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Cyanoamino Compounds in Synthesis
Syntheses of Some Heterocycles

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Transformations of some heterocyclic cyanoamino compounds leading to various heterocyclic systems are described. *s*-Triazolo(1,5—*a*)azines are obtained either in a direct synthetic approach or via the substituted aminotetrazoles, substituted 3-amino-5-oxo-1,2,4-oxadiazolines, and from *N*-ethoxycarbonyl *N'*-heteroaryl thioureas or *N*-heteroaryl *N'*-hydroxyguanidine. The cyanoamino group reacts also with *o*-difunctional benzenes to give the corresponding substituted derivatives of benzimidazole, benzoxazole or benzothiazole.

(Keywords: Cyclization with N—N *bond formation; Heterocyclic compounds; Rearrangements)*

Cyanoamino-Verbindungen in der Synthese. Synthesen von einigen Heterocyclen

Umwandlungen von einigen heterocyclischen Cyanoamino-Verbindungen in verschiedene heterocyclische Systeme werden beschrieben. *s*-Triazolo-(1,5—*a*)azine konnten in einem direkten Syntheseschritt oder über die substituierten Aminotetrazole, substituierten 3-Amino-5-oxo-1,2,4-oxadiazoline und aus *N*-Ethoxycarbonyl-*N'*-Heteroaryl-Thioharnstoffen oder *N*-Heteroaryl-*N'*-Hydroxyguanidin erhalten werden. Die Cyanoamino-Gruppe reagiert auch mit einigen *o*-disubstituierten Benzolderivaten; es wurden damit Derivate von Benzimidazol, Benzoxazol oder Benzothiazol dargestellt.

Introduction

Organic compounds with different functional groups are often employed as synthons for heterocyclic compounds. There is, however, little known about the reactivity and synthetic application of cyanoamino compounds, in particular in the heterocyclic series. Since we have recently developed methods for efficient preparation of heterocyclic cyanoamines[1,2] it seemed worthwhile to exploit their use as synthons.

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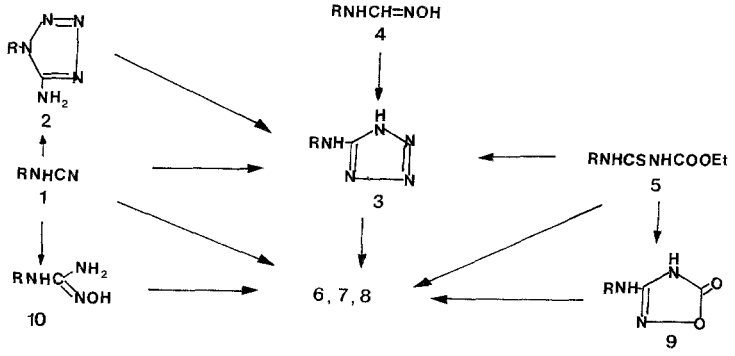
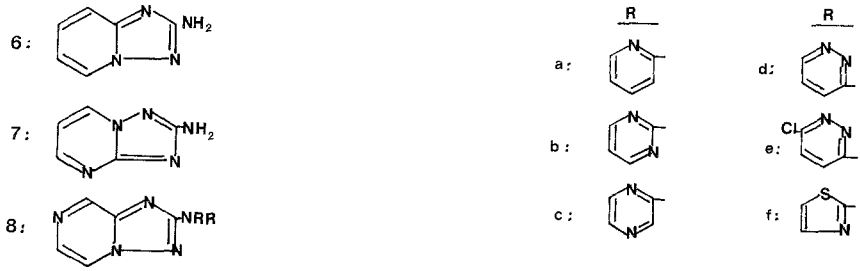
Results

The starting cyanoamino compounds **1** reacted with azides in two ways, forming either 1-heteroaryl 5-aminotetrazoles **2** or 5-heteroaryl-aminotetrazoles **3**. It appears that under milder reaction conditions compounds of the first type are formed, whereas in higher boiling solvents or if azidotrimethylsilane is used the thermodynamically more stable heteroarylamino derivatives **3** are obtained. The latter ones are obtainable also by rearrangement of the 1-substituted derivatives or from the amidoxime **4**. In the last mentioned case, the reaction proceeds most probably first by dehydration and the formed cyano-amino compound reacts then with the azide. It is interesting to note that also the *N*-ethoxycarbonyl thioureas **5 b** and **5 c** react with sodium azide in *N*,*N*-dimethylformamide (*DMF*) to give the corresponding tetrazoles **3**, although in low yield.

