Synthesis of symmetrical di(pyrimidin-2-yl)-1,2,4-triazoles and di(pyrimidin-2-yl)-1,2,4,5-tetrazines

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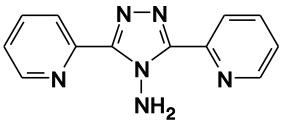
The reactions of pyrimidine-2-carbonitrile and 4,6-dimethylpyrimidine-2-carbonitrile with hydrazine hydrate were investigated. Intermediates in the route of successive transformations of pyrimidine-2-carbonitrile (pyrimidine-2-carbamidrazone and 1,2-bis[amino(pyrimidin-2-yl)methylidene]hydrazine) into trinuclear heterocyclic compounds, *viz.*, symmetrical di(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazines and di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amines (potential polydentate ligands), were isolated. The oxidative dehydrogenation of di(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazines afforded the corresponding 3,6-di(pyrimidin-2-yl)-1,2,4,5-tetrazines.

Key words: pyrimidine-2-carbonitrile, 4,6-dimethylpyrimidine-2-carbonitrile, pyrimidine-2-carbamidrazone, 3,6-di(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazines, 3,6-di(pyrimidin-2-yl)-1,2,4,5-tetrazines, 3,5-di(pyrimidin-2-yl)-1*H*-1,2,4-triazole, 3,5-di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amines.

Substituted 1*H*- and 4*H*-1,2,4-triazoles exhibit properties of metal corrosion inhibitors.[1] These compounds are used also as ligands for the synthesis of transition metal complexes, being coordinated to metal ions through the N(1),N(2) or N(2),N(4) atoms of the triazole ring to form oligo- or polynuclear complexes.[2] Transition metal complexes with triazoles can exhibit ferro- or antiferromagnetic exchange interactions.[3,4] For the Fe^{II} complexes, the spin transition $^1A_1 \Leftrightarrow {}^5T_2$ and the thermochromism can be observed.[5—7] 4*H*-1,2,4-Triazol-4-amines, unlike parent 1*H*-1,2,4-triazole, are usually coordinated to metal atoms as bidentate-bridging ligands through the N(1) and N(2) atoms of the triazole ring.[2] The introduction of a heterocyclic substituent containing the pyridine-type nitrogen atom into the triazole ring (Tri) can lead to a substantial change in the structure of the resulting complex due to the appearance of additional coordination sites. In addition, the presence of functional groups in the heterocyclic substituent can impart new properties to the complexes or mutually enhance their properties (synergism). In the last two decades, researchers focussed on the synthesis and investigation of transition metal coordination compounds containing 3,5-bis(2-pyridyl)-1,2,4-triazol-4-amine (**1**) as the ligand.[8,9]



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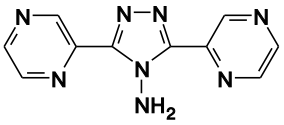

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Triazol-4-amines containing other azinyl groups as substituents in the triazole ring are of great interest in view of the extension of the range of structurally related ligands. However, only the synthesis of 3,5-di(pyrazin-2-yl)-1,2,4-triazol-4-amine (**2**) was documented.[10] Other ligands of this type are unknown. We synthesized for the first time two compounds belonging to this class, *viz.*, 3,5-di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (**3**) and 3,5-bis(4,6-dimethylpyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (**4**), which allowed us to begin studies aimed at synthesizing metal complexes with these ligands. Complexes based on symmetrical dipyrimidinyltriazoles containing mesogenic groups in the pyrimidine rings are of particular interest in view of the design of new multifunctional spin-transition materials, which simultaneously exhibit liquid-crystalline properties.

Known 3,5-diazinyl-4*H*-1,2,4-triazol-4-amines were synthesized according to a standard procedure involving

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1760—1768, September, 2010.

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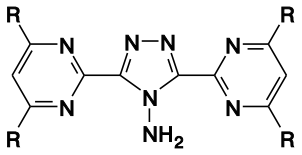


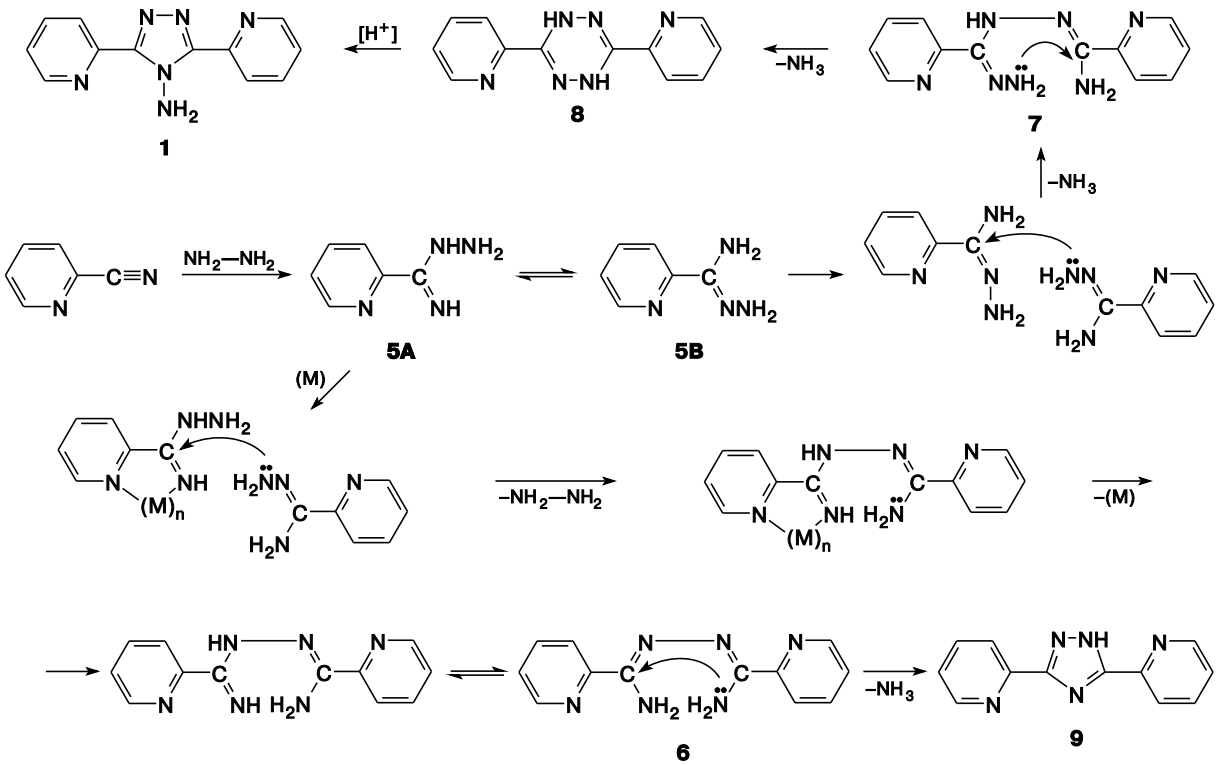
3, 4

R = H (**3**), Me (**4**)

