			Tautomer A			Tautomer T		
			H(5) ($J_{5,6}$)	H(6) ($J_{6,5}$)	Phenyl ring protons	H(7) ($J_{7,8}$)	H(8) ($J_{8,7}$)	Phenyl ring protons
7	$CDCl_3$	100:0	6.68 (5.5)	8.47 (5.5)	12.97 (s, 1 H, H(2')O); 6.94 (m, 2 H, H(3'), H(5')); 7.41 (m, 1 H, H(4')); 8.41 (dd, 1 H, H(6'), J = 8.0, J = 2.0)			
	Acetone-d_6	97:3	6.91 (5.5)	8.68 (5.5)	12.99 (s, 1 H, H(2')O); 6.93 (m, 2 H, H(3'), H(5')); 7.41 (m, 1 H, H(4')); 8.37 (dd, 1 H, H(6'), J = 8.3, J = 2.0)	8.58 (6.3)	8.13 (6.3)	7.15 (m, 2 H, H(3'), H(5')); 7.60 (m, 1 H, H(4'))
	DMSO-d_6	71:29	7.04 (5.5)	8.74 (5.5)	13.10 (s, 1 H, H(2')O); 6.98 (m, 2 H, H(3'), H(5')); 7.44 (m, 1 H, H(4')); 8.30 (dd, 1 H, H(6'), J = 8.2, J = 2.0)	8.55 (6.5)	8.26 (6.5)	11.13 (s, 1 H, H(2')O); 7.07 (m, 2 H, H(3'), H(5')); 7.55 (m, 1 H, H(4')); 8.08 (dd, 1 H, H(6'), J = 8.2, J = 2.0)

* The signals of these protons overlap.

Table 2. Parameters of the ^{1}H NMR spectra of 4-azido-2-(2'-hydroxyphenyl)quinazoline (**8A**) and 5-(2'-hydroxyphenyl)tetrazolo[1,5-*c*]quinazoline (**8T**) and the ratios between these compounds under equilibrium conditions

Solvent	Percentages of the tautomers, A : T	δ, *J*/Hz					
		Tautomer **8A***	Tautomer **8T**				
		Phenyl ring protons	H(7), dd (J)	H(8), td (J)	H(9), td (J)	H(10), dd (J)	Phenyl ring protons
$CDCl_3$	39:61*	13.88 (s, 1 H, H(2')O); 7.00 (m, 2 H, H(3'), H(5')); 7.39 (m, 1 H, H(4')); 8.52 (dd, 1 H, H(6'), J = 8.0, J = 2.0)	8.08	7.97	7.82	8.70 (8.0; 1.2)	13.28 (s, 1 H, H(2')O); 7.13 (m, 2 H, H(3'), H(5')); 7.55 (m, 1 H, H(4')); 9.36 (dd, 1 H, H(6'), J = 8.5, J = 1.5)
Acetone-d_6	19:81**	13.67 (s, 1 H, H(2')O); 7.00 (m, 2 H, H(3'), H(5')); 7.47 (m, 1 H, H(4')); 8.58 (dd, 1 H, H(6'), J = 8.5, J = 2.1)	8.34 (8.0; ~1)	8.15 (8.0; 1.8)	8.00 (8.0; 1.3)	8.70 (8.0; 1.3)	12.79 (s, 1 H, H(2')O); 7.21 (m, 2 H, H(3'), H(5')); 7.65 (m, 1 H, H(4')); 9.20 (dd, 1 H, H(6'), J = 8.5, J = 2.1)
DMSO-d_6	0:100		8.24 (8.0; 1)	8.08 (8.0; 1.5)	7.96**	8.64 (8.0; 1.7)	10.71 (s, 1 H, H(2')O); 7.08 (m, 2 H, H(3'), H(5')); 7.54 (m, 1 H, H(4')); 7.96** (dd, 1 H, H(6'))

* H(5)—H(8): in $CDCl_3$ the signals of three protons overlap with the H(7)—H(9) signals of the tetrazole tautomer, one signal overlaps with the signal of H(4') of the tetrazole; in acetone-d_6, one of these signals is recorded as a multiplet at 7.70 ppm, the signals of the three other protons overlap with the H(8) and H(9) signals of the tetrazole.
** The signals overlap.