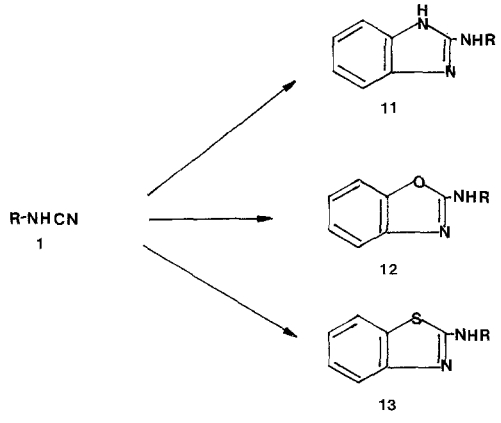




In another new type of transformation, the corresponding *N*-ethoxycarbonyl thioureas **5** reacted with free hydroxylamine at room temperature to give substituted 3-amino-1,2,4-oxadiazol-5-ones **9**. Apparently, the thioxo group is replaced first to give the corresponding

hydroxyimino derivative which is subsequently cyclized with the participation of the ethoxycarbonyl group. There is no evidence for another possibility, i.e. that first the corresponding hydroxamic acid is formed, followed by cyclization. In this case 1,2,4-oxadiazol-3-ones would be formed and these would react further in a different way as observed. The obtained 1,2,4-oxadiazol-5-ones **9** are readily transformed upon heating into the corresponding azoloazines, for example **7** or **8** ($R = H$). The reaction involves elimination of carbon dioxide from **9** and participation of the ring nitrogen of the corresponding heterocycles in the five-membered ring formation. These 2-amino-*s*-triazolo-(**1**,5—*a*)azines are available also by several other synthetic routes. These involve either elimination of a molecule of nitrogen from **3** in the presence of hot polyphosphoric acid, or reaction of **5** with hydroxylamine upon heating. These transformations may proceed most probably via the intermediate **9** since the reaction between 2-pyridylthiourea and hydroxylamine did not afford **6**. 2-Amino-*s*-triazolo(1,5—*a*)pyrimidine (**7**) could be prepared in one step reaction when reacting the corresponding cyanoamino compound **1 b** with hydroxylamine *O*-sulfonic acid. In another variant, the cyanoamino compound **1 c** was transformed first into the corresponding hydroxyguanidine (**10 c**) which afforded upon treatment with hot polyphosphoric acid the triazolopyrazine (**8**, $R = H$). All these reactions represent new synthetic pathways to the corresponding 2-amino-*s*-triazolo(1,5—*a*)azines. Some of these compounds, particularly in the pyridine and pyrimidine series, were prepared before by either rearrangement of the corresponding isomeric 3-amino(4,3—*a*)-systems or by treatment of the corresponding hydrazinoazines with cyanogen chloride[3,4].

The cyanoamino group can also serve as one carbon unit in the



formation of the corresponding benzimidazoles **11**, benzoxazoles **12** or benzothiazoles **13**. It appears that the reaction with *o*-phenylenediamine and *o*-aminothiophenol makes no difficulties, except that in some cases prolonged reaction time was required to obtain moderate yields of the products. *o*-Aminophenol reacts not so readily and higher temperatures and prolonged reaction time were necessary, a situation which we have encountered previously when using *N*,*N*-dimethylformamide dialkyl acetals for ring closure[5].

Discussion

In a recent paper the reaction between 2-pyridyl isothiocyanate and HN_3 was described to yield **3a** and sulfur. It was also claimed that at 200 °C compound **3a** is isomerized into **2a**[6] what contrasts our observations. The reverse structural assignment, as presented here, follows from other synthetic approaches, like the synthesis of **3** from **4** and **5**, from the transformation of **3** into azoloazines and from the reaction between **2** and *N*,*N*-dimethylformamide dimethyl acetal in which case the corresponding formamidine is formed[7]. The later reaction would not proceed with **3**, except that eventual methylation would take place as experienced with some other heterocycles possessing a NH-group[8]. Isomerization of **2** to **3** paralells the ready thermal isomerization of 5-mercapto-1-aryltetrazoles into 5-arylamino 1,2,3,4-thiatriazoles[9]. Also on hand of NMR spectra it may be possible to distinguish between both isomers **2** and **3**. In the case of **2a** the signal for NH_2 group appears at about 7.60, whereas in the case of **3a** signals for NH-groups appear at about 10-12. This is the case also with other compounds of the type **3**.

