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SYNTHESIS AND STUDY OF 3-(PYRIMIDIN-2-YL)AMINO-1(2)H-1,2,4-TRIAZOLE DERIVATIVES

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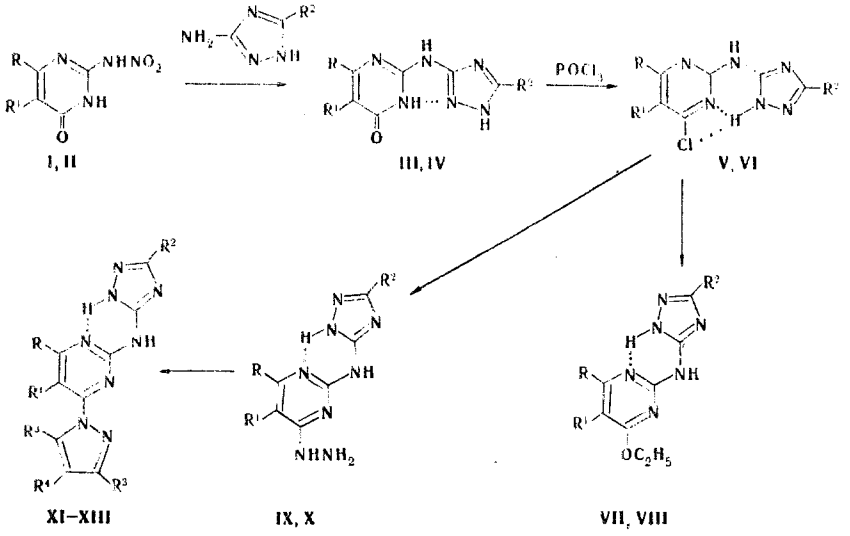
The previously unknown 3-[4(3H)-pyrimidinon-2-yl]amino-1H-1,2,4-triazoles, which were converted to 3-[4-chloro-, 3-(4-ethoxy)-, 3-(4-hydrazinopyrimidin-2-yl)]-amino-2(4)H-1,2,4-triazoles, were obtained by the reaction of 2-nitroamino-4(3H)-pyrimidinones with 3-amino-5-hexyl-1H-1,2,4-triazole. The condensation of the initial products with β-diketones gave 3-[4-(1H-pyrazol-1-yl)pyrimidin-2-yl]-amino-2(4)H-1,2,4-triazoles. The IR, UV, and PMR spectra of the synthesized compounds were studied.

3-(2-Pyrimidin-2-yl)amino-1(2)H-1,2,4-triazole derivatives have not been described in the literature. However, like 3-(pyrimidin-4-yl)amino-1(2)H-1,2,4-triazoles [1], they are of interest as polydentate ligands that are potentially capable of reacting with metal salts to give complexes, including those that are stabilized by additional metal chelates that include an intramolecular hydrogen bond (IHB).

We have obtained some 3-(pyrimidin-2-yl)amino-1(2)H-1,2,4-triazole derivatives (III-XIII), the synthesis of which was realized via the scheme



I—XIII R=CH_3; III—XIII R^2=C_6H_{13}; I, III, V, VII, IX, XI, XIII R^1=H; II, IV, VI, VIII, X, XII R^1=C_2H_5; XI, XII R^3=CH_3, R^4=H; XIII R^3=C_3H_7, R^4=C_2H_5

In addition to the results of elementary analysis of III-XIII (Table 1), we also studied their IR, UV (Table 2), and PMR (Table 3) spectra.

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TABLE 1. Characteristics of III-XIII