region, which unambiguously indicates the presence of azide tautomer **7A**. The ^{1}H NMR spectrum of a $CDCl_3$ solution contains only signals of azide **7A**, while in solutions in acetone-d_6 or DMSO-d_6, the tetrazole form **7T**, whose proportion varies in parallel with the polarity of the solvent (see Table 1), also appears. The presence of broad smeared bands with maxima at 2400—2800 cm^{-1} in the IR spectra, for example, in $CHCl_3$, and also the low-field chemical shifts of the protons of the *o*-hydroxyl group indicate the presence of a strong intramolecular H-bond in tautomers **7A** and **7T**. The fact that the ^{1}H NMR signal of the OH group in azide **7A** is recorded in a lower field than that for tetrazole **7T** indicates that the intramolecular H-bond in the former is stronger, and this accounts for the displacement of the azide-tetrazole equilibrium toward the azide form. In our opinion, the

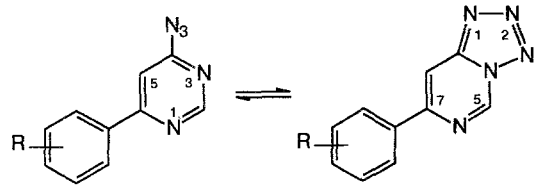
difference between the energies of intramolecular H-bond in tautomers is due to the high proton-acceptor ability of the aza atom of the chelate ring in azide **7A** compared to the tetrazole form **7T**. This is caused by the fact that the electron-withdrawing tetrazole ring decreases the electron density at this atom, whereas the azide group, conversely, increases it, due to the $+M$ effect,[17] since it is conjugated with the N(1) atom of the pyrimidine ring.

Thus, the *o*-phenolic hydroxyl in compound **7** stabilizes azide form **7A** owing to the formation of the chelate ring, whose effect is greater in magnitude than the electron-releasing effect of this group located in the *para*-position and acting in a direction opposite to it (*cf.* azides **2** and **7**).

We obtained similar experimental data for *o*-hydroxyphenylquinazoline **8** (Table 2). The presence of the **8A** $\rightleftharpoons$ **8T** azide-tetrazole equilibrium in solutions in $CDCl_3$ or acetone-d_6 also results from the greater strength of the chelate ring in **8A** compared to **8T**, but benzoannelation of the pyridine ring substantially decreases the effect of intramolecular H-bond on the tautomeric equilibrium (*cf.* compound **7**).

On going from 2-substituted 4-azidopyrimidines **1A—4A** to the series of 6-substituted 4-azidopyrimidines (**9A—11A**), the *ortho*-arrangement of the aryl substituent with respect to the N(3) reaction center changes to the *para*-arrangement, which is a significant factor in elucidating the electronic influence of substituents with $-I$ and $+M$ effects on an azide-tetrazole equilibrium.[18] The IR spectra of these compounds recorded in KBr exhibit no absorption band in the 2100—2200 cm^{-1} region corresponding to the azide group; this band is very weak in a DMSO solution, and in a $CHCl_3$ solution it is strong. The ^1H NMR spectra recorded in solutions in $CDCl_3$, acetone-d_6, or DMSO-d_6 contain signals of both azide and tetrazole forms. As the polarity of the medium increases, the tautomeric equilibrium shifts to the more polar tetrazole tautomer, **9T—11T** (Scheme 3, Table 3).

Scheme 3



9A—11A **9T—11T**

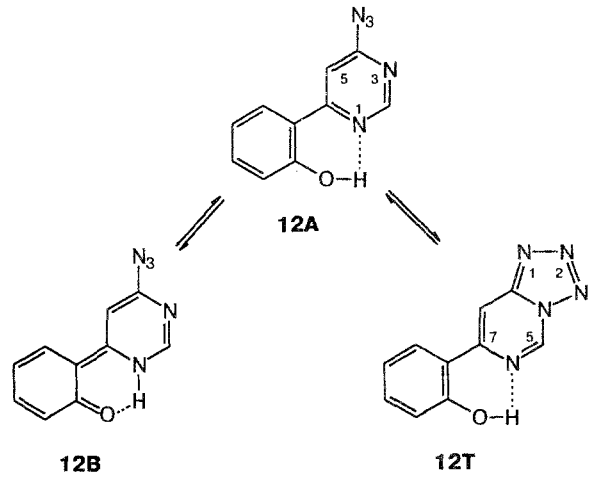
R = H (**9**), 4'-OMe (**10**), 2'-OMe (**11**)