3-Substituted 1,2,4-oxadiazol-5-ones have been prepared so far from the corresponding amidoximes and ethyl chloroformate[10,11] and from an oxaziridine and phenyl isocyanate[12]. Although 1,2,4-oxadiazoles are known to undergo a variety of rearrangements[13], to the best of our knowledge a transformation of the 1,2,4-oxadiazol-5-ones **9** into fused azoloazines, like **6**, **7** or **8** has not been described before. It appears that the driving force for this transformation is the relative easy thermal elimination of carbon dioxide. For example, compound **9c** is transformed into **8** already at room temperature after several days.

The oxadiazolone system **9** is also a potentially tautomeric one and two lactam forms, a zwitterionic and a hydroxy form are theoretically possible. Tautomerism was studied so far only in the case of 3-phenyl-1,2,4-oxadiazol-5-one and controversal assignments for the preponderant tautomeric form have been published on hand of spectroscopic data[14,15]. However, the lactam forms appear to be most probably the prevailing ones[16]. It should be noted that the related pyrimidinyl and

pyrazinyl compounds **9b** and **9c** revealed a difference in carbonyl absorption in their IR spectra, i.e. at 1770 cm^{-1} for **9b** and 1680 cm^{-1} for the other compound.

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Experimental

Melting points were determined on a *Kofler* hot plate m.p. apparatus. ^1H NMR spectra were recorded on a JEOL JNM C-60 HL spectrometer and mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6 L spectrometer (*TMS* as internal standard, δ-values in ppm). Elemental analyses (C, H, N) were in agreement with the formulas given for **2a**, **3a**, **3b**, **6**, **7**, **8**, **9b**, **9c**, **10c**, **11a**, **11c**, **11d**, **11e**, **11f**, **12b**, **13c**, **13d**, and **13f**. The synthesis of the starting cyanoamino compounds **1**, the hydroxyiminomethyleneamino compounds **4**, and the *N*-ethoxycarbonyl *N'*-heteroaryl thioureas **5** have been described before[1,2,17–19].

5-Amino-1-(pyridyl-2')tetrazole (**2a**)

a) A mixture of 0.36 g **1a**, 0.5 g NaN_3, 0.5 g NH_4Cl and 20 ml of *Et*OH was heated under reflux for 15 h. The solvent was evaporated, the residue was treated with 10 ml of water and the separated product was filtered. The crude product was extracted with $CHCl_3$ to obtain **2a** (0.13 g, 27%). The residue was identified as **3a** (75 mg, 15%). Compound **2a** had m.p. 178–188 °C with isomerization into compound **3a** with m.p. 245–250 °C. The isomerization can be effected also upon heating **2a** at 150 °C/0.5 mm or in a solution of *DMSO*. The following spectroscopic data for **2a** have been recorded: MS (*m/e*): 162 (M^+); NMR (*DMSO-d*$_6$): 7.88 (ddd, H_3), 8.18 (ddd, H_4), 7.42 (ddd, H_5), 8.53 (ddd, H_6), $J_{3,4} = 8.0$, $J_{3,5} = 2.0$, $J_{3,6} = 0.9$, $J_{4,5} = 6.6$, $J_{4,6} = 1.8$, $J_{5,6} = 5.0$ Hz.

b) A mixture of 35 mg **1a**, 0.17 g NaN_3, 0.25 ml hydrochloric acid (1:1) and 5 ml of *Et*OH was left at room temperature for 1 week. During this time, two times 30 mg of NaN_3 and 0.25 ml of hydrochloric acid (1:1) were added to the reaction mixture. The solvent was then evaporated, 3 ml of water were added and the product was filtered. There were obtained 10 mg (21%) of compound **2a**, identical in all respects with the product obtained as described under a).

