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Features of the Synthesis of 1,1'-Phenylenebis(1*H*-tetrazoles) and Their Transformations in Basic Environment

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Abstract—Reactions of substituted 1,3- and 1,4-phenylenediamines with sodium azide and triethyl orthoformate in the presence of acetic acid led to the formation in high yields of the corresponding 1,12 -phenylenebis(1*H*-tetrazoles). The presence of electron-acceptor groups in the molecules of the initial diamines reduces the yield of the target heterocycles. With 2-nitro-1,4-phenylenediamine the prevailing product was 2-nitro-4-(1*H*-tetrazol-1-yl)aniline. The obtained bistetrazoles in basic environment suffer an opening of one or both heterocycles forming cyanamides.

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The growing interest to the synthesis of new functionally substituted tetrazole derivatives is due to the inherent to this class compounds biological activity, chemical and metabolic stability, high energy store and capability of complex formation [1–3].

Bi- and polynuclear tetrazoles attract attention as chelating agents and initial compounds for building up one-, two-, and three-dimensional metal-containing supramolecular structures and developing materials with unusual magnetic properties, photo- and thermochromism ([3–5] and references cited there). Besides bicyclic tetrazoles are promising for the synthesis both of tetrazole-containing and other bifunctional and macroheterocyclic systems [6], and also of linear oligoheterocycles [7]. The application of 1,12 -(1,3-phenylene)bistetrazole was described as an effective ligand in the catalyzed by palladium salts cross-coupling of aryl halides and arylboric acids [8].

Although a large amount of information exists on the opportunities of 1,3- and 1,4-phenylenebistetrazoles application, the development of approaches to their synthesis is scanty. An efficient procedure for preparation of 1-substituted tetrazoles by the heterocyclization of appropriate amines under the treatment with sodium azide and triethyl orthoformate in acetic acid was poorly studied with respect to the synthesis of phenylenebistetrazoles. In the preceding research [9, 10] concerning a limited range of substrates with equivalent or similar in the reactivity amino groups it was demonstrated that both amino groups of phenylenediamine underwent the heterocyclization disregarding the reaction conditions and the reagents ratio. The opening of the tetrazole ring under the action of bases practically important for the synthesis of N-arylcyanamides and 5-amino-1-aryltetrazoles [10–13] was not virtually investigated on the mentioned phenylenebistetrazoles: Only the behavior was described of two simplest compounds of this series lacking other substituents [10]. The published data are insufficient for evaluating the applicability of these reactions to the functionally-substituted phenylenediamines and phenylenebistetrazoles. In the present study we attempted to reveal the features of this processes depending on the presence and the type of substituents in the initial compounds.

In the synthesis of phenylenebistetrazoles a series of appropriate 1,3- and 1,4-phenylenediamines was used containing substituents with donor and acceptor electronic effects (CH_3, OCH_3, Cl, NO_2) that were located symmetrically and unsymmetrically with respect to amino groups. With phenylene-diamines **Ia, Ib, Id** the

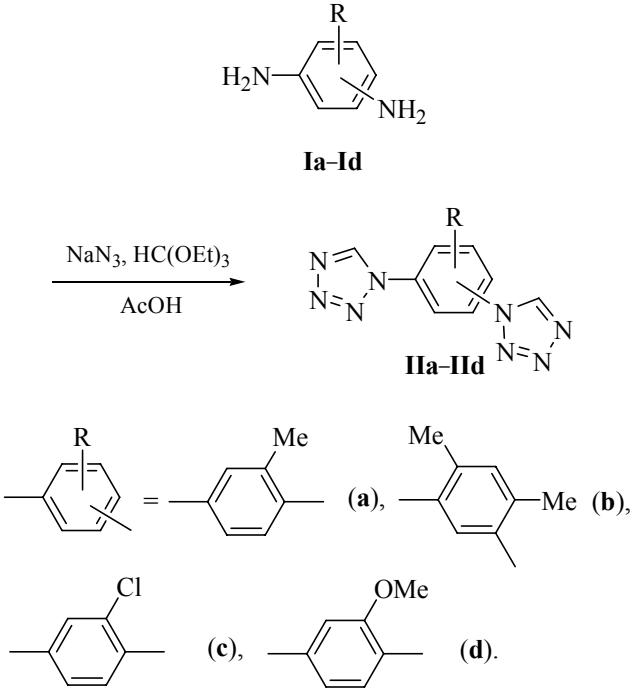
heterocyclization readily proceeded resulting in the corresponding bistetrazoles **IIa, IIb, IId** in high yields (Scheme 1). 1,12 -(2-Chloro-1,4-phenylene)bis(1*H*-tetrazole) (**IIc**) was obtained in a considerably lower yield as was known to be characteristic of the heterocyclization of the *ortho*-halosubstituted arylamines due to the steric hindrances and the negative inductive effect of halogen atoms reducing the basicity of the amino group [13].

