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Synthesis of 1- and 5-(pyrazolyl)tetrazole amino and nitro derivatives

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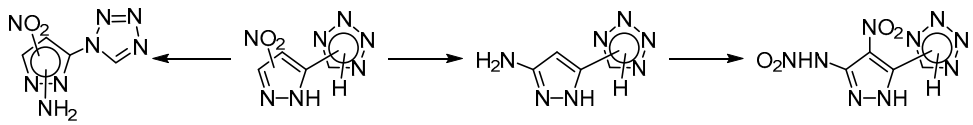


Regioselective introduction of nitro groups was studied in the case of pyrazoles containing a 1- or 5-tetrazole substituent at position 3(5). All the possible isomeric *C*-mononitropyrazoles were synthesized. The reduction of these compounds gave the respective 3(5)-amino-5(3)-tetrazolylpyrazoles, which were nitrated to 3(5)-nitramino-4-nitro-5(3)-tetrazolylpyrazoles. The reaction of 1-(nitropyrazol-3(5)-yl)tetrazoles with hydroxylamine-*O*-sulfonic acid produced the respective *N*-amino derivatives.

Keywords: nitropyrazole, tetrazole, *N*-amination, multinuclear NMR, nitration, reduction, regioselectivity, X-ray structural analysis.

The pyrazole ring is widely used for the design of various biologically active compounds, components of dyes and luminophores,[1] and high-energy materials.[2] A current trend in the chemistry of pyrazoles is the increasingly frequent use of nitropyrazoles as effective building blocks.[3] The powerful activating and directing influence of nitro group in nucleophilic substitution reactions at the carbon atoms of pyrazole ring, as well as in electrophilic reactions at the unsubstituted nitrogen atom of this ring has substantially expanded the synthetic possibilities of *C*- and *N*-functionalization in the pyrazole series.[4–6]

The concept of designing hybrid molecules,[7] which represent a combination of several heterocycles, is widely used in the chemistry of nitrogen-oxygen systems[8] for conferring the necessary set of properties to the target compounds. This often allows not only to optimize the specific properties, but also to obtain compounds with new properties and extended range of practical applications.

In recent years, we have used this approach to develop synthetic methods and to study the reactivity of hybrid heteronuclear pyrazole-containing compouds that combine an aromatic heterocycle with several nitrogen atoms and a nitropyrazole ring that is linked to it.[9–12]

Taking into account the many fields of use for tetrazole derivatives,[13] we recently developed a method for the synthesis of 1-(*N*-nitropyrazolyl)-1*H*-tetrazoles, a new type of heteronuclear *N*-nitropyrazoles.[9] In order to further develop this direction, it was considered to be worthwhile to synthesize and study compounds combining tetrazole rings with *N*-unsubstituted pyrazole rings bearing nitro groups at the carbon atoms. The goal of this work was to develop effective methods for the synthesis of such compounds (Fig. 1), where the aforementioned rings are linked with a C–N (type **A**) or a C–C bond (type **B**), and to study their properties.

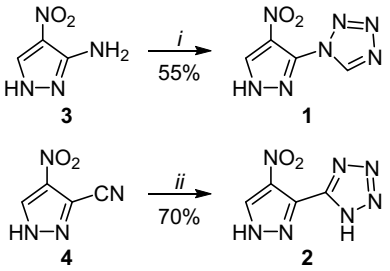
It should be noted that only two such compounds have been described in the literature, namely, 1- and 5-(4-nitro-1*H*-pyrazol-3(5)-yl)tetrazoles (**1**)[9] and (**2**).[14] As shown in Scheme 1, the key step in the published methods for building the heteronuclear system was the formation of a

A **B**

Figure 1. The types of target pyrazolyltetrazoles **A** and **B**.

tetrazole ring from the respective amino- and cyanopyrazoles **3** and **4** that already contained a nitro group. An alternative method for the synthesis of 1- and 5-(pyrazolyl)-tetrazole nitro derivatives of types **A** and **B** can be nitration, which has been commonly used for the preparation of nitropyrazoles.[3]