the reaction of heteroaromatic carbonitriles with hydrazine.[10—14] Based on investigations of this reaction for a series of aromatic substrates, suggestions were made about the structures of certain intermediates in the route of successive chemical transformations, and the general hypothetical scheme was proposed based on the observations on the influence of the components of the reaction medium and the reaction conditions on the formation of particular final products (as an example, Scheme 1 represents the transformations of pyridine-2-carbonitrile).[10—15] The reaction of carbonitrile with hydrazine starts with the formation of arylcarbamidrazone **5**, which, in turn, accumulates in the reaction medium and begins to regioselectively react with different reaction centers of the starting compounds and products and, depending on the reaction conditions and the chemical nature of these compounds, can give bis(carbamidine) **6** and/or adduct **7**. These products can undergo further transformations to form 3,6-bis-(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine (**8**), 3,5-bis(2-pyridyl)-4*H*-1,2,4-triazol-4-amine (**1**), or 3,5-bis(2-pyridyl)-1*H*-1,2,4-triazole (**9**) as the final products.

In the case of the pyridine, pyrazine, and related derivatives, the above-mentioned transformations can be significantly influenced by the specific effects of solvation and complexation with metal ions. Thus, using pyridine-2-carbonitrile as an example, it was shown that the reactions with hydrazine afford dihydrotetrazines **8** as the major products, whereas the alternative pathway giving triazole **9** requires the presence of metal ions M^{2+} in the reaction mixture.[14,15] To explain this fact, the reactivity of intermediate pyridine-2-carbamidrazone (**5**) was investigated, and the conclusion was made about the favorable formation of the chelate M^{II} complex for tautomer **5A** (compared to tautomer **5B**). The complexation leads to an increase in the electrophilicity of the C=N bond in the substrate, thus facilitating the attack on the second carbamidrazone molecule. The subsequent elimination of the hydrazine molecule from the adduct affords 1,2-bis-(aminomethylidene)hydrazine **6**. In the absence of M^{2+} ions in the reaction mixture, tautomer **5B** is the major species in the medium, and, consequently, adduct **7** can undergo cyclization accompanied by the elimination of two ammonia molecules and the formation of dihydrotetrazine **8**.[14,15] The subsequent transformations of bis-(aminomethylidene)hydrazines into triazoles[16,17] and of

Scheme 1



dihydrotetrazines into *N*-aminotriazoles[10–12] have been studied in detail.

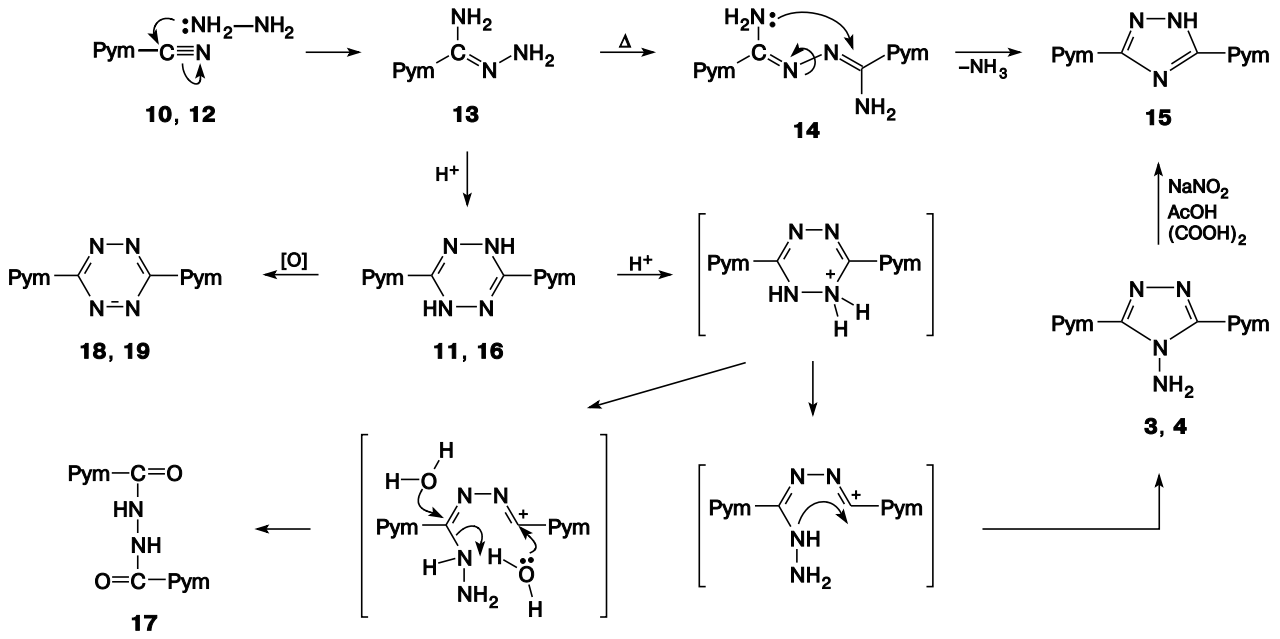
In these investigations, different approaches were used for the synthesis of disubstituted triazolamines, including those containing the pyrazinyl and pyridyl groups, either by the two-step procedure with the isolation (or without the isolation) of the corresponding dihydrotetrazines, which can be then rearranged into the target compounds using homogeneous acid catalysis,[11–13] or according to the one-pot procedure in neutral solvents at higher temperatures.[10,14]

The methods developed previously for the synthesis of pyridine analogs, which prevent the complexation with metals, seemed to be the most convenient for the synthesis of pyrimidinyl derivatives of 1,2,4-triazol-4-amine and 1,2,4,5-tetrazine. Nevertheless, taking into account the higher electrophilicity of the cyano group at position 2 of the pyrimidine ring compared to the cyano derivatives of pyridine and pyrazine, the possible deviations in the above-mentioned transformation, including those associated with the transformation of the pyrimidine ring (Pym), cannot be ruled out. Hence, we initially investigated the behavior of 4,6-dimethylpyrimidine-2-carbonitrile (**10**) in the reaction with hydrazine hydrate under different conditions, because the presence of two electron-releasing methyl groups in the even positions of the pyrimidine ring partially compensates the electron-withdrawing effect of the second nitrogen atom. Hence, the reactivity of this substrate should not be substantially different from that of pyridine-2-carbonitrile derivatives.

We examined several methods for the synthesis of the target pyrimidinyl-substituted triazolamines with the aim of choosing the best procedure. One method was based on the one-step approach, which has been developed for the synthesis of pyridyl derivatives of triazolamine and which involves the reaction of pyridinecarbonitrile with hydrazine dihydrochloride in a solution of hydrazine hydrate.[10] In another method, the same reaction was carried out in two steps. Initially, the reaction of carbonitrile **10** with hydrazine hydrate performed under mild conditions gave 3,6-disubstituted 1,4-dihydrotetrazine **11**, which was rearranged into 3,5-disubstituted triazolamine **4** without the isolation and purification (Scheme 2). In the third method, the reaction was divided into two steps with the isolation of individual dihydrotetrazine **11** followed by its transformation into triazolamine **4** by analogy with the procedure described previously.[11] A comparison of all three methods for the synthesis of these compounds did not reveal advantages of a particular method because the yields of the target product **4** were equal and were at most 25%. In the above-described syntheses, we used 98% hydrazine hydrate.