The heterocyclization of 2-nitro-1,4-phenylenediamine (**Ie**) proceeded differently. According to the data of ^{1}H and ^{13}C NMR the reaction led to the formation of a mixture of a bistetrazole and a tetrazolylaniline (the product of tetrazole formation from one of the amino groups) in a ratio 1:9. This is indicated by the presence in the ^{1}H NMR spectrum of the mixture obtained of three signals with the chemical shifts characteristic of hydrogen atoms of 1-aryl-tetrazoles (δ 9.97, 10.09, and 10.31 ppm, intensity ratio 9:1:1) and a broad proton signal of a primary amino group (δ 7.79 ppm). The positions, type, and intensity of the other signals confirm the assumed composition of the mixture.

The structure of the obtained tetrazolylaniline was established with the use of a number of one-and two-dimensional NMR procedures. The assignment of the signals of three hydrogen atoms of the aromatic ring was done based on the character and the parameters of their spin-spin couplings in the ^{1}H NMR spectrum. The signals of three corresponding unsubstituted carbon atoms in the ^{13}C NMR spectrum were identified using the spectrum with the polarization transfer (DEPT), and also the spectrum of the hetronuclear correlation [^{1}H, ^{13}C] HSQC. The analysis of the correlation spectrum [^{1}H, ^{13}C] HMBC made it possible to assign the signals of the other carbon atoms of the tetrazolylaniline molecule. It is important that in the homonuclear correlation spectrum [^{1}H, ^{1}H] COSY the signal of the tetrazole hydrogen (δ 9.97 ppm) has two cross-peaks of similar intensity with hydrogen atoms belonging to the arene system (δ 7.86 and 8.44 ppm). This interaction shows the contiguity of the tetrazole substituent to the two unsubstituted positions of the aryl fragment. It is possible to conclude from the above analysis that the compound obtained is 2-nitro-4-(tetrazol-1-yl)aniline (**IIIe**). The corresponding 3-nitroisomer **IVe** was not found in the reaction products even in traces (Scheme 2).

The reaction of phenylenediamine **Ie** under more stringent conditions and also in the presence of excess reagents did not result in larger yield of bistetrazole **IIe**. The attempts on heterocyclization of tetrazolylaniline **IIIe** isolated by column chromatography failed evidently because of its low basicity.

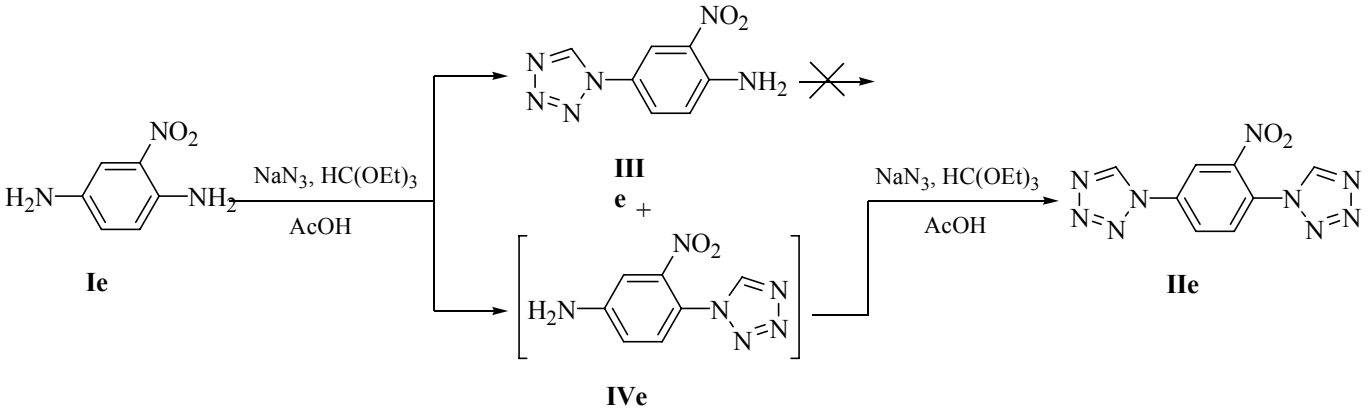
Scheme 1.