An analysis of the experimental data on the azide-tetrazole equilibria of 4-azido-6-arylpyrimidines **9A—11A** and 4-azido-2-arylpyrimidines **1A**, **3A**, and **5A** (see Tables 1 and 3) allows one to draw the following conclusions. First, in both series the proportion of the tetrazole form is higher when the methoxy group is introduced into the *ortho*-position of phenyl than into the *para*-position. Second, the tetrazole tautomers of compounds **9—11** are more stable than those of compounds **1**, **3**, and **5**. This is due to the change in the electron-donating properties of the pyrimidine N(3) atom participating in cyclization, since in the former case, the aryl group increases the electron density at this atom owing to conjugation, and, conversely, in the latter case, it decreases the electron density owing to the predominating influence of the $-I$ effect on the reaction center.

The experimental data obtained are in agreement with the results of *ab initio*[19] and MNDO[20] quantum-chemical studies of azide-tetrazole tautomerism, according to which cyclization occurs in several steps, and interaction between the unshared electron pair of the aza atom with the terminal nitrogen atom of the azide group acts as the driving force of the process.

In 4-azido-6-(2'-hydroxyphenyl)pyrimidine (**12A**), as in azides **7A**, **8A**, a strong O—H...N intramolecular H-bond between the hydroxyl group and the aza atom of the ring is also formed, which is evidenced by the presence of broad diffusion absorption bands in the 2400—3000 cm^{-1} region of the IR spectrum recorded in $CHCl_3$. The tautomeric equilibrium of compound **12** can be represented by Scheme 4.

Scheme 4



12A

12B **12T**

The UV spectrum of compound **12** in $CHCl_3$ exhibits a long-wave absorption maximum at 342 nm (ε 8600), and the ^{17}O NMR signal of the phenolic oxygen is recorded at 96.5 ppm ($\Delta\nu_{1/2}$ = 450 Hz). These spectral parameters are similar to the data obtained for compound **7** (see above) and also indicate that the **12A** $\rightleftharpoons$ **12B** prototropic equilibrium is almost completely shifted to the formation of tautomer **12A**.

Table 3. Parameters of the ^{1}H NMR spectra of 4-azido-6-arylpyrimidines **9A—12A** and 7-aryltetrazolo[1,5-*c*]pyrimidines **9T—12T** and the ratios between these compounds under equilibrium conditions