Compound	mp,[a] °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
III	260,5—261,5	56,6	7,0	30,6	$C_{13}H_{20}N_6O$	56,5	7,3	30,4	62,0
IV	232,0—234,0	59,3	7,8	27,3	$C_{15}H_{24}N_6O$	59,2	7,9	27,6	59,5
V	167,0—168,0	52,9	6,7	28,5	$C_{13}H_{19}N_6Cl$	53,2	6,5	28,5	67,1
VI	176,0—177,0	55,7	7,2	25,8	$C_{15}H_{23}N_6Cl$	55,9	7,1	26,0	64,0
VII	124,0—125,5	59,4	8,0	27,8	$C_{15}H_{24}N_6O$	59,2	8,0	28,0	67,5
VIII	104,0—105,5	61,7	8,6	25,1	$C_{17}H_{28}N_6O$	61,4	8,1	25,3	62,5
IX	192,0—194,0	53,5	7,8	38,8	$C_{13}H_{22}N_8$	53,8	7,6	38,6	65,5
X	202,0—204,0	56,4	8,4	35,0	$C_{15}H_{26}N_8$	56,7	8,2	35,2	50,0
XI	153,0—154,0	61,3	7,1	31,4	$C_{18}H_{26}N_8$	61,0	7,4	31,6	48,5
XII	156,0—158,0	62,7	8,0	29,0	$C_{20}H_{30}N_8$	62,8	7,9	29,3	46,2
XIII	104,5—106,0	66,0	8,6	25,4	$C_{24}H_{38}N_8$	65,7	8,7	25,6	61,5

[a]Compounds III, IV, IX, and X were recrystallized from ethanol, while V-VIII and XI-XIII were recrystallized from heptane.

TABLE 2. IR and UV Spectra of III-XIII

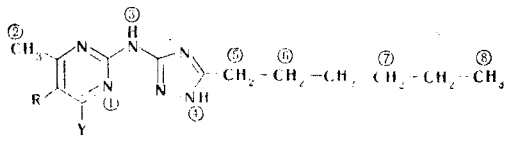
Compound	IR spectrum, ν_{NH}, cm^{-1}		UV spectra, λ_{max}, nm (log ε)
	$CHCl_3$	CCl_4	
III	1682 (980)[a]		242 (4,13), 276 (4,03)
IV	1690 (1194)[a]		249 (4,01), 271 (3,95), 291 (3,88)
V	3410 (167), 3260 (25)	3436 (236), 3200—2600[b]	257 (4,38), 295 (3,54)
VI	3415 (153), 3261 (29)	3432 (213), 3200—2600[b]	256 (4,24), 288 (3,66)
VII	3432 (198), 3380 (159) 3290 (80)	3446 (210), 3406 (164)	251 (4,33)
VIII	3432 (132), 3370 (119), 3280 (70)	3449 (164), 3401 (97)	253 (4,23), 278 (3,80)
IX	3440 (18), 3345 (106) 3280 (155), 3235 (155)		234 (4,28), 244 (4,24), 249 (4,23)
X	3451, 3270[c], 3190[c]		233 (4,27), 255 (4,24), 287 (3,92)
XI	3425 (179), 3390 (177)[c]	3440 (205), 3410 (200)[c]	260 (4,58), 298 (4,01)
XII			258 (4,47), 292 (3,65)
XIII	3441 (170), 3388 (192)[c]	3454 (210), 3410 (204)	261 (4,49), 302 (4,16)

[a]The $\nu_{C=O}$ values are presented.
[b]Diffuse band.
[c]Broad band.

The IR spectra of solutions of III and IV in $CHCl_3$ contain an intense band in the region of stretching vibrations at 1682-1690 cm^{-1}, which is characteristic for $\nu_{C=O}$ of 4(3H)-pyrimidinoses [2] and a broad band with a fine structure of 3000-3500 cm^{-1}. which has a number of maxima at 3425, 3360, 3320, 3275, and 3200 cm^{-1}. The band at 3425 cm^{-1} can be assigned to ν_{NH} of a dihetarylamino group, since a similar band is found at 3425-3440 cm^{-1} in the spectra of 2-arylaminopyrimidines [2, 3]. However, it is impossible to draw a conclusion regarding the structures of III and IV on the basis of the IR spectra. The PMR spectra proved to be more informative in this case and supplement the data from the IR spectra. Thus the PMR spectra of III and IV in $CDCl_3$ contain, in addition to signals of C—H protons, signals of N—H protons: $\delta_{NH}^{III,IV}$ = 13.30 ppm (triazole ring), δ_{NH}^{III} = 13.00 ppm, δ_{NH}^{IV} = 12.74 ppm (amide groupings of the pyrimidine ring), and $\delta_{NH}^{III,IV}$ = 13.30 ppm (dihetarylamino groups); in this case the latter two signals are shifted markedly to weak field as compared with those in the spectrum of 2-(N-p-butylanilino)-4(3H)-pyrimidinone, for which the corresponding δ_{NH} values are 11.0 and 9.3 ppm [2]. The latter can be explained by the presence in III and IV of an IHB formed by the N—H group of the pyrimidinone ring and the sp^2-hybridized nitrogen atom in the 2 or 4 position of the triazole ring.