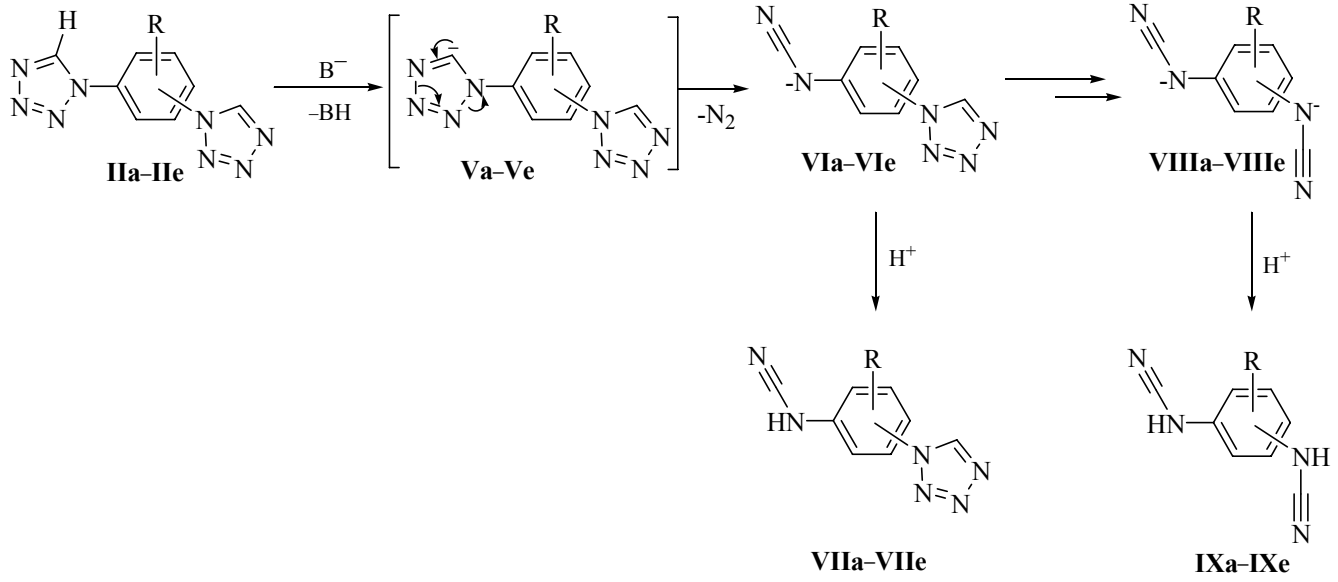
This uncommon behavior of 2-nitro-1,4-phenylenediamine under the heterocyclization conditions apparently originates from the significant difference in the reactivity of the groups both in the initial compound and in the monotetrazole derivatives **IIIe** and **IVe**. The essentially higher basicity of the amino group located in the *meta*-position with respect to the nitro group of the initial phenylenediamine resulted in higher probability of the reaction involving this group. Presuming that the heterocyclization of the amino groups of phenylenediamines proceeds successively, it is possible to conclude that the main product of the first stage is 2-nitro-4-tetrazolylaniline (**IIIe**). π-Acceptor properties of the tetrazolyl substituent in the molecule of tetrazolylaniline **IIIe** result in the additional decrease in the basicity of the second amino group, therefore the proceeding of the second reaction state with the formation of bistetrazole **IIe** becomes impossible, and tetrazolylaniline **IIIe** remains intact to the end of the process. On the contrary, the basicity of the amino group in the minor product **IVe** containing electron-acceptor substituents in the meta- and para-positions remains sufficient for the reaction, and this isomer totally converts into bistetrazole **IIe**.

The described reaction is the first example of tetrazolation proceeding selectively involving only one of

Scheme 2.



Scheme 3.



the amino groups of a diamine. This result has both a theoretical importance consisting in the outlining the factors influencing the heterocyclization of primary amines and in the extending the limits of the method application, and practical prospects of the use in multistage processes including stages of regioselective functionalization.

The obtained phenylenebistetrazoles **IIa–IIe** were subjected to transformation under basic conditions yielding cyanamides **VII** and **IX** aiming at extension of the application field and at the study of the special features of this reaction possessing a significant practical potential (Scheme 3). The mechanism of the process involves the abstraction of a hydrogen atom from the tetrazole ring followed by the elimination of a nitrogen molecule from unstable heterocyclic carbanion **V** and the formation of cyanamide anion **VI** or **VIII**. The rate of the process is affected by the strength of the base, properties of the solvent, and the lability of the hydrogen of the heterocycle that is sufficient in most 1-aryltetrazoles for the ready occurring of the reaction [13].