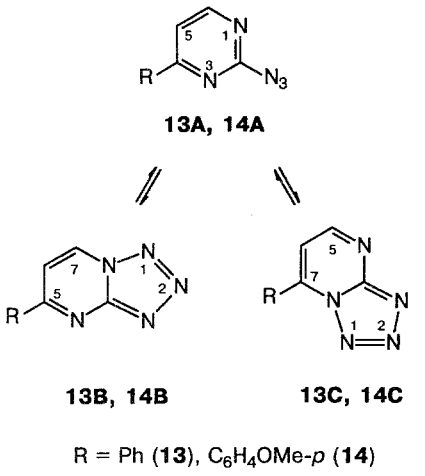
Compound	Solvent	Percentages of the tautomers, A:T	δ, *J*/Hz					
			Tautomer **A**			Tautomer **T**		
			H(2) ($J_{2,5}$)	H(5) ($J_{5,2}$)	Phenyl ring protons	H(5) ($J_{5,8}$)	H(8) ($J_{8,5}$)	Phenyl ring protons
9	$CDCl_3$	59:41	8.96 (~1)	7.16 (~1)	8.01 (m, 2 H, H(2'), H(6')); 7.50* (m, 3 H, H(3'), H(4'), H(5'))	9.69 (1.5)	8.24 (1.5)	8.12 (m, 2 H, H(2'), H(6')); 7.50* (m, 3 H, H(3'), H(4'), H(5'))
	Acetone-d_6	20:80	8.97 (~1)	7.48 (~1))	8.21 (m, 2 H, H(2'), H(6')); 7.58* (m, 3 H, H(3'), H(4'), H(5'))	10.09 (1.5)	8.60 (1.5)	8.33 (m, 2 H, H(2'), H(6')); 7.58* (m, 3 H, H(3'), H(4'), H(5'))
	DMSO-d_6	3:97	9.03 (~1)	7.56*	8.19 (m, 2 H, H(2'), H(6')); 7.56* (m, 3 H, H(3'), H(4'), H(5'))	10.27 (1.5)	8.82 (1.5)	8.28 (m, 2 H, H(2'), H(6')); 7.56* (m, 3 H, H(3'), H(4'), H(5'))
10	$CDCl_3$	57:43	8.91 (~1)	7.09 (~1)	8.01 (d, 2 H, H(2'), H(6'), *J* = 8.8); 6.98 (d, 2 H, H(3'), H(5'), *J* = 8.8); 3.86 (s, 3 H, 4'-MeO)	9.64 (1.5)	8.13 (1.5)	8.09 (d, 2 H, H(2'), H(6'), *J* = 9.0); 7.05 (d, 2 H, H(3'), H(5'), *J* = 9.0); 3.89 (s, 3 H, 4'-MeO)
	Acetone-d_6	21:79	8.90 (~1)	7.40 (~1)	8.21 (d, 2 H, H(2'), H(6'), *J* = 9.0); 7.07 (d, 2 H, H(3'), H(5'), *J* = 9.0); 3.88 (s, 3 H, 4'-MeO)	10.03 (1.5)	8.46 (1.5)	8.30 (d, 2 H, H(2'), H(6'), *J* = 9.0); 7.13 (d, 2 H, H(3'), H(5'), *J* = 9.0); 3.90 (s, 3 H, 4'-MeO)
11	$CDCl_3$	45:55	8.96 (~1)	7.46 (~1)	3.88 (s, 3 H, 2'-MeO); 6.95—7.19* (m, 2 H, H(3'), H(5')); 7.38—7.53* (m, 1 H, H(4')); 8.00 (dd, 1 H, H(6'), *J* = 8.0, *J* = 2.0)	9.66 (1.5)	8.73 (1.5)	3.97 (s, 3 H, 2'-MeO); 6.95—7.19* (m, 2 H, H(3'), H(5')); 7.38—7.53* (m, 1 H, H(4')); 8.21 (dd, 1 H, H(6'), *J* = 8.0, *J* = 2.0)
12	$CDCl_3$	100:0	8.85 (~1)	7.24 (~1)	13.41 (s, 1 H, H(2')O); 6.99 (m, 2 H, H(3'), H(5')); 7.40 (m, 1 H, H(4')); 7.71 (dd, 1 H, H(6'), *J* = 8.0, *J* = 1.5)			
	Acetone-d_6	80:20	8.99 (~1)	7.58 (~1)	13.30 (s, 1 H, H(2')O); 6.95 (m, 2 H, H(3'), H(5')); 7.42 (m, 1 H, H(4')); 8.03 (dd, 1 H, H(6'), *J* = 8.0, *J* = 1.8)	10.20 (1.5)	8.76 (1.5)	11.15 (br.s, 1 H, H(2')O); 7.03 (m, 2 H, H(3'), H(5')); 7.42 (m, 1 H, H(4')); 8.21 (dd, 1 H, H(6'), *J* = 8.0, *J* = 1.8)
	Acetonitrile-d_3	77:23	8.89 (~1)	7.44 (~1)	13.43 (br.s, 1 H, H(2')O); 7.13—6.83* (2 H, H(3'), H(5')); 7.51—7.29* (m, 1 H, H(4')); 7.90 (dd, 1 H, H(6'), *J* = 8.5, *J* = 1.5)	9.87 (1.5)	8.53 (1.5)	11.17 (s, 1 H, H(2')O); 7.13—6.83* (m, 2 H, H(3'), H(5')); 7.51—7.29* (m, 1 H, H(4')); 8.01 (dd, 1 H, H(6'), *J* = 8.5, *J* = 1.5)
	DMF-d_7	28:72	9.09 (~1)	8.18 (~1)	13.13 (br.s, 1 H, H(2')O); 7.21—6.91* (m, 2 H, H(3'), H(5')); 7.52—7.33* (m, 1 H, H(4')); 8.18 (dd, 1 H, H(6'), *J* = 8.0, *J* = 2.0)	10.34 (1.5)	8.93 (1.5)	7.21—6.91* (m, 2 H, H(3'), H(5')); 7.52—7.33* (m, 1 H, H(4')); 8.31 (dd, 1 H, H(6'), *J* = 8.0, *J* = 2.0)
	DMSO-d_6	13:87	9.03 (~1)	7.77 (~1)	12.70 (s, 1 H, H(2')O); 7.04* (m, 2 H, H(3'), H(5')); 7.35* (m, 1 H, H(4')); 8.09 (dd, 1 H, H(6'), *J* = 8.0, *J* = 1.8)	10.24 (1.5)	8.82 (1.5)	10.90 (s, 1 H, H(2')O); 7.04* (m, 2 H, H(3'), H(5')); 7.35* (m, 1 H, H(4')); 8.18 (dd, 1 H, H(6'), *J* = 8.0, *J* = 1.8)

* The signals of these protons overlap.