N-(Tetrazolyl-5')-2-pyridylamine (**3a**)

a) A mixture of 0.4 g **1a**, 1 ml azidotrimethylsilane and 10 ml of *o*-dichlorobenzene was heated under reflux for 2.5 h. Upon cooling the separated product was filtered (0.17 g, 31%). M.p. 246–248 °C (Lit.[6] m.p. 242–244 °C for the erroneously assigned structure as **2a**). MS (*m/e*): 162 (M^+), NMR (*DMSO-d*$_6$): 7.11 (ddd, H_3), 7.77 (ddd, H_4), 6.98 (ddd, H_5), 8.33 (ddd, H_6), 12–10 (broad, NH), $J_{3,4} = 8.4$, $J_{3,5} = 1.2$, $J_{3,6} = 0.9$, $J_{4,5} = 7.2$, $J_{4,6} = 1.8$, $J_{5,6} = 5.0$ Hz.

b) A mixture of 0.12 g **4a**, 0.2 g NaN_3 and 2 ml of *DMF* was heated under reflux for 5.5 h. Upon cooling, 5 ml of water were added and the mixture was

acidified with hydrochloric acid. The product was filtered (55 mg, 39%) and found identical in all respects with the product obtained as described under a).

N-(Tetrazolyl-5')-2-pyrimidinylamine (**3 b**)

a) A mixture of 0.12 g **1 b**, 0.13 g NaN_3 and 5 ml of *DMF* was heated under reflux for 1 h. The cold reaction mixture was diluted with 10 ml of water and acidified with hydrochloric acid (1:1). The separated product (85 mg, 52% yield) was crystallized from *DMF*, m. p. 291–293 °C (dec.). MS (*m/e*): 163 (M^+). NMR (*DMSO-d*$_6$): 8.63 (d, H_4 and H_6), 7.06 (t, H_5), 11.5 (broad, NH), $J_{4,5} = J_{5,6} = 4.9$ Hz.

b) Compound **5 b** (70 mg) and 0.1 g of NaN_3 in 2 ml of *DMF* were heated under reflux for 9 h. The cold reaction mixture was treated with 5 ml of water and acidified with hydrochloric acid (1:1). The product (5 mg, 10%) which separated after 2 days was found identical in all respects with the compound obtained as described under a).

N-(Tetrazolyl-5')-2-pyrazinylamine (**3 c**)

a) By the same procedure as described for the synthesis of compound **3 b** under a), but after 5 h under reflux, the compound **3 c** was obtained in 58% yield (95 mg), m. p. 295–300 °C (dec.) (from *DMF*). MS (*m/e*): 163 (M^+). NMR (*DMSO-d*$_6$): 8.40 (d, H_3), 8.12 (d, H_5), 8.21 (dd, H_6), 11.35 (broad, NH), $J_{3,6} = 1.5$, $J_{5,6} = 2.7$ Hz.

b) Following the procedure as described for the preparation of compound **3 a** under b) compound **3 c** could be prepared from **4 c** after 3 h under reflux in 68% yield.

c) In the same manner as described for compound **3 b** under b) compound **3 c** could be prepared from **5 c** after 35 min under reflux in 29% yield.

2-Amino-s-triazolo(1,5—a)pyridine (**6**)

a) A mixture of 15 mg **3 a** and 1 g polyphosphoric acid was heated at 200 °C for 0.5 h. Upon cooling and dilution with 20 ml of water, the solution was neutralized with $NaHCO_3$ and extracted with $CHCl_3$. The compound (3 mg, 24%) was found to be identical with the product as described under b).

b) 2.25 g of **5 a** were suspended in 100 ml of ethanolic solution of free hydroxylamine (prepared from 0.7 g sodium, ethanol and 3.5 g of hydroxylamine hydrochloride) and the mixture was heated under reflux for 2 h. During the reaction hydrogen sulfide was evolved. The solvent was then evaporated in vacuo and the residue was extracted with $CHCl_3$. The oily residue was crystallized from benzene (0.84 g, 63%), m. p. 110–112 °C (Lit.[3] m. p. 108–109 °C). MS (*m/e*): 134 (M^+). NMR ($CDCl_3$): 7.88 (m, H_5), 6.50 (m, H_6), 7.00 (m, H_7 and H_8), 4.60 (broad, NH_2).