Unsubstituted pyrimidine-2-carbonitrile (**12**) exhibited the most complex behavior in the reaction with hydrazine (see Scheme 2). Depending on the temperature conditions, the order of the mixing of the reagents, and their ratio, the reaction affords different series of products. Our observations are consistent with the conclusions drawn in the study,[18] where the experimental conditions of the synthesis of carbamidrazones in a series of substituted

Scheme 2



Pym is pyrimidin-2-yl (**3**, **12**—**18**), 4,6-dimethylpyrimidin-2-yl (**4**, **10**, **11**, **19**).

pyridines were varied. Thus, we isolated pyrimidine-2-carbamidrazone (**13**) in good yield in the reaction of carbonitrile **12** with a large excess of hydrazine hydrate at room temperature, as opposed to the results of the study,[19] where the condensation was performed in 96% ethanol and gave this compound in a yield of at most 6%. Such a low yield is apparently attributed to the high affinity of amidrazone **13** for water as a result of the formation of intramolecular hydrogen bonds between water molecules and the endocyclic nitrogen atoms of the pyrimidine ring and the NH_2 groups of the amidrazone moiety. The latter fact indicates that the extraction of this compound from aqueous solutions by organic solvents is inefficient and could lead to a substantial loss of the product in the experiment.[19] The characteristic structural feature of amidrazone **13** is that its ^{1}H NMR spectrum shows two closely spaced broad signals of NH_2 groups at δ 5.5—5.6.[20]

We found that carbamidrazone **13** is the key compound in the chain of further chemical transformations. The amidrazone molecules have the amphiphilic reactivity and can either react with the starting carbonitrile to give 1,2-bis(aminomethylidene)hydrazines or undergo dimerization accompanied by the elimination of two ammonia molecules and the formation of disubstituted dihydrotetrazines.[10,14—16] Among the known bis(aminomethylidene)-hydrazines, the derivative containing the 2-pyridyl group[21,22] is most closely related to the compounds under study. Other heterocyclic derivatives remained unknown until recent years, and only in the recent past the X-ray diffraction data for pyrimidinyl analog **14** prepared as dihydrate have been published;[23] however, details of the synthesis and complete characteristics of this compound were not published. We succeeded in isolating compound **14** in 35% yield. Compound **14** was characterized analytically and spectroscopically and was studied by powder X-ray diffraction. The results of the powder X-ray diffraction study are in complete agreement with the single-crystal X-ray diffraction data.[23] In addition, we transformed compound **13** into triazole derivative **15** and dihydrotetrazine derivative **16** by the thermolysis of a dry sample and using homogeneous acid catalysis (see Scheme 2).

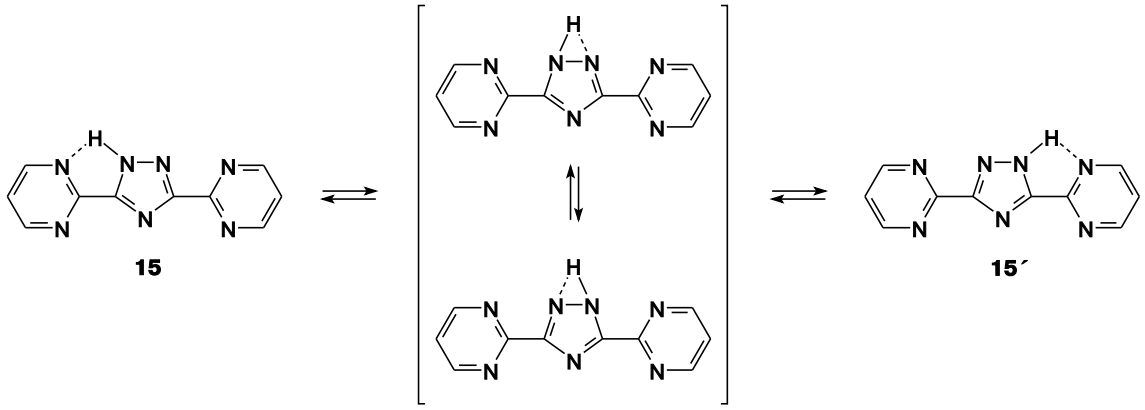
We found that the heating of pyrimidinecarbamidrazone **13** at temperatures above the melting point leads to the elimination of ammonia and affords 1,2-di[amino(pyrimidin-2-yl)methylidene]hydrazine, $C_{10}H_{10}N_8$ (**14**), containing an impurity (TLC data and ^{1}H and ^{13}C NMR spectra). The latter gives a peak at *m/z* 225 in the mass spectrum corresponding to the molecular formula $C_{10}H_7N_7$ for 3,5-di(pyrimidin-2-yl)-1*H*-1,2,4-triazole (**15**). In addition, the mass spectrum of the mixture has the most intense peak at *m/z* 197, relatively intense peaks at *m/z* 198 and 171, and a peak at *m/z* 144 characteristic of compound **15**. The ^{1}H NMR spectrum of the mixture shows a double set of triplets for the H(5) atom and doublets for the H(4) and H(6) atoms of the pyrimidine rings. The ^{13}C NMR spectrum also has a double set of signals for the C(5), C(4), and C(6) atoms, whose chemical shifts are exactly equal to the shifts observed for individual compounds **14** and **15** (see the Experimental section). According to the spectroscopic data, both compounds were present in the mixture in comparable amounts, with compound **14** slightly predominating. Compound **14** is the precursor giving triazole **15**. The similar thermal heterocyclization of aryl analogs of compound **14** has been observed previously.[17]

A sample of individual di(pyrimidin-2-yl)triazole **15** was synthesized by the diazotization of triazolamine **3** in the presence of oxalic acid. This compound is characterized by a very broad NH signal shifted to 14—15 ppm in the ^{1}H NMR spectrum (in DMSO-d_6), which is consistent with the data for 1,2,4-triazole[24] and its 3,5-diphenyl derivative.[25] It should be noted that the NH signal of di(pyrimidin-2-yl)triazole **15**, which is present in a mixture with bis(aminomethylidene)hydrazine **14**, is substantially broadened (up to 11—14 ppm) and is not observed at all in the case of the deuterium exchange in the presence of CD_3OD. The substantial broadening of the NH signal of compound **15** is apparently attributed to the fact that it exists mainly as the 1*H* tautomer (this fact was proved for the majority of 1,2,4-triazoles in the studies[24,26,27]) and to the intramolecular migration of the proton between the adjacent nitrogen atoms of the strongly solvated triazole and pyrimidine rings in degenerate structures **15** and **15′** (Scheme 3).