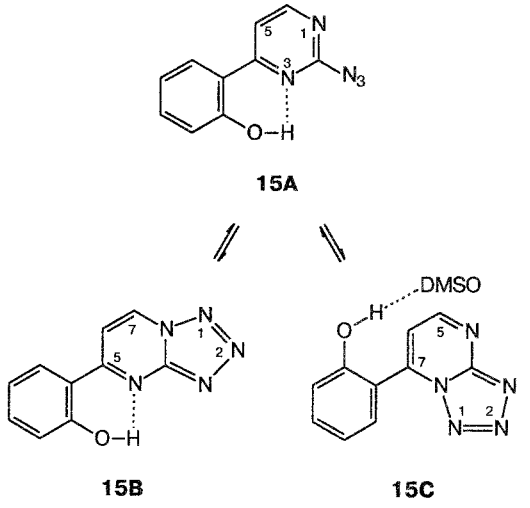
The IR spectra of compound **12** recorded in the crystalline state and in $CHCl_3$ or DMSO solutions exhibit a strong absorption band of the azide group in the 2100—2200 cm^{-1} region, which unambiguously indicates the presence of tautomer **12A**. In the ^{1}H NMR spectrum in $CDCl_3$, only the signals of azide **12A** are recorded, while in more polar solvents, acetone-d_6 or DMSO-d_6, tetrazole form **12T** also appears (see Table 3). The low-field signals of the OH groups in these tautomers indicate that they participate in intramolecular H-bond, and the fact that this signal of azide **12A** is recorded in a lower field than that of tetrazole **12T** is due to the higher proton-acceptor properties of the N(1) atom participating in the intramolecular H-bond in azide **12A**. The reason for the substantial difference between the strengths of the intramolecular H-bonds in compounds **12A** and **12T** is similar to that considered above for tautomers **7A** and **7T**.

The peculiarities of 2-azido-4-R-pyrimidines (**13A**, **14A**) are, first, the presence of two nonequivalent reaction centers due to the asymmetry of the molecule, and therefore, the possibility of the formation of tetrazoles **13C**, **14C** and/or **13B**, **14B** by intramolecular cyclization of the azide group (Scheme 5). Second, the substituents in these structures are located in the *ortho*- and *para*-positions with respect to the N(3) and N(1) aza atoms,

Scheme 5



Scheme 6



respectively, *i.e.*, their mutual arrangement corresponds to both series of the above-considered azides.

The IR spectra of compounds **13** and **14** recorded in KBr exhibit no absorption band of the azide group at 2100—2200 cm^{-1}; in a DMSO solution, this band is weak, and in $CHCl_3$, it is strong. The ^1H NMR spectra recorded in $CDCl_3$, acetone-d_6, or DMSO-d_6 contain signals of azide forms **13A**, **14A** and two tetrazole forms **13B**, **14B** and **13C**, **14C**; the cyclization of the azide group at the N(1) aza atom predominates. The higher values of the spin coupling constants in tautomers **B** than in tautomers **C** are diagnostic markers of the direction of the cyclization of the azide group. Previously,[21] based on ^1H NMR spectra, the structure of only tetrazole **13B** was ascribed to compound **13** in DMSO (Table 4). We obtained similar results in an IR- and NMR-spectroscopic study of the azide-tetrazole equilibrium in 2-azido-4-(*o*-hydroxyphenyl)pyrimidine (**15A**) (see Table 4). The formation of tetrazole **15C** is accompanied by simultaneous cleavage of the intramolecular H-bond in azide **15A** and formation of an intermolecular hydrogen bond between the phenolic hydroxyl and DMSO (Scheme 6).