At room temperature in bistetrazoles containing methyl (**IIa, IIb**) and methoxy (**IId**) groups the transformation occurs with only one tetrazole ring notwithstanding the amount of the base in the reaction mixture. The second heterocycle reacts with a notable rate only at the temperature exceeding 60–70°C. This results are consistent with previously published findings

on the behavior of unsubstituted 1,3- and 1,4-phenylenebistetrazoles in basic environment [10]. The observed difference in the reactivity of two heterocycles in the molecules of phenylenebistetrazoles evidently originate from a strong electron-donor effect of the anion form of the cyanamide group in the intermediate **VI** sharply decreasing the mobility of the hydrogen atom in the second tetrazole ring. The reaction of phenylenebistetrazoles **IIc** and **IIe** results in the transformation of both heterocycles already at room temperature as shows the lack in the IR spectra of the reaction products of the characterictic absorption band in the region 3120–3145 cm^{-1} corresponding to the stretching vibrations of C–H bond. This fact may be due to the partial compensation of the donor effect of the cyanamide anion by the electron-acceptor functional groups (Cl and NO_2 respectively) present in the molecules of these substrates The high reactivity of dicyanamides **IX** led to the formation *in situ* of intractable products of their hydrolysis and solvolysis [13] impeding the separation of compounds **IX** in a pure state.

Our interest attracted the factors governing the prevailing direction of attack of the basic agent in the case of phenylenebistetrazoles with unsymmetrical location of substituents. To this end bistetrazoles **IIa, IIc–IIe** were brought into the reaction with an equimolar amount of NaOH. The ratio of isomeric tetrazolylphenylcyanamides **VII** and **VII'** was measured by the methods of one-and two-dimensional NMR. ^1H NMR spectra of obtained isomeric mixtures contained two signals in the region characteristic of CH protons of 1-aryltetrazoles (δ 9.5–10.5 ppm). In the spectra [^1H, ^1H] NOESY these signals have cross-peaks with the proton signals of the aryl fragment presnt in the ortho-position with respect to the tetrazole moiety. In the spectra of isomers **VII** one cross-peak is observed with a doublet signal having a coupling constant of 8.5 Hz. In contrast, isomers **VII'** in each case gave two cross-peaks of the hydrogen atom of the heterocycle with protons observed in the ^1H NMR spectrum as a narrow doublet (1.8 Hz) and a doublet of doublets (8.5 and 1.8 Hz). From these data we assigned the signals of heterocyclic protons to regioisomeric structure **VII** and **VII'**, and from the integral curve we estimated their quantitative ratio (see the table). The validity of signals assignment was confirmed by the presence of cross peaks between the methyl and heterocyclic protons in structures **VIIa** and **VIIe**, and also the adequate correlation NMR spectra [^1H, ^{13}C] HSQC and HMBC.

The ratio of isomeric products of reaction between substituted 1,4-phenylenebistetrazoles and NaOH–DMSO

Initial bistetrazole	R	Cleavage products ratio, %
IIa	CH_3	**VIIa, VII'a**, 80:20
IIc	Cl	**VIIc, VII'c**, 66:34
IId	OCH_3	**VIId, VII'd**, 95:5
IIe	NO_2	**VIIe, VII'e**, 30:70

The results of analyses showed that two tetrazole rings in the initial compounds are not equivalent with respect to the base attack. The substituent in the aryl fragment builds up steric hindrances reducing the possibility of the base attack on the tetrazole ring located in the *ortho*-position. However this effect is not decisive due to noncoplanar position of the tetrazole and aryl rings in the molecules of 1-aryltetrazoles demonstrated by XRD studies and quantum-chemical calculations [14–16]. A significant role belongs to the electronic effect of the substituent: The effect of the electron-donor groups acts in the same direction as their steric influence, whereas the electron-acceptor groups increase the possibility of the cleavage of the tetrazole ring in the *ortho*-position. In the series of studied bistetrazole the ratio of isomeric cleavage products varied from 30:70 to 95:5 (see the table). The reason here consists also in the influence of the electronic effect of the substituents on the mobility of the hydrogen atoms of the tetrazole rings, first of all the ring situated in the *ortho*-position to this substituent.

The effect of the reaction conditions and of the type of applied base on the direction of the process and the isomers ratio was studied by an example of 2-methyl-1,4-phenylenebistetrazole (**IIa**). It was established that the temperature maintained in the course of the reaction between the base and the tetrazole affects the rate of the process and the extent of the side reactions (hydrolysis or solvolysis of cyanamides [13]), but not the ratio of the regioisomers **VIIa:VII' a**.

For instance, at 0°C the reaction completion by the data of TLC monitoring required about 20 h. The HPLC of the products revealed the presence of isomeric cyanamides **VIIa** and **VII'a** at the content of their hydrolysis products less than 1%. At 20°C the reaction completed in 1 h; therewith the extent of cyanamide hydrolysis reached ~15%. The maintaining the reaction mixture at 80°C for 20 min besides the completion of ring opening led to virtually total hydrolysis of cyanamides whose content was <3%. The ratio of isomeric

tetrazolyl-arylcyanamides and also of their hydrolysis products in all cases remained approximately constant. The use for bases of sodium methylate and butyllithium also did not affect this ratio. The reaction with sodium methylate completed at 20°C within 1 h and afforded a mixture of isomeric cyanamides **VIIa** and **VII'a** free of impurities of their hydrolysis or solvolysis products.