N-(5-Oxo-Δ²-1,2,4-oxadiazolin-3-yl)-2-pyrimidinylamine (**9 b**)

To a solution of free hydroxylamine (prepared from 0.184 g sodium, 30 ml *Et*OH, 0.7 g hydroxylamine hydrochloride and filtered from sodium chloride) 0.452 g of **5 b** were added and the mixture was left at room temperature for 21 h. The separated product was filtered (0.255 g, 71%) and in the filtrate the

presence of 2-amino-*s*-triazolo(1,5—*a*)pyrimidine (**7**) was detected by TLC. The product had a m. p. of about 150 °C with decomposition and formation of **7**. MS (*m/e*): 179 (M^+), 135 (M^+—CO_2). NMR (*DMSO-d*$_6$): 8.23 (d, H_4 and H_6), 6.77 (t, H_5), $J_{4,5} = J_{5,6} = 4.5$ Hz.

2-Amino-s-triazolo(1,5—a)pyrimidine (**7**)

a) A suspension of 50 mg **9b** in 5 ml of water was heated under reflux for 30 min. Upon evaporation in vacuo, the residue was crystallized from *n*-butanol (14 mg, 37%), m. p. 202–203 °C (Lit.[4] m. p. 191–193 °C). MS (*m/e*): 135 (M^+). NMR (*DMSO-d*$_6$): 8.05 (dd, H_5), 6.63 (dd, H_6), 8.49 (dd, H_7), 6.01 (broad, NH_2), $J_{5,6} = 4.5$, $J_{5,7} = 1.8$, $J_{6,7} = 6.4$ Hz.

b) A mixture of 50 mg **3b** and 2 g polyphosphoric acid was heated at 200 °C for 3 h. The mixture was poured into 20 ml of water, neutralized with $NaHCO_3$ and the solvent evaporated in vacuo. The residue was extracted with 20 ml of hot *Me*OH and the obtained product (15 mg, 36%) was found to be identical with the compound as described under a).

c) A mixture of 60 mg **1b**, 70 mg hydroxylamine *O*-sulfonic acid and 3 ml of *DMF* was heated under reflux for 2 h. The cold reaction mixture was filtered, the filtrate was evaporated to dryness and the residue was extracted with hot *n*-butanol. The solvent was evaporated to dryness and the residue was purified by TLC on silica gel 60 F-254 using a mixture of *Me*OH and $CHCl_3$ (1:5) as the mobile phase. Upon elution of the corresponding zone with *n*-butanol there were obtained 2 mg of the pure compound **7**, identical with the product obtained as described under a).

N-(Pyrazinyl-2)-N'-hydroxyguanidine (**10c**)

A methanolic solution of hydroxylamine, prepared from 70 mg sodium, 30 ml *Me*OH and 0.21 g hydroxylamine hydrochloride, was treated with 0.12 g of **1c** and the mixture was left at room temperature for 54 h. The solvent was evaporated to dryness and the residue was suspended in 10 ml of water. The product was filtered and crystallized from water (65 mg, 43%), m. p. 185–187 °C (dec.). MS (*m/e*): 153 (M^+). NMR (*DMSO-d*$_6$): 8.12 (d, H_3), 7.51 (d, H_5), 7.64 (dd, H_6), $J_{3,6} = 1.2$, $J_{5,6} = 2.5$ Hz. By TLC it could be established that in the filtrate also 2-pyrazinylurea is present.

N-(5-Oxo-Δ²-1,2,4-oxadiazolin-3-yl)-2-pyrazinylamine (**9c**)

The compound was prepared in essentially the same way as described for **9b**, except that the reaction mixture was left to stand at room temperature for 9 h. The obtained product (53% yield) decomposed upon heating at about 150 °C and compound **8** ($R = H$) is formed. The later was also detected by TLC in the filtrate. For compound **9c** the following data were determined: MS (*m/e*): 179 (M^+), 135 (M^+—CO_2). NMR (*DMSO-d*$_6$): 8.49 (d, H_3), 7.66 (d, H_5), 7.79 (dd, H_6), $J_{3,6} = 1.4$, $J_{5,6} = 2.5$ Hz.