The transformations of dihydrotetrazines into 4-aminotriazoles are generally carried out by refluxing solutions of dihydrotetrazines in dilute mineral acids. We found that in the case of the dimethylpyrimidyl derivative of dihydrotetrazine **11**, triazolamine **4** that is formed under these conditions can be isolated in the rather pure form in moderate yield. Under these conditions, the corresponding derivative of dihydrotetrazine **16**, which does not contain methyl groups, gives di(pyrimidin-2-yl)triazolamine **3** along with 1,2-di(pyrimidin-2-yl)hydrazine (**17**) as the minor product in 14% yield. Apparently, the formation of the latter product occurs in the step of the opening of the protonated dihydrotetrazine ring (Tetr) in accordance with the proposed mechanism of recyclization.[10,11] The repeated cyclization leading to the formation of a new C—N bond in the triazole molecule is accompanied by the side reaction resulting in the addition of water molecules at two C-electrophilic centers of the substrate and the elimination of the hydrazine molecule (see Scheme 2).

1,2-Di(pyrimidin-2-yl)hydrazine (**17**) was identified in the mixture after chromatography and recrystallization of the product, which allowed us to increase the percentage of this component in the mixture to ~30%. Further attempts to purify and isolate this compound in the pure form failed. The structure of this compound was assigned based on the comparison of the IR, NMR, and mass spec-

Scheme 3



tra of the mixture with the spectra of individual di-(pyrimidin-2-yl)triazolamine **3**. The IR spectrum of the mixture shows two characteristic C=O stretching bands of the —NH(C=O)—NH(C=O)— moiety at 1678—1710 cm^{-1}. In the ^1H NMR spectrum, this moiety is manifested as a two-proton signal shifted downfield compared to the NH_2 signal of triazolamine **3** (*cf.* the published data[28,29] for symmetrical dipyridylhydrazines). The molecular formula $C_{10}H_8N_6O_2$ determined from the high-resolution mass spectrum is also consistent with the proposed structure of the by-product.

The purification of triazolamine **3** from the impurity of dipyrimidinylhydrazine **17** that is difficult to separate is a serious problem. Hence, the latter procedure is worse than the previous method. The best result was obtained when the recyclization of dihydrotetrazine **16** to triazolamine **3** was carried out by heating in THF in the presence of catalytic amounts of hydrazine dihydrochloride.

The structures of triazolamines **3** and **4** and of dihydrotetrazines **11** and **16** were determined based on the NMR spectroscopic and mass spectrometric data with the use of the known generalizations for structurally related compounds.[10,12] The single-crystal X-ray diffraction study of triazolamine **3** (Fig. 1) showed that two crystallographically independent molecules have the same planar geometry (the rms deviations of the atoms are 0.104 and 0.074 Å), which is similar to that of pyridyl analog **1**.[30] The nonplanar amino groups are linked to the nitrogen atoms of the pyrimidine rings by intramolecular N—H...N hydrogen bonds (H...N, 2.11(2)—2.28(2) Å; N—H...N, 122(2)—129(1)°). In the crystals, the molecules are linked by C—H...N hydrogen bonds (H...N, 2.40(2)—2.54(2) Å; C—H...N, 165(1)—176(1)°) into planar layers parallel to the (*a*—*c*,*b*) plane. Among interlayer interactions, let us mention N—H...N hydrogen bonds (2.55(2) Å, 137°) and π-stacking interactions of the molecules with the centroid—centroid distances of 3.5780(9)—3.9330(9) Å.

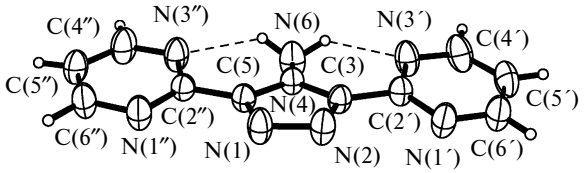


Fig. 1. Molecular structure of **3** with nonhydrogen atoms represented as displacement ellipsoids drawn at the 50% probability level (only one crystallographically independent molecule is shown).

Investigations of the characteristic features of the complexation of the ligands, which we have synthesized, with transition metal salts are currently underway. In the present study, we synthesized the first of these compounds, *viz.*, the Fe^{II} complex with bis(dimethylpyrimidinyl)triazolamine **3**.

In summary, we carried out successive transformations of pyrimidine-2-carbonitrile **12** and its 4,6-dimethyl-substituted derivative **10** into pyrimidinyl-substituted 1,4-dihydro-1,2,4,5-tetrazines **16** and **11** and 1,2,4-triazol-4-amines **3** and **4**, respectively. Pyrimidine-2-carbamidrazone **13** and the corresponding 1,2-bis(aminomethylidene)hydrazines **14**, which are the key intermediates in the route to trinuclear polynitrogen heterocyclic compounds, were isolated and characterized for the first time. These compounds are potential polydentate ligands. Tetrazine derivatives **18** and **19** were synthesized by the oxidative dehydrogenation of di(pyrimidin-2-yl)dihydrotetrazines **11** and **16**, respectively.

Experimental

The IR spectra were recorded on a Bruker Vector 22 spectrophotometer in KBr pellets. The IR spectrum of the Fe^{II} complex with triazolamine **3** was measured on a BOMEM MB-102 spectrophotometer in the region of 200—400 cm^{-1}. The UV-Vis spectra of solutions of tetrazine dyes in $CHCl_3$ were recorded on

a Specord M-40 spectrophotometer. The mass spectra were obtained on a DFS instrument (EI, 70 eV, direct inlet). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300 and Bruker AV-400 spectrometers with the use of the signals of the solvents as the internal standards: DMSO-d_6, (δ_H 2.50, δ_C 39.50) for compounds **3**, **4**, **11**, and **13—17** and $CDCl_3$ (δ_H 7.24, δ_C 76.90) for compounds **18** and **19**. The microanalysis was carried out on a Carlo Erba analyzer. The water content in the Fe^{II} complex with triazolamine **3** was determined gravimetrically based on the weight loss after storage of the samples *in vacuo*. The purity of the compounds was checked by TLC on Silufol UV-254 plates with the use of an EtOAc—EtOH—concentrated NH_4OH mixture (2 : 2 : 1) as the eluent; the spots were visualized under UV light.