Thus the procedure of the synthesis of 1-substituted tetrazoles by the heterocyclization of primary amines, triethyl orthoformate, and sodium azide in acetic acid in the majority of cases is suitable for preparation of binuclear tetrazoles from the corresponding *m*- and *p*-phenylenediamines. In the presence in the molecule of the initial phenylenediamine of an electron-acceptor substituent the yield of the phenylenebistetrazole decreases and appears a possibility of the formation of a monotetrazole product. The obtained phenylenebis-tetrazoles in the system NaOH–DMSO undergo the heterocycle opening forming the corresponding cyanamides. The direction of the base attack is affected by the position and electronic effects of the substituents in the aryl ring of the substrate, whereas the reaction conditions and the type of the applied base influence only the rate of the process and also the probability and character of the side processes to which are prone the obtained cyanamides.

EXPERIMENTAL

In syntheses were used reagents and solvents of no less than "pure" grade or additionally purified. The solutions of sodium methylate and butyllithium were prepared by procedures from [17]. The melting points of compounds synthesized were measured on a device Electrothermal IA9200 in open capillaries. IR spectra wre recorded on an IR Fourier spectrophotometer Nicolet Protege 460 from pellets with KBr. One-dimensional (^{1}H and ^{13}C) and two-dimensional NMR spectra ([^{1}H, ^{1}H] COSY, [^{1}H, ^{1}H] NOESY, [^{1}H, ^{13}C] HSQC, and [^{1}H, ^{13}C] HMBC) were registered on a spectrometer Bruker Avance 500 [operating frequencies 500 (^{1}H) and 125 MHz (^{13}C)] using the standard programs. $(CD_3)_2SO$ was used as solvent, concentration of measured solutions 20 mg/ml. Chemical shifts are reported with respect to the residual signals of solvent. The individuality of compounds synthesized was proved by TLC on Merck 60 F_{254} plates. The quantitative estimation of the composition of isomeric mixtures was carried out by HPLC. The system included a Waters 600E pump, a spectrophotometer detector Waters 996 (λ 254 nm), a column Purospher RP-18 (250×4.6 mm), packed with silica gel C_{18} with an average particle diameter 5 μm and porosity 90 Å. As mobile phases acetonitrle mixtures with water were used supplied to the column on conditions of linear gradient.

Heterocyclization of phenylenediamines Ia–Ie. To a dispersion of 0.01 mol of phenylenediamine **Ia–Ie** and 1.43 g (0.022 mol) of sodium azide in 10 ml (0.06 mol) of triethyl orthoformate was added dropwise at vigorous stirring 9.2 ml (0.16 mol) of glacial acetic acid, the mixture was stirred for 4 h at 70–80°C. On cooling to the reaction mixture was added 200 ml of 3% HCl. The separated precipitate was filtered off, washed with water, and dried in a vacuum.

In event of the heterocyclization of 2-nitro-1,4-phenylenediamine (**Ie**) the precipitate was dissolved in a minimum volume of methanol, the solution was applied to a column packed with silica gel L 40/100, and subjected to chromatography, eluent ethyl acetate–methanol, 5 : 1. We obtained 105 mg (8%) of bis-tetrazole **IIe** and 745 mg (72%) of 2-nitro-4-(tetrazol-1-yl)aniline (**IIIe**).

1,12-(2-Methyl-1,4-phenylene)bis(1*H*-tetrazole) (IIa). Yield 82%, mp 183–184°C (decomp.). IR spectrum, ν, cm^{-1}: 3113 (C–H), 1470 (C^5=N^4), 1389 (C^5–N^1), 1096, 1042, 1015, 995 (tetrazole). ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3), 7.87 d (1H_{arom}, *J* 8.5 Hz), 8.03 d.d (1H_{arom}, *J* 2.2, *J* 8.5 Hz), 8.16 d (1H_{arom}, *J* 1.8 Hz), 9.93 s (1H_{Ht}), 10.20 s (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 17.4 (CH_3), 119.7 (CH_{arom}), 123.8 (CH_{arom}), 128.1 (CH_{arom}), 133.4 (C_{arom}), 134.9 (C_{arom}), 135.9 (C_{arom}), 142.5 (CH_{Ht}), 144.7 (CH_{Ht}). Found, %: C 47.49; H 3.36; N 49.33. $C_9H_9N_8$. Calculated, %: C 47.37; H 3.53; N 49.10.