The IR spectra of dilute solutions of V-VIII and XI-XIII in CCl_4 contain a band in the region of stretching vibrations at 3432-3454 cm^{-1}, which is characteristic for ν_{NH} of 2-

TABLE 3. PMR Spectra[a] of the Synthesized Compounds with the General Formula



Compound	R			1 (s)	2 (s)	3 (s)	4 (s)	5 (t)	6 (m)	7 (m)	8 (t)	Y
	H (c)	C_2H_5										
		CH_3 (t)	CH_2 (q)									
III	5,44			13,00	2,20	13,32	13,32	2,62	1,74	1,36	0,89	Y=O
IV		1,07	2,32	12,74	2,13	13,34	13,34	2,61	1,72	1,32	0,89	Y=O
V	6,66				2,48	12,30	12,30	3,00	1,80	1,32	0,86	Y=Cl
VI		1,19	2,74		2,53	12,15	12,15	3,00	1,80	1,34	0,86	Y=Cl
VII					2,38	10,80	12,15	2,96	1,78	1,34	0,86	Y=OCH_2CH_3: 4,36 (q, CH_2), 1,40 (t, CH_3)
VIII		1,06	2,53		2,39	12,50	12,50	2,73	1,75	1,31	0,86	Y=OCH_2CH_3: 4,39 (q, CH_2), 1,37 (t, CH_3)
IX	6,17				2,18	11,01	12,40	2,56	1,73	1,34	0,88	Y=$NHNH_2$: 10,80 (s, NH), 3,39 (s, NH_2)
X		0,99	2,28		2,38	10,94	12,47	2,32	1,79	1,32	0,86	Y=$NHNH_2$: 9,38 (s, NH), 2,56 (s, NH_2)
XI	7,34				2,51	10,00	12,00	2,75	1,77	1,30	0,86	Y=3,5-dimethyl-1H-pyrazol-1-yl: 2,29 (s, 3-CH_3), 6,00 (s, 4-H), 2,62 (s, 5-CH_3)
XII		1,04	2,83		2,60	11,84	11,84		1,73	1,26	0,89	Y=3,5-dimethyl-1H-pyrazol-1-yl: 2,29 (s, 3-CH_3), 5,98 (s, 4-H), 2,62 (s, 5-CH_3)
XIII	7,30				2,49	9,00	9,00	2,70	1,30	1,85	0,89	Y=4-ethyl-3,5-dipropyl-1H-pyrazol-1-yl: 0,89 (t), 1,40—1,70 (m), 3,00 (t, 1-CH_2, 2-CH_2, 3-CH_2 in 3-C_3H_7), 1,10 (t), 2,36 (q, CH_2, CH_2 in 4-C_2H_5), 2,57 (t), 1,40—1,70 (m), 1,02 (t, 1-CH_2, 2-CH_2, 3-CH_3 in 5-C_3H_7)

[a]For 0.2 M solutions of III, IV, and VI-XIII in $CDCl_3$ and of V in CCl_4; the numbers of the substituents and the character of the signal (in parentheses) are presented.

arylaminopyrimidines [2, 3], as well as a broad and markedly shifted (to the long-wave region) ν_{NH} band of the triazole ring; in the case of VII, VIII, and XI-XIII this band is found at 3400-3410 cm^{-1}, whereas it is diffuse and located at 2600-3200 cm^{-1} in the case of V and VI. The data from the IR spectra make it possible to conclude that V-VIII and XI-XIII in solutions in low-polarity organic solvents are stabilized by an IHB; the IHB is stronger in the case of V and VI. The latter provides a basis for the assumption that V and VI are stabilized by a three-center IHB formed by the 2-NH or 4-NH group of the triazole ring, the sp^2-hybridized N_3 atom of the pyrimidine ring, and the chlorine atom, whereas the IHB in VII, VIII, and XI-XIII is formed by the 2-NH or 4-NH group of the triazole ring and the sp^2-hybridized N_1 atom of the pyrimidine ring.