Reaction of 4,6-dimethylpyrimidine-2-carbonitrile with hydrazine hydrate

3,6-Bis(4,6-dimethylpyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (11). A mixture of carbonitrile **10** (2.66 g, 20 mmol) and hydrazine hydrate (2 mL, 2.1 g, 42 mmol) was heated at 90 °C under argon for 3.5 h and then cooled to room temperature. Ethanol (5 mL) and water (5 mL) were added to the reaction mixture, and the mixture was kept in a refrigerator. The orange product was filtered off and successively washed with water, 50% ethanol (2×0.5 mL), and diethyl ether. The product was crystallized from ethanol and dried *in vacuo*. The yield was 1.20 g (42%), m.p. 253—255 °C (EtOH), R_f 0.90. Found (%): C, 56.87; H, 5.74; N, 37.90. $C_{14}H_{16}N_8$. Calculated (%): C, 56.74; H, 5.44; N, 37.81. MS, *m/z* (I_{rel} (%)): 296 $[M]^+$ (63), 134 $[C_7H_8N_3]^+$ (100), 108 $[C_6H_8N_2]^+$ (11), 107 $[C_7H_8N_3—HCN]^+$ (15), 67 (21). High-resolution MS, found: *m/z* 296.1496 $[M]^+$. $C_{14}H_{16}N_8$. Calculated: M = 296.1498. IR, ν/cm^{-1}: 3366 (NH), 2919, 2850 (Me), 1594, 1540, 1446, 1344 (Pym). ^{1}H NMR, δ: 2.48 (s, 12 H, 4 Me); 7.37 (s, 2 H, H(5) 2 Pym); 8.89 (s, 2 H, 2 NH). ^{13}C NMR, δ: 23.53 (Me); 120.74 (C(5) Pym); 145.19 (C(3), C(5) Tetr); 155.20 (C(2) Pym); 167.04 (C(4), C(6) Pym).

3,5-Bis(4,6-dimethylpyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (4). ***A.*** A mixture of pyrimidinecarbonitrile **10** (1.33 g, 10 mmol), hydrazine hydrate (1.5 mL, 1.6 g, 32 mmol), hydrazine dihydrochloride (1.05 g, 10 mmol), and ethylene glycol (5 mL) was heated at 130—140 °C under argon for 3 h until the elimination of ammonia ceased. Then the reaction mixture was cooled to room temperature, and water (20 mL) was added. After storage for many hours in a refrigerator, the almost colorless precipitate that formed was filtered off and washed with water (2×0.5 mL). The product was recrystallized from ethanol and dried. The yield was 0.38 g (25%), m.p. 266.5—267.5 °C, R_f 0.80. Found (%): C, 56.74; H, 5.54; N, 37.74. $C_{14}H_{16}N_8$. Calculated (%): C, 56.74; H, 5.44; N, 37.81. MS, *m/z* (I_{rel} (%)): 296 $[M]^+$ (100), 201 (4), 134 $[C_7H_8N_3]^+$ (70), 108 $[C_6H_8N_2]^+$ (32), 107 $[C_7H_8N_3—HCN]^+$ (21), 67 (23). IR, ν/cm^{-1}: 3291 (NH_2), 2956, 2920 (Me), 1595, 1558, 1536, 1440 (Pym). ^{1}H NMR, δ: 2.55 (s, 12 H, 4 Me); 7.42 (s, 2 H, H(5) 2 Pym); 7.84 (s, 2 H, NH_2). ^{13}C NMR, δ: 23.44 (Me); 120.13 (C(5) Pym); 148.08 (C(3), C(5) Tri); 154.85 (C(2) Pym); 167.13 (C(4), C(6) Pym).

B. A solution of hydrazine hydrate (3.0 mL, 60 mmol) in ethylene glycol (10 mL) was added dropwise with stirring to a mixture of pyrimidinecarbonitrile **10** (4.0 g, 30 mmol), hydrazine dihydrochloride (2.1 g, 20 mmol), and ethylene glycol (5 mL). The reaction mixture was heated at 100 °C under argon for 1.5 h. A 2 *M* HCl solution (5 mL) was added to the voluminous dark-orange product, and the resulting red-brown solution was refluxed for 20 min until the solution became colorless. The pale-yellow solution was brought to pH 9 by adding 2 *M* NH_4OH, concentrated *in vacuo* to 5 mL, and extracted with $CHCl_3$. The extract was concentrated, and the residue was recrystallized from ethanol. The yield of triazolamine **4** was 1.1 g (25%), m.p. 264.5—266 °C.

C. A solution of dihydrotetrazine **11** (0.75 g, 2.5 mmol) in 2 *M* HCl (7 mL) was heated under slight reflux in an argon atmosphere for 0.5 h until the solution became colorless. The pale-yellow solution was concentrated *in vacuo* to 3 mL, ammonia was added to pH 9, and the solution was again concentrated and extracted with $CHCl_3$. The extract was concentrated, and the residue was recrystallized from ethanol. The yield of triazolamine **4** was 0.42 g (56%), m.p. 262—266 °C.

Reaction of pyrimidine-2-carbonitrile with hydrazine hydrate

Pyrimidine-2-carbamidrazone (13). A solution of pyrimidine-2-carbonitrile (**12**) (0.42 g, 4 mmol) in THF (1.5 mL) was added dropwise with stirring to hydrazine hydrate (2 mL, 2.1 g, 42 mmol). The reaction mixture was stirred at room temperature for 4 h and concentrated *in vacuo*. The oily viscous residue was dissolved in anhydrous ethanol (5 mL) and again concentrated *in vacuo*. This operation was repeated two times. The residue was triturated with benzene (5 mL), after which the slow crystallization started. After 10 h, the product was pressed on the filter, washed with benzene and then with hexane, and dried on the filter. The yield was 0.52 g (90%), m.p. 98—101 °C (in a capillary) (*cf.* lit. data[19]: m.p. 109—110 °C), R_f 0.72. MS, *m/z* (I_{rel} (%)): 137 $[M]^+$ (100), 109 $[M - N_2]^+$ (51), 108 $[M - CHNH_2]^+$ (48), 106 (51), 94 (6), 82 (6), 81 (49), 80 $[C_4H_4N_2]^+$ (43), 79 $[C_4H_3N_2]^+$ (52), 78 (12), 58 (7), 55 (7), 54 (26), 53 (24), 52 (20). High-resolution MS, found: *m/z* 137.0698 $[M]^+$. $C_5H_7N_5$. Calculated: M = 137.0701. IR, ν/cm^{-1}: 3434, 3327, 3195 (NH_2), 1642 (N—NH_2, C=N), 1561, 1449, 1377 (Pym). ^{1}H NMR, δ: 5.55 (br.s, 2 H, =NNH_2); 5.65 (br.s, 2 H, =CNH_2); 7.39 (t, 1 H, H(5) Pym, ^3J = 4.8 Hz); 8.77 (d, 2 H, H(4), H(6) Pym, ^3J = 4.8 Hz). ^{13}C NMR, δ: 120.02 (C(5) Pym); 141.65 (N=C—NH_2); 156.99 (C(4), C(6) Pym); 159.14 (C(2) Pym).