Attention is engaged by the fact that the ratio between the tautomers of **15** is comparable to that for compounds incorporating no chelate rings, **13** and **14**. This weak influence of the intramolecular H-bond in azide **15** on the azide-tetrazole equilibrium is especially pronounced in comparison with the substantial destabilization of the tetrazole ring in compounds **7**, **8**, and **12**. In our opinion, this is caused by the decrease in the proton-acceptor ability of the N(3) aza atom and, hence, by weakening of the intramolecular H-bond in azide **15** owing to the $-I$ effect of the azide group, since the electron-donating ability of a "pyridine" type nitrogen atom in α-substituted heteroaromatic compounds is mostly determined by the inductive effect of the substituent.[22,23]

Thus, the analysis of the effect of intramolecular H-bonds on the azide-tetrazole equilibria in the above-discussed compounds showed that the chelate H-ring acts as a "probe" that makes it possible to observe the variation of the electron-donating properties of the aza atom as a function of the location of the azide group with respect to this atom, and the greater strength of the intramolecular H-bond in the azide form compared to the tetrazole form is the cause for destabilization of the latter.

In polar aprotic solvents,[24] the intramolecular H-bonds in compounds **7**, **8**, **12**, and **15** are partially or entirely cleaved to give complexes containing intermolecular H-bonds between solvent molecules and the phenolic hydroxyls in the tautomers. This results in a decrease in the effect of an intramolecular H-bond on the stabilization of the azide form and in a displacement of the azide-tetrazole equilibria toward the tetrazole tautomer. The data that we obtained on the ratio between the tautomers of compounds **9** and **12** dissolved in acetonitrile-d_3 or DMF-d_7, whose dielectric constants ε are very similar, but whose basicities are substantially different,[25] serve as experimental evidence of this solvent effect. The ratios between the tautomers of compound **9** in CD_3CN and DMF-d_7 solutions are similar (**9A** : **9T** = 15 : 85 and 8 : 92, respectively), since in this case, the equilibrium is governed mostly by nonspecific intermolecular interactions of the tautomers with solvent molecules. The positions of the tautomeric equilibria of compound **12** in DMF-d_7 and CD_3CN, unlike those of compound **9**, are substantially different (see Table 3). The fact that the proportion of tetrazole **12T** in DMF-d_7 is larger than that in CD_3CN implies the occurrence of the competing process, *viz.*, the formation of intermolecular H-bonds with solvent molecules, which results in the stabilization of azide form **12A** by the intramolecular H-bond becoming less effective. The significance and the relative contributions of

Table 4. Parameters of the ^1H NMR spectra of 2-azido-4-arylpyrimidines **13A—15A** and 5-aryl- and 7-aryltetrazolo[1,5-*a*]pyrimidines (**13B—15B** and **13C—15C**, respectively) and the ratios between these compounds under equilibrium conditions