The PMR spectra of V-XIII are in agreement with the data from the IR spectra and confirm their structures (Table 3).

A special communication will be devoted to the study of the complexing ability of the synthesized compounds.

EXPERIMENTAL

The UV spectra of $(1.9\text{-}7.5)\cdot10^{-5}$ mole/liter solutions of the compounds in ethanol were recorded with a Shimadzu MPS-50L spectrophotometer. The IR spectra of solutions of the compounds in $CHCl_3$ (10^{-2} mole/liter) and CCl_4 (10^{-4} mole/liter) at 2600-3600 cm^{-1} were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Varian X-100-12 spectrometer (100 MHz) with tetramethylsilane as the internal standard.

6-Methyl-2-nitroamino-4(3H)-pyrimidinones I and II were obtained by the method in [4], while 3-amino-5-hexyl-1H-1,2,4-triazole was obtained by the method in [1].

5-Hexyl-3-[6-methyl-4(3H)-pyrimidinon-2-yl]amino-1H-1,2,4-triazole (III). A mixture of 17.6 g (0.1 mole) of I and 30.8 g (0.2 mole) of 3-amino-5-hexyl-1H-1,2,4-triazole was heated at 140°C for 3 h, after which it was cooled and recrystallized from ethanol. The yield and results of analysis are presented in Table 1. The UV and IR spectra are presented in Table 2, and the PMR spectrum is presented in Table 3.

5-Hexyl-3-[5-ethyl-6-methyl-4(3H)-pyrimidinon-2-yl]amino-1H-1,2,4-triazole (IV). This compound was similarly obtained from II and 3-amino-5-hexyl-1,2,4-triazole.

5-Hexyl-3-(4-chloro-6-methylpyrimidin-2-yl)amino-2(4)H-1,2,4-triazole (V). A 14-g (0.071 mole) sample of III was refluxed in 50 ml of phosphorus oxychloride in the presence of 1 ml of triethylamine for 3 h, after which the mixture was cooled and poured over ice. The aqueous mixture was neutralized with concentrated ammonium hydroxide to pH 9, and the precipitate was removed by filtration, dried, and recrystallized from heptane.

5-Hexyl-3-(4-chloro-5-ethyl-6-methylpyrimidin-2-yl)amino-2(4)H-1,2,4-triazole (VI). This compound was similarly obtained from IV.

5-Hexyl-3-(4-ethoxy-6-methylpyrimidin-2-yl)amino-2(4)H-1,2,4-triazole (VII). A 1.4-g (5 mmole) sample of IV was refluxed in 50 ml of a solution of 0.1 g (5 mmole) of sodium metal in ethanol for 4 h, after which the mixture was cooled and diluted with 25 ml of water, and the precipitate was removed by filtration, dried, and recrystallized from heptane.

5-Hexyl-3-(5-ethyl-4-ethoxy-6-methylpyrimidin-2-yl)amino-2(4)triazole (VIII). This compound was similarly obtained from VI.

5-Hexyl-3-(4-hydrazino-6-methylpyrimidin-2-yl)amino-1(2,4)H-1,2,4-triazole (IX). A 2.8-g (0.01 mole) sample of V was refluxed in 30 ml of ethanol containing 1 ml (0.02 mole) of 99% hydrazine hydrate for 3 h, after which the mixture was cooled, and the precipitate was removed by filtration, washed on the filter with water, dried, and recrystallized from ethanol.

5-Hexyl-3-(5-ethyl-4-hydrazino-6-methylpyrimidin-2-yl)amino-1(2,4)H-1,2,4-triazole (X). This compound was similarly obtained from IV.

5-Hexyl-3-[6-methyl-4-(1H-pyrazol-1-yl)pyrimidin-2-yl]amino-2(4)H-1,2,4-triazoles (XI-XIII). A mixture of 0.03 mole of IX or X and 0.03 mole of the corresponding β-diketone in 50 ml of ethanol was refluxed for 4 h, after which the ethanol was removed by vacuum distillation, and the residue was recrystallized twice from heptane.

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