1,2-Bis[amino(pyrimidin-2-yl)methylidene]hydrazine (14). ***A.*** A mixture of pyrimidinecarbamidrazone **13** (85 mg, 0.6 mmol), ethyl formate (50 mg, 0.7 mmol), and benzene (2.5 mL) was refluxed for 3 h. Then the reaction mixture was concentrated *in vacuo*, ethanol (1 mL) was added, and the reaction mixture was brought to reflux and kept in a refrigerator. The precipitate that formed was filtered off, washed with 50% ethanol, and dried *in vacuo*. The product, which was obtained in a yield of 70 mg, was purified by crystallization from boiling ethanol with the gradual addition of benzene until the solution became turbid. After storage of the solution in a refrigerator, the yellow product that precipitated was separated, washed with benzene, and dried *in vacuo*. The yield was 31 mg (35%), m.p. 200—205 °C (in a capillary). After cooling, the melt crystallized and again melted at 303—305 °C, R_f 0.75. Found (%): C, 42.08; H, 4.87; N, 38.80. $C_{10}H_{10}N_8 \cdot 2.5\,H_2O$. Calculated (%): C, 41.81; H, 5.26;

N, 39.01. MS, *m/z* (I_{rel} (%)): 242 $[M]^+$ (40), 227 (14), 226 (100), 225 (46), 197 (45), 171 (10), 163 (90), 108 (21), 106 (25), 81 (25), 80 $[C_4H_4N_2]^+$ (35), 79 $[C_4H_3N_2]^+$ (33), 53 (18), 52 (10). High-resolution MS, found: *m/z* 242.1026 $[M]^+$. $C_{10}H_{10}N_8$. Calculated: M = 242.1028. IR, ν/cm^{-1}: 3431, 3357, 3274 (NH_2), 1619 (C=N), 1560, 1427, 1372 (Pym). ^{1}H NMR, δ: 6.63 (br.s, 4 H, 2 NH_2); 7.59 (t, 2 H, H(5) 2 Pym, ^3J = 4.7 Hz); 8.93 (d, 4 H, H(4), H(6) 2 Pym, ^3J = 4.7 Hz). ^{13}C NMR, δ: 121.62 (C(5) Pym); 152.48 (C(=N)NH_2); 157.74 (C(4), C(6) Pym); 158.86 (C(2) Pym).

B. Pyrimidinecarbamidrazone **13** (140 mg, 1 mmol) was heated to a temperature above 200 °C until the elimination of ammonia started. Then the reaction mixture was heated *in vacuo* until the elimination of ammonia ceased. The residue was treated with boiling ethanol and filtered. The filtrate was concentrated to 1 mL, and then benzene (3 mL) and hexane (3 mL) were added. After storage of the reaction mixture in a refrigerator, the precipitate was filtered off and dissolved under reflux in $CHCl_3$ (30 mL). The solution was passed through a 2 cm layer of Al_2O_3, the eluate was concentrated, and the residue was recrystallized from a THF—ethanol mixture. The product was obtained in a yield of 43 mg (35%) as a mixture of 1,2-bis[amino(pyrimidin-2-yl)methylidene]hydrazine (**14**) and 3,5-di(pyrimidin-2-yl)-1*H*-1,2,4-triazole (**15**) in a ratio of 1.5 : 1, m.p. ~200 °C. Upon cooling, the melt crystallized and melted at 301—303 °C; R_f 0.75 (**14**) and 0.29 (**15**). MS, *m/z* (I_{rel} (%)): 242 $[M]^+$ (34) (**14**), 226 (100), 225 $[M]^+$ (66) (**15**), 197 (92), 171 (22) (**15**), 163 (76), 144 (15) (**15**), 108 (21), 106 (29), 81 (21), 80 $[C_4H_4N_2]^+$ (39), 79 $[C_4H_3N_2]^+$ (34). ^{1}H NMR, δ: 6.68 (br.s, 4 H, 2 NH_2 (**14**)); 7.60 (t, 2 H, H(5) 2 Pym (**14**), ^3J = 4.7 Hz); 7.62 (t, 2 H, H(5) 2 Pym (**15**), ^3J = 4.8 Hz); 8.94 (d, 4 H, H(4), H(6) 2 Pym (**14**), ^3J = 4.7 Hz); 9.00 (d, 4 H, H(4), H(6) 2 Pym (**15**), ^3J = 4.8 Hz). ^{13}C NMR, δ: 121.66 (C(5) Pym (**14** + **15**)); 152.50 (C(=N)NH_2 (**14**)); 157.39 (C(4), C(6) Pym (**14**) + C(3), C(5) Tri (**15**)); 157.95 (C(4), C(6) Pym (**15**)); 158.86 (C(2) Pym (**14** + **15**)).

3,6-Di(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (16). Hydrazine hydrate (6 mL, 6.12 g, 122 mmol) was added dropwise with stirring to a suspension of pyrimidinecarbonitrile **12** (6.3 g, 60 mmol) in THF (3 mL). The reaction mixture was kept at room temperature for 20 min and then heated at 90—95 °C for 4.5 h, after which the elimination of ammonia ceased, the mixture hardened, and a voluminous orange precipitate formed. After cooling of the reaction mixture, the precipitate was pressed on the filter, washed with 50% methanol (1 mL) and then twice with methanol (2×0.5 mL), and dried first on the filter and then at 100 °C *in vacuo* over P_2O_5. The yield was 3.95 g (55%), m.p. 215—218 °C (EtOH), R_f 0.68. Found (%): C, 48.82; H, 3.41; N, 45.41. $C_{10}H_8N_8 \cdot 0.5\,H_2O$. Calculated (%): C, 48.19; H, 3.64; N, 44.96. MS, *m/z* (I_{rel} (%)): 240 $[M]^+$ (98), 106 (100), 80 $[C_4H_4N_2]^+$ (27), 79 $[C_4H_3N_2]^+$ (60), 53 (39), 52 (17). High-resolution MS, found: *m/z* 240.0863 $[M]^+$. $C_{10}H_8N_8$. Calculated: M = 240.0872. IR, ν/cm^{-1}: 3471 and 3326 (NH), 1632 (C=N), 1567, 1452, 1421, 1354 (Pym). ^{1}H NMR, δ: 7.62 (t, 2 H, H(5) 2 Pym, ^3J = 4.8 Hz); 8.93 (d, 4 H, H(4), H(6) 2 Pym, ^3J = 4.8 Hz); 9.05 (s, 2 H, 2 NH Tetr). ^{13}C NMR, δ: 122.20 (C(5) Pym); 145.15 (C(3), C(6) Tetr); 155.82 (C(2) Pym); 157.74 (C(4), C(6) Pym).

The filtrates were combined, the product was extracted with $CHCl_3$, the extract was concentrated *in vacuo*, the residue was triturated with methanol (2 mL), and the mixture was kept in a refrigerator overnight. The straw-yellow precipitate that formed was filtered off, washed with methanol, and dried on the filter. The product was recrystallized from ethanol in the presence of DMF and dried *in vacuo* at 100 °C. The yield of 3,5-di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (**3**), which is identical with that described below, was 0.55 g (7%).