Compound	Solvent	Percentages of tautomers, A:B:C*	δ, *J*/Hz					
			Tautomer **A**			Tautomer **T**		
			H(5) ($J_{5,6}$)	H(6) ($J_{6,5}$)	Phenyl ring protons	H(6) ($J_{6,7}$)	H(7) ($J_{7,6}$)	Phenyl ring protons
13	$CDCl_3$	87:13:0	7.45 (5.3)	8.61 (5.3)	8.09 (m, 2 H, H(2'), H(6')); 7.50 (m, 3 H, H(3'), H(4'), H(5'))	7.72 (7.3)	9.05 (7.3)	8.24 (m, 2 H, H(2'), H(6')); 7.58 (m, 3 H, H(3'), H(4'), H(5'))
	Acetone-d_6	42:55:3	7.78 (5.5)	8.72 (5.5)	8.21 (m, 2 H, H(2'), H(6')); 7.56 (m, 3 H, H(3'), H(4'), H(5'))	8.14 (7.3)	9.57 (7.3)	8.39 (m, 2 H, H(2'), H(6')); 7.63 (m, 3 H, H(3'), H(4'), H(5'))
	DMSO-d_6	10:88:2	7.88 (5.3)	8.78 (5.3)	8.17 (m, 2 H, H(2'), H(6')); 7.58 (m, 3 H, H(3'), H(4'), H(5'))	8.22 (7.3)	9.80 (7.3)	8.37 (m, 2 H, H(2'), H(6')); 7.65 (m, 3 H, H(3'), H(4'), H(5'))
14	$CDCl_3$	82:18:0	7.36 (5.5)	8.54 (5.5)	8.07 (d, 2 H, H(2'), H(6'), J = 9.0); 6.99 (d, 2 H, H(3'), H(5'), J = 9.0); 3.87 (s, 3 H, 4'-MeO)	7.64 (7.3)	8.96 (7.3)	8.23 (d, 2 H, H(2'), H(6'), J = 9.0); 7.06 (d, 2 H, H(3'), H(5'), J = 9.0); 3.91 (s, 3 H, 4'-MeO)
	Acetone-d_6	36:64:0	7.71 (5.2)	8.64 (5.2)	8.20 (d, 2 H, H(2'), H(6'), J = 9.0); 7.10 (d, 2 H, H(3'), H(5'), J = 9.0); 3.91 (s, 3 H, 4'-MeO)	8.50 (6.2)	7.99 (6.2)	8.39 (d, 2 H, H(2'), H(6'), J = 9.0); 7.18 (d, 2 H, H(3'), H(5'), J = 9.0); 3.95 (s, 3 H, 4'-MeO)
	DMSO-d_6	6:92:2	7.82 (5.5)	8.69 (5.5)	8.17 (d, 2 H, H(2'), H(6'), J = 9.0); 7.10 (d, 2 H, H(3'), H(5'), J = 9.0); 3.84 (s, 3 H, 4'-MeO)	8.16 (7.3)	9.70 (7.3)	8.36 (d, 2 H, H(2'), H(6'), J = 9.0); 7.16 (d, 2 H, H(3'), H(5'), J = 9.0); 3.88 (s, 3 H, 4'-MeO)
15	$CDCl_3$	89:11:10	7.51 (5.5)	8.62 (5.5)	12.67 (s, 1 H, H(2')O); 6.97 (m, 2 H, H(3'), H(5')); 7.40** (m, 1 H, H(4')); 7,77** (dd, 1 H, H(6'), J = 8.0, J = 1.5)	8.34 (7.3)	9.05 (7.3)	7.40** (m, 1 H, H(4')); 7.77** (1 H, H(6'))
	Acetone-d_6	44:56:0	7.89 (5.5)	8.75 (5.5)	7.01** (m, 2 H, H(3'), H(5')); 7.41 (m, 1 H, H(4')); 8.02 (dd, 1 H, H(6'), J = 8.0, J = 1.5)	8.26 (7.3)	9.58 (7.3)	7.01** (m, 2 H, H(3'), H(5')); 7.53 (m, 1 H, H(4')); 8.21 (dd, 1 H, H(6'), J = 8.0, J = 1.5)
	DMSO-d_6	8:87:5	8.01 (5.5)	8.77 (5.5)	11.46 (s, 1 H, H(2')O); 8.04 (dd, 1 H, H(6'))	8.25 (7.3)	9.71 (7.3)	11.49 (s, 1 H, H(2')O); 6.96 (m, 2 H, H(3'), H(5')); 7.49 (m, 1 H, H(4')); 8.10 (dd, 1 H, H(6'), J = 8.0, J = 1.5)

* The spectral parameters for tautomer **13C** in DMSO-d_6, δ: 9.18 (d, 1 H, H(5), $J_{5,6}$ = 4.6 Hz); 7.84 (d, 1 H, H(6), $J_{6,5}$ = 4.6 Hz), the signals of the Ph-group protons overlap with the corresponding signals of tautomers **A** and **B**; in acetone-d_6: 9.16 (d, 1 H, H(5), $J_{5,6}$ = 4.4 Hz); 7.74 (d, 1 H, H(6), $J_{6,5}$ = 4.4 Hz); for tetrazole **14C** in DMSO-d_6: 9.12 (d, 1 H, H(5), $J_{5,6}$ = 4.4 Hz); for tetrazole **15C** in DMSO-d_6: 10.48 (br.s, 1 H, H(2')O); 9.16 (d, 1 H, H(5), $J_{5,6}$ = 4.5 Hz); 7.69 (d, 1 H, H(6), $J_{6,5}$ = 4.5 Hz).

** The signals of these protons overlap.

these two opposing effects to the position of the azide-tetrazole equilibrium of compound **12** are clearly demonstrated by the fact that the proportions of tautomers **12A** and **12T** in acetone-d_6 and acetonitrile-d_3 are close, although the dielectric constant of the latter is almost twice as large as that of acetone.