1,12-(2,4-Dimethyl-1,4-phenylene)bis(1*H*-tetrazole) (IIb). Yield 60%, mp 206–207°C (decomp.). IR spectrum, ν, cm^{-1}: 3137 (C–H), 1478 (C^5=N^4), 1401 (C^5–N^1), 1095, 1046, 1016, 1000 (tetrazole). ^{1}H NMR spectrum, δ, ppm: 2.23 s (6H, CH_3), 7.21 s (1H_{arom}), 7.91 s (1H_{arom}), 9.87 s (2H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 17.1 (CH_3), 124.0 (CH_{arom}), 131.2 (C_{arom}), 134.4 (CH_{arom}), 136.1 (C_{arom}), 144.7 (CH_{Ht}). Found, %: C 49.37; H 4.21; N 46.14. $C_{10}H_{10}N_8$. Calculated, %: C 49.58; H 4.16; N 46.26.

1,12-(2-Chloro-1,4-phenylene)bis(1*H*-tetrazole) (IIc). Yield 38%, mp 161–162°C (decomp.). IR spectrum, ν, cm^{-1}: 3145, 3124 (C–H), 1462 (C^5=N^4), 1396 (C^5–N^1), 1092, 1057, 1011, 995 (tetrazole). ^{1}H NMR spectrum,

δ, ppm: 8.13 d (1H_{arom}, *J* 8.6 Hz), 8.23 d.d (1H_{arom}, *J* 1.9, *J* 8.6 Hz), 8.51 d (1H_{arom}, *J* 1.9 Hz), 10.02 s (1H_{Ht}), 10.26 s (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 121.0 (CH_{arom}), 123.0 (CH_{arom}), 130.1 (CH_{arom}), 130.3 (C_{arom}), 131.7 (C_{arom}), 136.0 (C_{arom}), 142.8 (CH_{Ht}), 145.1 (CH_{Ht}). Found, %: C 39.01; H 2.11; N 45.29. $C_8H_5ClN_8$. Calculated, %: C 38.65; H 2.03; N 45.07.

1,12-(2-Methoxy-1,4-phenylene)bis(1*H*-tetrazole) (IId). Yield 63%, mp 182–183°C (decomp.). IR spectrum, ν, cm^{-1}: 3177, 3155 (C–H), 1483 (C^5=N^4), 1370 (C^5–N^1), 1093, 1024, 1002, 989 (tetrazole). ^{1}H NMR spectrum, δ, ppm: 4.00 s (3H, CH_3), 7.75 d.d (1H_{arom}, *J* 2.0, *J* 8.5 Hz), 7.92 d (1H_{arom}, *J* 1.9 Hz), 8.00 d (1H_{arom}, *J* 8.5 Hz), 9.89 s (1H_{Ht}), 10.24 s (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 57.2 (CH_3), 106.4 (CH_{arom}), 113.4 (CH_{arom}), 123.0 (C_{arom}), 127.4 (CH_{arom}), 135.7 (C_{arom}), 142.6 (CH_{Ht}), 144.8 (CH_{Ht}), 152.8 (C_{arom}). Found, %: C 44.49; H 3.12; N 45.67. $C_9H_8N_8O$. Calculated, %: C 44.26; H 3.30; N 45.88.

1,12 -(2-Nitro-1,4-phenylene)bis(1*H*-tetrazole) (IIe). Yield 8%, mp 182–183°C (decomp.). IR spectrum, ν, cm^{-1}: 3150 (C–H), 1458 (C^5=N^4), 1412 (C^5–N^1), 1087, 1058, 1046, 1028, 995 (tetrazole). ^{1}H NMR spectrum, δ, ppm: 8.27 d (1H_{arom}, *J* 8.7 Hz), 8.57 d.d (1H_{arom}, *J* 2.0, *J* 8.6 Hz), 8.93 d (1H_{arom}, *J* 2.2 Hz), 10.03 C (1H_{Ht}), 10.32 C (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 118.7 (CH_{arom}), 126.3 (C_{arom}), 126.7 (CH_{arom}), 130.5 (CH_{arom}), 135.7 (C_{arom}), 143.0 (CH_{Ht}), 143.9 (C_{arom}), 144.8 (CH_{Ht}). Found, %: C 36.89; H 1.90; N 48.88. $C_8H_5N_9O_2$. Calculated, %: C 37.07; H 1.94; N 48.64.