3,5-Di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (3). ***A.*** Hydrazine hydrate (1.5 g, 30 mmol) was added dropwise with stirring to a mixture of pyrimidinecarbonitrile **12** (1.05 g, 10 mmol), hydrazine dihydrochloride (1.05 g, 10 mmol), and methyl cellosolve (5 mL). The reaction mixture slightly warmed up, the precipitate gradually dissolved, and the color of the solution became more intense. The temperature was raised until the elimination of ammonia started. After 0.5 h, the temperature of the bath was brought to 115 °C, and the reaction mixture was kept at this temperature for 6 h. After the completion of the reaction, the mixture was kept in a refrigerator for 16 h. The precipitate that formed was pressed on the filter, repeatedly washed with a minimum amount of anhydrous ethanol, treated with concentrated NH_4OH, and concentrated to dryness. Then the precipitate was refluxed in ethanol (50 mL) in the presence of activated carbon. The solution was filtered, and the filtrate was concentrated *in vacuo* to 15 mL and kept in a refrigerator. The crystalline precipitate that formed was filtered off, washed with anhydrous ethanol, and dried *in vacuo* at 100 °C. The yield was 0.87 g (72%), m.p. 257—259 °C (in a capillary); R_f 0.55. Found (%): C, 49.75; H, 3.37; N, 46.59. $C_{10}H_8N_8$. Calculated (%): C, 50.00; H, 3.36; N, 46.64. MS, *m/z* (I_{rel} (%)): 240 $[M]^+$ (100), 106 (46), 79 (32), 53 (8). High-resolution MS, found: *m/z* 240.0863 $[M]^+$. $C_{10}H_8N_8$. Calculated: M = 240.0872. IR, ν/cm^{-1}: 3326 (NH_2), 1566, 1452 и 1421 (Pym). ^{1}H NMR, δ: 7.54 (s, 2 H, NH_2); 7.69 (t, 2 H, H(5) 2 Pym, ^3J = 4.8 Hz); 9.07 (d, 4 H, H(4), H(6) 2 Pym, ^3J = 4.8 Hz). ^{13}C NMR, δ: 121.72 (C(5) Pym); 149.00 (C(3), C(5) Tri); 155.50 (C(2) Pym); 157.94 (C(4), C(6) Pym).

B. A suspension of 3,6-di(pyrimidin-2-yl)-1,4-dihydrotetrazine **16** (0.69 g, 2.5 mmol) in 2 *M* HCl (6 mL) was carefully heated with stirring and a gradual rise of the temperature. After the dissolution of the precipitate, the temperature was raised to reflux. After ~30 min, the reaction solution, whose color changed from dark-red to straw-yellow, was concentrated *in vacuo*, the residue was treated with concentrated NH_4OH, and the mixture was again concentrated. The product was extracted with boiling ethanol. The extract was concentrated to 3 mL and kept in a refrigerator. After the separation of the precipitate, the filtrate was concentrated to one half of the initial volume, and an additional amount of the product was obtained. The total yield was 0.43 g (69%), m.p. 235—245 °C. According to the spectroscopic data, the product consisted of 3,5-di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (**3**) and 1,2-di(pyrimidin-2-yl)hydrazine (**17**) in a ratio of ~4 : 1 and other minor compounds.

To purify the mixture from the minor compounds, 0.30 g of the mixture was refluxed with ethyl acetate. The resulting solution was passed through a 3-cm layer of silica gel. After the column chromatography, the major fraction was gradually concentrated until the crystallization started. After the formation of a precipitate of triazolamine **3** (0.06 g), the mother liquor was carefully decanted and kept at room temperature and then in a refrigerator. The white fine-crystalline precipitate that slowly formed was filtered off, washed with ethyl acetate, and dried *in vacuo*. A mixture (0.14 g) of triazolamine **3** and di(pyrimidinecarbonyl)hydrazine **17** in the **3**/**17** ratio of ~2 : 1 was ob-

tained, m.p. 275—278 °C. MS, *m/z* (I_{rel} (%)): 244 $[M]^+$ (37) (**17**), 240 $[M]^+$ (78) (**3**), 165 (10), 109 (15) (**17**), 107 (33) (**17**), 106 (34) (**3**), 81 (31), 80 (52), 79 $[C_4H_3N_2]^+$ (100), 53 (44), 52 (18). High-resolution MS, found: *m/z* 244.0698 $[M]^+$, $C_{10}H_8N_6O_2$ and 240.0877 $[M]^+$, $C_{10}H_8N_8$. Calculated: M = 244.0708 (**17**) and M = 240.0872 (**3**). IR of the mixture, ν/cm^{-1}: 3405, 3316, and 3139 (NH, NH_2), 1710 and 1678 (C=O), 1565, 1424, and 1386 (Pym). ^{1}H NMR, δ: 7.54 (s, 2 H, NH_2, (**3**)); 7.69 (t, 2 H, H(5) 2 Pym, **3**, ^3J = 4.9 Hz); 7.75 (t, 2 H, H(5) 2 Pym, **17**, ^3J = 4.9 Hz); 9.02 (d, 4 H, H(4), H(6) 2 Pym, **17**, ^3J = 4.9 Hz); 9.07 (d, 4 H, H(4), H(6) 2 Pym, **3**, ^3J = 4.9 Hz); 10.87 (br.s, 2 H, NH—NH, **17**). ^{13}C NMR, δ: 121.69 (C(5) Pym, **3**); 123.46 (C(5) Pym, **17**; 148.98 (C(3), C(5) Tri, **3**); 155.48 (C(2) Pym, (**3**)); 157.37 (C(2) Pym, **17**); 157.82 (C(4), C(6) Pym, **17**); 157.86 (C(4), C(6) Pym, **3**); 161.44 (C=O, **17**).

3,5-Di(pyrimidin-2-yl)-1*H*-1,2,4-triazole (15). A solution of $NaNO_2$ (0.14 g, 2 mmol) in water (0.3 mL) was added dropwise with stirring to a solution of triazolamine **3** (0.12 g, 0.5 mmol) in a mixture of oxalic acid (0.27 g, 3 mmol), acetic acid (0.6 mL), and water (0.6 mL). The reaction mixture was stirred for 0.5 h, after which the precipitate that formed was filtered off and washed with water. Then 2 *M* NH_4OH was added to the precipitate, and the mixture was extracted with chloroform. The extract was concentrated, and the residue was crystallized from anhydrous ethanol. After storage in a refrigerator for 3 days, the colorless fine-crystalline precipitate was filtered off and dried *in vacuo* at 100 °C. The yield was 0.04 g (35%), m.p. 299—302 °C; R_f 0.27. Found (%): C, 52.86; H, 3.22; N, 43.77. $C_{10}H_7N_7$. Calculated (%): C, 53.33; H, 3.13; N, 43.54. MS, *m/z* (I_{rel} (%)): 225 $[M]^+$ (90), 197 (100), 196 (33), 171 (32), 144 (18), 106 (15), 79 (21), 65 (13). High-resolution MS, found: *m/z* 225.0760 $[M]^+$. $C_{10}H_7N_7$. Calculated: M = 225.0763. IR, ν/cm^{-1}: 3432 (NH), 1567, 1509, 1451, 1429, 1410, 1391 и 1376 (Pym). ^{1}H NMR, δ: 7.62 (t, 2 H, H(5) 2 Pym, ^3J = 4.9 Hz); 9.00 (d, 4 H, H(4), H(6) 2 Pym, ^3J = 4.9 Hz); 14.90 (br.s, 1 H, NH). ^{13}C NMR, δ: 121.60 (C(5) Pym); 156.69 (C(3), C(5) Tri); 157.97 (C(4), C(6) Pym); 158.37 (C(2) Pym).