2-Amino-s-triazolo(1,5—a)pyrazine (**8**, $R = H$)

a) A suspension of 50 mg **9c** in 5 ml of water heated under reflux for 2 h. The cold solution was extracted with $CHCl_3$ and the obtained product was

crystallized from *n*-butanol (7 mg, 18%), m. p. 207-208 °C. MS (*m/e*): **135** (M^+). NMR (*DMSO-d*$_6$): 8.25 (dd, H_5), 7.58 (d, H_6), 8.40 (d, H_8), 3.90 (broad, NH_2), $J_{5,6} = 4.0$, $J_{5,8} = 1.2$ Hz.

b) A mixture of 65 mg **10 c** and 2 g polyphosphoric acid was heated at 90-100 °C for 2.5 h. Upon dilution with 10 ml of water, neutralization with $NaHCO_3$ and extraction with $CHCl_3$ the product was obtained in 19% yield (11 mg). It was found to be identical with the compound as described under a). The above transformation takes place also if the starting compound is heated at 140-160 °C/20 mm.

c) In essentially the same manner as described under b) the product was obtained upon heating **3 c** in polyphosphoric acid at 210 °C for 50 min. If the filtrate upon extraction with $CHCl_3$ was evaporated to dryness and extracted with hot *Me*OH some more of the product was obtained (total yield 67%). However, if the reaction mixture in this experiment was heated up to 290 °C, a mixture of **8** ($R = H$) and 2-aminopyrazine was obtained.

2-Dimethylaminomethyleneamino-s-triazolo(1,5—a)pyrazine
(**8**, $RR = CHNMe_2$)

a) A mixture of 50 mg **9 c**, 0.3 ml *N*,*N*-dimethylformamide dimethyl acetal and 4 ml of *Me*OH was heated under reflux for 2 h. The solvent was evaporated and the residue was crystallized from toluene (40 mg, 75%), m. p. 210-211 °C. MS (*m/e*): 190 (M^+). NMR (*DMSO-d*$_6$): 8.72 (dd, H_5), 7.98 (d, H_6), 8.95 (d, H_8), 8.51 (s, CH), 3.0 and 3.10 (s, NMe_2), $J_{5,6} = 4.5$, $J_{5,8} = 1.5$ Hz.

b) If a mixture of 50 mg **8** ($R = H$), 0.25 ml *N*,*N*-dimethylformamide dimethyl acetal and 3 ml of toluene was heated under reflux for 1 h, the product was obtained in 67% yield (47 mg). It was found to be identical in all respects with the compound obtained as described under a).

N-(Pyridyl-2')-2-benzimidazolylamine (**11 a**)

A mixture of 0.119 g **1 a**, 0.108 g *o*-phenylenediamine and 10 ml of *Et*OH was heated under reflux for 7 h. Upon cooling the separated product was filtered and crystallized from *Et*OH (70 mg, 33%), m. p. 259-260 °C. MS (*m/e*): 210 (M^+). NMR (*DMSO-d*$_6$): 7.64 (ddd, $H_{4'}$), 8.20 (ddd, $H_{6'}$), 6.75-7.44 (m, $H_{3'}$, $H_{5'}$, H_4, H_5, H_6, H_7), $J_{3',4'} = 8.1$, $J_{4',5'} = 7.2$, $J_{4',6'} = 1.8$, $J_{3',6'} = 0.9$, $J_{5',6'} = 5.0$ Hz.

In essentially the same manner the following compounds were synthesized:

N-(Pyrazinyl-2')-2-benzimidazolylamine (**11 c**)

Obtained in 33% yield (6 h under reflux), m. p. over 300 °C (from aqueous *Et*OH). MS (*m/e*): 211 (M^+). NMR (*DMSO-d*$_6$): 8.54 (d, $H_{3'}$), 8.01 (d, $H_{5'}$), 8.15 (dd, $H_{6'}$), 6.86-7.07 and 7.18-7.40 (m, H_4, H_5, H_6, H_7), $J_{3',6'} = 1.4$, $J_{5',6'} = 2.8$ Hz.