2-Nitro-4-(1*H*-tetrazol-1-yl)aniline (IIIe). Yield 72%, mp 210–211°C (decomp.). IR spectrum, ν, cm^{-1}: 3138 (C–H), 1462 (C^5=N^4), 1393 (C^5–N^1), 1088, 1053, 1008 (tetrazole). ^{1}H NMR spectrum, δ, ppm: 7.19 d (1H, CH^6, *J* 9.1 Hz), 7.79 br.s (2H, NH_2), 7.86 d.d (1H, CH^5, *J* 1.9, *J* 9.0 Hz), 8.44 d (1H, CH^3, *J* 1.9 Hz), 9.97 s (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 118.5 (C^3H), 120.7 (C^6H), 121.7 (C^4), 129.0 (C^5H), 129.2 (C^2), 142.2 (CH_{Ht}), 146.5 (C^1). Found, %: C 40.67; H 2.77; N 40.93. $C_7H_6N_6O_2$. Calculated, %: C 40.78; H 2.93; N 40.76.

Cleavage of phenylenebistetrazoles with bases. *a***.** With 0.01 mol of phenylenebistetrazole was mixed 10% solution of NaOH (4.5 or 9.0 ml depending on the plan to involve into the reaction one or both tetrazole rings). The dispersion obtained was brought to the minimum controlled temperature providing a sufficient reaction rate (20–60°C), and at constant stirring was added dropwise 10–15 ml of DMSO. Therewith a vigorous gas evolution was observed, and the reaction mixture self-heated. The stirring was continued for 15–20 min after the visual end of nitrogen liberation. The completion of the reaction was monitored by TLC. The reaction mixture was 5-fold diluted with water, filtered, and acidified with HCl to pH 3–4. The precipitate was filtered off, washed with water, and dried in a vacuum.

The cleavage of bistetrazole **IIe** under the above conditions proceeded very vigorously with the formation of a mixture of tetrazolylphenylcyanamides, phenylenedicyanamide, unreacted initial compound, and hydrolysis products. The attempts to isolate the target cyanamides from the mixture resulted in their further degradation. Therefore the cleavage of this bistetrazole was carried out in DMSO-d_6. The composition of the product obtained was immediately evaluated by NMR.

[3- and 2-Methyl-4-(1*H*-tetrazol-1-yl)phenyl]-cyanamides VIIa, VII'a. Yield 88%. IR spectrum, ν, cm^{-1}: 3137 (C–H), 2222 (C≡N). Found, %: C 53.71; H 3.89; N 41.77. $C_9H_8N_6$. Calculated, %: C 53.99; H 4.03; N 41.98.

[3-Methyl-4-(1*H*-tetrazol-1-yl)phenyl]cyanamide (VIIa). ^{1}H NMR spectrum, δ, ppm: 2.10 s (3H, CH_3), 6.99 d.d (1H, CH^6, *J* 1.8, *J* 8.2 Hz), 7.06 d (1H, CH^2, *J* 1.8 Hz), 7.50 d (1H, CH^5, *J* 8.4 Hz), 9.77 s (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 17.6 (CH_3), 111.7 (CN), 113.7 (C^6H), 117.4 (C^2H), 128.3 (C^4), 128.9 (C^5H), 135.8 (C^1), 141.0 (C^3), 145.0 (CH_{Ht}).

[2-Methyl-4-(1*H*-tetrazol-1-yl)phenyl]cyanamide (VII'a). ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, CH_3), 7.26 d (1H, CH^6, *J* 8.1 Hz), 7.74–7.77 m (2H, CH^3, CH^5), 9.99 s (1H, CH_{Ht}). ^{13}C NMR spectrum, δ, ppm: 17.5 (CH_3), 112.4 (CN), 116.4 (C^6H), 120.6 (C^5H), 124.1 (C^3H), 127.0 (C^2), 128.9 (C^4), 138.4 (C^1), 142.4 (CH_{Ht}).

[2,4-Dimethyl-5-(1*H*-tetrazol-1-yl)phenyl]-cyanamide (VIIb). Yield 89%, ppm 180°C. IR spectrum, ν, cm^{-1}: 3133 (C–H), 2235 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.04 s (3H, CH_3), 2.25 s (3H, CH_3), 7.15 s (1H_{arom}), 7.34 s (1H_{arom}), 9.83 s (1H_{Ht}). ^{13}C NMR spectrum, δ, ppm: 16.7 (CH_3), 17.3 (CH_3), 112.5 (CN), 113.2 (CH_{arom}), 127.6 (C_{arom}), 128.2 (C_{arom}), 131.6 (C_{arom}), 134.3 (CH_{arom}), 136.1 (C_{arom}), 144.9 (CH_{Ht}). Found, %: C 56.07; H 4.71; N 39.23. $C_{10}H_{10}N_6$. Calculated, %: C 56.19; H 4.40; N 38.97.