Experimental

IR spectra were recorded on a UR-20 spectrometer; UV were run on a Specord UV-VIS instrument. ^1H NMR spectra (200.13 MHz) and ^{17}O NMR spectra (54.24 MHz) were recorded at 22 °C on Bruker WP-200 SY and AM 400 pulse spectrometers with stabilization with respect to deuterium NMR signals of the solvent. Chemical shifts were referred to the residual protons of the solvent ($CDCl_3$, δ 7.24; DMSO-d_6, δ 2.50; acetone-d_6, δ 2.04) or to the resonance absorption of the water oxygen (an external standard). The solvents (except $CDCl_3$) were preliminarily dried with molecular sieves: acetone-d_6 and DMSO-d_6 were dried over 4 Å sieves and DMF-d_7 was dried over 4 and 9 Å sieves. Mass spectra were obtained on a Finnigan MAT 8200 instrument.

5-Phenyltetrazolo[1,5-*c*]quinazoline (6T). A solution of 4-chloro-2-phenylquinazoline (5 mmol), NaN_3 (10 mmol), and anhydrous LiCl (10 mmol) in 50 mL of dry DMF was stirred at ambient temperature until the starting compound

disappeared (the reaction was monitored by TLC on Silufol UV-254 plates). The reaction mixture was poured into water, and the resulting precipitate was filtered off, washed with water, and dried to give compound **6T**, m.p. 162—163 °C (*cf.* Ref. 14: m.p. 162—163 °C). The molecular weight found by high-resolution mass spectrometry was 247.0839. $C_{14}H_9N_5$. Calculated: 247.0858.

5-(2′-Hydroxyphenyl)tetrazolo[1,5-*c*]quinazoline (8T) was prepared from 4-chloro-2-(2′-hydroxyphenyl)quinazoline and LiN_3 under the above-described conditions, m.p. 168—170 °C (from an ethanol—dioxane mixture). Found (%): C, 63.93; H, 3.43; N, 26.51. $C_{14}H_9N_5O$. Calculated (%): C, 63.87; H, 3.45; N, 26.61.

4-Azido-6-(4′-methoxyphenyl)pyrimidine (10A) was prepared from 4-chloro-6-(4′-methoxyphenyl)pyrimidine and LiN_3 under the above-described conditions, m.p. 190—192 °C (from a benzene—dioxane mixture). The molecular weight found by high-resolution mass spectrometry was 227.0796. $C_{11}H_9N_5O$. Calculated: 227.0807.

4-Azido-6-(2′-methoxyphenyl)pyrimidine (11A) was prepared from 4-chloro-6-(2′-methoxyphenyl)pyrimidine and LiN_3 similarly to compound **6T**, m.p. 113—115 °C (from ethanol). Found (%): C, 57.81; H, 4.00; N, 30.88. $C_{11}H_9N_5O$. Calculated (%): C, 58.14; H, 3.99; N, 30.82.

2-Azido-4-(2′-hydroxyphenyl)pyrimidine (15A). A solution of $NaNO_2$ (0.09 g, 1.3 mmol) in 2 mL of water was added dropwise over a period of ~15 min to a solution of 2-hydrazino-4-(2′-hydroxyphenyl)pyrimidine (0.2 g, 1 mmol) in 7 mL of 70 % acetic acid cooled by ice water. The reaction mixture was stirred for an additional 1.5 h at ~0 °C and the precipitate was filtered off, washed with water, and dried to give 0.16 g (76 %) of azide **15A**, m.p. 185—186.5 °C (from an ethanol—benzene mixture). Found (%): C, 56.67; H, 3.62; N, 32.66. $C_{10}H_7N_5O$. Calculated (%): C, 56.33; H, 3.31; N, 32.85.

4-Azido-2-(4′-hydroxyphenyl)pyrimidine (2A) was prepared from 4-hydrazino-2-(4′-hydroxyphenyl)pyrimidine under the conditions of the previous experiment, m.p. 185—187 °C (from ethanol). Found (%): C, 56.28; H, 3.37; N, 32.70. $C_{10}H_7N_5O$. Calculated (%): C, 56.33; H, 3.31; N, 32.85.

2-Azido-4-(4′-methoxyphenyl)pyrimidine (14A) was synthesized by nitrosation of 2-hydrazino-4-(4′-methoxyphenyl)-pyrimidine similarly to the synthesis of azide **15A**, m.p. 180—182 °C (from an ethanol—benzene mixture). The molecular weight found by high-resolution mass spectrometry was 227.0804. $C_{11}H_9N_5O$. Calculated: 227.0807.

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