N-(Pyridazinyl-3')-2-benzimidazolylamine (**11 d**)

As solvent a mixture of *Et*OH and water (3:1) was used and reaction time was 9.5 h. The product was obtained in 30% yield, m. p. over 310 °C (from aqueous *Et*OH) and from the filtrate unchanged **1 d** was recovered in 40% yield. MS (*m/e*): 211 (M^+). NMR (*DMSO-d*$_6$, 130 °C): 7.60 (dd, $H_{4'}$), 8.59 (dd, $H_{6'}$), 6.85-7.45 (m, $H_{5'}$; H_4, H_5, H_6, H_7), $J_{4',5'} = 8.9$, $J_{4',6'} = 1.8$, $J_{5',6'} = 4.0$ Hz.

N-(6'-Chloropyridazinyl-3')-2-benzimidazolylamine (**11e**)

The compound was obtained in 49% yield after 3.5 h of reaction time, m. p. 295-305 °C (dec.) (from *Et*OH). MS (*m/e*): 245 (M^+). NMR (*DMSO-d*$_6$, 110 °C): 7.70 (d, $H_{4'}$), 7.50 (d, $H_{5'}$), 6.90-7.12 (m, H_4, H_5, H_6, H_7), $J_{4',5'} = 9.5$ Hz.

N-(Thiazolyl-2')-2-benzimidazolylamine (**11f**)

After 7 h reaction time the compound was obtained in 42% yield, m. p. 267-271 °C (from aqueous *Et*OH). MS (*m/e*): 216 (M^+).

N-(Pyrimidinyl-2')-2-benzoxazolylamine (**12b**)

A mixture of 60 mg **1b**, 55 mg *o*-aminophenol and 5 ml of *DMF* was heated under reflux for 11 h. The product, which separated upon cooling, was filtered and crystallized from aqueous *Et*OH (50 mg, 47%), m. p. 241-242 °C. MS (*m/e*): 212 (M^+). NMR (*DMSO-d*$_6$): 8.67 (d, $H_{4'}$ and $H_{6'}$), 7.00-7.70 (m, $H_{5'}$, H_4, H_5, H_6, H_7), $J_{4',5'} = J_{5',6'} = 5.0$ Hz.

N-(Pyrazinyl-2')-2-benzothiazolylamine (**13c**)

A mixture of 0.12 g **1c**, 0.135 g *o*-aminothiophenol and 10 ml of *Et*OH was heated under reflux for 5 h. The separated product (0.115 g, 50%) was crystallized from aqueous *Et*OH, m. p. 241 °C. MS (*m/e*): 228 (M^+). NMR (*DMSO-d*$_6$): 8.59 (d, $H_{3'}$), 8.18 (d, $H_{5'}$), 8.33 (dd, $H_{6'}$), 7.01-7.96 (m, H_4, H_5, H_6, H_7), $J_{3',6'} = 1.4$, $J_{5',6'} = 2.7$ Hz. If the filtrate was poured in water, a compound separated (70 mg) and was identified as di(*o*-aminophenyl)disulfide[20].

N-(Thiazolyl-2')-2-benzothiazolylamine (**13f**)

The compound was prepared following the above procedure (3.5 h under reflux) in 75% yield, m. p. 235-237 °C (from *Et*OH), MS (*m/e*): 233 (M^+).

N-(Pyridazinyl-3')-2-benzothiazolylamine (**13d**)

A mixture of 0.12 g **1d**, 0.16 g *o*-aminothiophenol and 10 ml of *Et*OH was heated under reflux for 5 h. Upon cooling the product was filtered and to the filtrate 0.15 g of *o*-aminothiophenol and 10 ml of *Et*OH were added and the mixture was heated for another 5 h. Upon cooling some more of the product were obtained, total yield amounting 66% (0.15 g), m. p. 298-300 °C (from aqueous *Et*OH). MS (*m/e*): 228 (M^+). NMR (*DMSO-d*$_6$): 8.81 (dd, $H_{6'}$), 6.95-7.95 (m, $H_{4'}$, $H_{5'}$, H_4, H_5, H_6, H_7), $J_{4',6'} = 2.1$, $J_{5',6'} = 3.9$ Hz.

In the filtrate di(*o*-aminophenyl)disulfide[20] was detected by TLC.

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