[4-(1*H*-Tetrazol-1-yl)-3- and -2-chlorophenyl]-cyanamides VIIc and VII'c. Yield 77%. IR spectrum, ν, cm^{-1}: 3134 (C–H), 2241 (C≡N). Found, %: C 43.64; H 2.21; N 15.83. $C_8H_5ClN_6$. Calculated, %: C 43.55;

H 2.28; N 16.07.

[4-(1*H*-Tetrazol-1-yl)-3-chlorophenyl]cyanamide (VIIc). ^{1}H NMR spectrum, δ, ppm: 7.17 d.d (1H, CH^6, *J* 1.7, *J* 8.7 Hz), 7.27 d (1H, CH^2, *J* 1.6 Hz), 7.76 d (1H, CH^5, *J* 8.6 Hz), 9.87 c ($1H_{Ht}$). ^{13}C NMR spectrum, δ, ppm: 110.9 (CN), 114.9 (C^6H), 116.3 (C^2H), 125.6 (C^4), 130.2 (C^5H), 130.4 (C^1), 142.6 (C^3), 145.3 (CH_{Ht}).

[4-(1*H*-Tetrazol-1-yl)-2-chlorophenyl]cyanamide (VII'c). ^{1}H NMR spectrum, δ, ppm: 7.43 d (1H, C^6H, *J* 8.8 Hz), 7.93 d.d (1H, C^5H, *J* 1.4, *J* 8.6 Hz), 8.13 d (1H, C^3H, *J* 1.4 Hz), 10.05 s ($1H_{Ht}$). ^{13}C NMR spectrum, δ, ppm: 111.5 (CN), 117.8 (C^6H), 120.8 (C^2), 121.9 (C^5H), 123.2 (C^3H), 129.2 (C^4), 137.0 (C^1), 142.5 (CH_{Ht}).

[3-Methoxy-4-(1*H*-tetrazol-1-yl)phenyl]-cyanamide (VIId). Yield 79%. IR spectrum, ν, cm^{-1}: 3141 (C–H), 2246 (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, CH_3), 6.74 d.d (1H, C^6H, *J* 2.1, *J* 8.5 Hz), 6.79 d (1H, C^2H, *J* 2.0 Hz), 7.64 d (1H, C^5H, *J* 8.5 Hz), 9.72 s ($1H_{Ht}$), 10.77 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 56.3 (CH_3), 99.4 (C^2H), 107.0 (C^6H), 111.3 (CN), 117.0 (C^4), 127.5 (C^5H), 141.9 (C^1), 144.7 (CH_{Ht}), 153.1 (C^3). Found, %: C 49.09; H 3.57; N 39.20. $C_9H_8N_6O$. Calculated, %: C 50.00; H 3.73; N 38.87.

[3-Nitro-4-(1*H*-tetrazol-1-yl)phenyl]cyanamide (VIIe). ^{1}H NMR spectrum, δ, ppm: 7.64 d ($1H_{arom}$, *J* 9.0 Hz), 8.33 d.d ($1H_{apOm}$, *J* 2.4, *J* 9.0 Hz), 8.71 d ($1H_{arom}$, *J* 2.4 Hz), 10.14 s ($1H_{Ht}$).

[2-Nitro-4-(1*H*-tetrazol-1-yl)phenyl]cyanamide (VII'e). ^{1}H NMR spectrum, δ, ppm: 7.86 d ($1H_{arom}$, *J* 2.6 Hz), 8.16 d.d ($1H_{arom}$, *J* 2.5, *J* 9.2 Hz), 8.39 d ($1H_{arom}$, *J* 9.3 Hz), 10.20 s ($1H_{Ht}$).

b. To a dispersion of 228 mg (1 mmol) of phenylenebistetrazole **IIa** in 2 ml of 0.5 M solution of sodium methylate in methanol was added dropwise at 20°C under constant stirring 2 ml of DMSO. The mixture was stirred for 15–20 min after the visual end of nitrogen liberation. The completion of the reaction was monitored by TLC. The reaction mixture was worked up as described in procedure *a*. The reaction product was identical to that obtained by method *a* (TLC, HPLC). Yield 154 mg (77%).

c. To a solution of 228 mg (1 mmol) of phenylenebistetrazole **IIa** in tetrahydrofuran at 0°C while constant stirring was added dropwise an equimolar amount of butyllithium in ether solution. The stirring was continued for 15–20 min after the visual end of nitrogen liberation. To the mixture was added a 5-fold volume of water, the organic solvents were distilled off in a vacuum at the temperature not exceeding 40°C, the solution was filtered and acidified with HCl to pH 3–4. The precipitate was filtered off, washed with water, and dried in a vacuum. The reaction product was identical to that obtained by method *a* (TLC, HPLC). Yield 171 mg (86%).

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