3,6-Di(pyrimidin-2-yl)-1,2,4,5-tetrazine (18). A solution of $NaNO_2$ (0.11 g, 1.6 mmol) in water (0.3 mL) was added dropwise with stirring to a cold solution of the substrate, which was prepared by the dissolution of dihydrotetrazine **16** (0.12 g, 0.5 mmol) in acetic acid (2 mL) at 30 °C. The solution immediately turned carmine-violet. After 0.5 h, the precipitate that formed was filtered off, washed with water and ethanol, and dried on the filter. The yield of tetrazine **18*** was 0.04 g (33%), m.p. 274—277 °C. MS, *m/z* (I_{rel} (%)): 238 $[M]^+$ (5), 105 (100), 78 (25), 53 (8), 52 (7). High-resolution MS, found: *m/z* 238.0714 $[M]^+$. $C_{10}H_6N_8$. Calculated: M = 238.0715. UV-Vis, λ_{max}/nm (logε): 260 (4.38), 535 (2.80). IR, ν/cm^{-1}: 3075, 2988, 2920, 1568, 1375, 1168. ^{1}H NMR ($CDCl_3$), δ: 7.61 (t, 2 H, H(5) 2 Pym, ^3J = 4.8 Hz); 9.16 (d, 4 H, H(4), H(6) 2 Pym, ^3J = 4.8 Hz). ^{13}C NMR, δ: 122.61 (C(5) Pym); 158.42 (C(4), C(6) Pym); 159.21 (C(2) Pym); 163.58 (C(3), C(5) Tetr).

3,6-Bis(4,6-dimethylpyrimidin-2-yl)-1,2,4,5-tetrazine (19). A solution of $NaNO_2$ (0.60 g, 10 mmol) in water (2 mL) was added dropwise with stirring to a cold solution of dihydrotetrazine **11** (0.60 g, 2 mmol) in acetic acid (6 mL). The reaction solution immediately turned violet, and the dark-violet fine-crystalline precipitate formed soon afterwards. After 0.5 h, the precipitate was filtered off, washed with ethanol, and dried *in vacuo* at 100 °C. The yield was 0.12 g (70%), m.p. 245—248 °C. Found (%): C, 57.03; H, 4.92; N, 38.32. $C_{14}H_{14}N_8$. Calculated (%): C, 57.13; H, 4.79; N, 38.07. MS, *m/z* (I_{rel} (%)): 294 $[M]^+$ (17), 134 (56), 133 $[C_7H_8N_3—H]^+$ (100), 132 (26), 107 (9), 106 $[C_7H_8N_3—HCN]^+$ (24), 105 (9), 80 (13), 67 (16), 66 (22), 65 (12). UV-Vis, λ_{max}/nm (logε): 267 (4.32), 535 (2.79). IR, ν/cm^{-1}: 2997, 2925, 1595, 1532, 1431, 1389, 1347. ^{1}H NMR ($CDCl_3$), δ: 2.69 (s, 12 H, 4 Me); 7.28 (s, 2 H, H(5) 2 Pym). ^{13}C NMR, δ: 24.11 (Me); 121.58 (C(5) Pym); 158.91 (C(2) Pym); 163.88 (C(3), C(5) Tetr); 168.35 (C(4), C(6) Pym).

Dithiocyanatobis[3,5-di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine]iron monohydrate, $[FeL_2(NCS)_2]\cdot H_2O$. A solution of KNCS (21 mg, 0.22 mmol) in MeOH (1 mL) was added to a solution of $Fe(ClO_4)_2\cdot H_2O$ (32 mg, 0.09 mmol) in MeOH (1 mL) containing an additive of ascorbic acid under argon. The precipitate that formed was filtered off, and the filtrate was added to a solution of triazolamine **3** (43 mg, 0.18 mmol) in MeOH (13 mL). After 15 min, the bright-red precipitate that formed was separated, washed with MeOH, and dried in air. The yield was 46.2 mg (77%). IR, ν/cm^{-1}: 3600—3400 (OH, NH), 2067 (NCS^-), 1580 sh, 1559, 1491 (Pym, Tri), 476 (NCS^-), 253 (Fe—N). Found (%): C, 39.51; H, 2.65; N, 36.48; Fe, 8.13; S, 9.96; H_2O, 3.0. $C_{22}H_{16}FeN_{18}S_2\cdot H_2O$. Calculated (%): C, 39.41; H, 2.71; N, 37.60; Fe, 8.33; S, 9.56; H_2O, 2.7.

X-ray diffraction study of a crystalline sample of 3,5-di(pyrimidin-2-yl)-4*H*-1,2,4-triazol-4-amine (3). A suspension of the complex $[FeL_2(NCS)_2]\cdot H_2O$ (0.1 g) in MeCN (3 mL) in the presence of several drops of DMF was prepared. The slow evaporation of the solvent for two months led to the formation of large well-faceted single crystals of ligand **3** over the layer of the fine-crystalline complex.

The X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer (graphite monochromator, λ(Mo-Kα) = = 0.71073 Å, 296 K, ϕ,ω-scanning technique). Colorless crystals belong to the monoclinic system, $C_{10}H_8N_8$, M = 240.24, space group $P2_1/c$, a = 7.8317(4) Å, b = 18.4894(8) Å, c = 14.5157(7) Å, β = 94.936(2)°, V = 2094.13(17) Å^3, Z = 8, d_{calc} =1.524 g cm^{-3}, μ = 0.106 mm^{-1}. The intensities of 30083 reflections were measured ($2\theta < 54°$) from a crystal with dimensions 0.25×0.28×0.30 mm, of which 4543 reflections were independent (R_{int} = 0.0459); 3569 reflections with $I \geq 2\sigma(I)$ were obtained, 389 parameters were refined, R_1 = 0.0411 (based on reflections with $I \geq 2\sigma(I)$), wR_2 = 0.1267, and GOOF = 1.029 (based on all reflections). The absorption correction was applied with the use of the SADABS program[32] (T_{min}/T_{max} = 0.89/0.96). The structure was solved by direct methods. The positions and thermal parameters of nonhydrogen atoms were refined first isotropically and then anisotropically by the full-matrix least-squares method. The hydrogen atoms were refined isotropically. All calculations were performed with the use of the SHELXTL program package.[33] The atomic coordinates and the thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 754771).

* In the study,[31] the m.p. for compound **18** was not reported.

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Received December 3, 2009;
in revised form July 16, 2010