Scheme 1



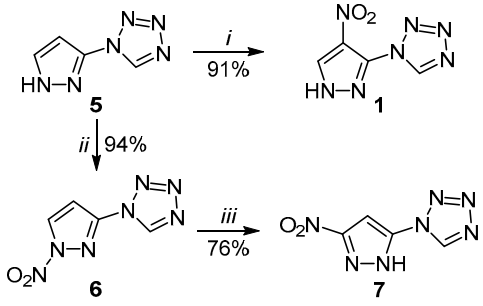
i: NaN_3, $CH(OEt)_3$, AcOH, 90°C, 3–4 h;
ii: NaN_3, NH_4Cl, DMF, 110°C, 6 h

It is known that direct acidic nitration allows to effectively introduce a nitro group at position 4 of pyrazole ring, while *N*-nitration with acyl nitrates followed by thermal isomerization of *N*-nitropyrazoles has been used as universal method for the synthesis of 3(5)-nitropyrazoles.[3,15] A combination of these two methods allows to obtain dinitropyrazoles. The possibilities for using analogous approaches for the preparation of isomeric pyrazolyltetrazoles were studied in this work.

The first stage of this work involved nitration of 1-(1*H*-pyrazol-3(5)-yl)-1*H*-tetrazole (**5**).[9] Tetrazole substituents are known to exhibit strong electron-withdrawing effects,[16] thus a pyrazole ring having a tetrazole substituent is deactivated with respect to electrophilic attack. Taking this into account, we attempted to perform nitration of pyrazole **5** under conditions that were analogous to those used for the nitration of 3(5)-nitropyrazole to 3(5),4-dinitropyrazole[17] (concd H_2SO_4 and HNO_3, 100°C, 4 h). However, complete destruction of the starting material occurred under these conditions, accompanied by vigorous evolution of gas and failure to contain the reaction mixture. The use of pure concd HNO_3 (20–25°C, 8 h) only led to slow decomposition of pyrazole **5**, while the formation of nitro derivative **1** was not detected (control by ^{1}H NMR spectroscopy).

We have shown for the first time that the nitration of pyrazoles containing a strong electron-withdrawing substituent can be successfully accomplished under mild conditions. It was found that the nitropyrazole **1** could be obtained in high yield from compound **5** by treatment with a nitrating mixture consisting of H_2SO_4, HNO_3, and H_2O in 20:3:1 ratio. The reaction mixture was not heated, but rather cooled to 5–10°C and maintained at that temperature for 5 h (Scheme 2). At the same time, increasing the reaction duration to 48 h led to a complete destruction of compound **1**. It is known that the pyrazole ring is highly stable during nitration reactions,[3,15] therefore the observed destruction of compounds **1** and **5** was apparently caused by the lability of the tetrazole moiety in these molecules. Nevertheless, in the narrow interval of reaction conditions identified by us the formation of product **1** prevailed over decomposition reactions.

Scheme 2



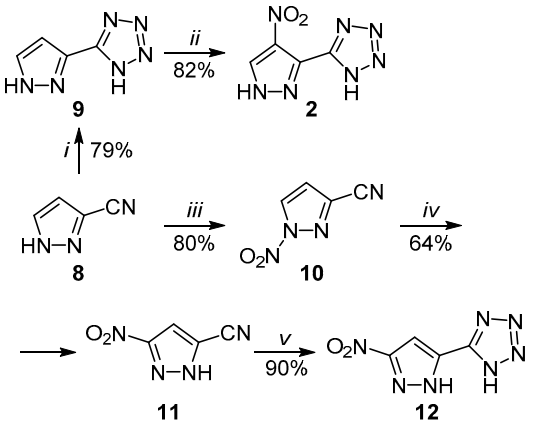
i: H_2SO_4–HNO_3–H_2O, 20:3:1, 5–10°C, 5 h;
ii: 100% HNO_3, Ac_2O, CF_3CO_2H, 5–10°C, 2 h;
iii: C_2Cl_4, 120°C, 10 h

A significant interest in the field of nitropyrazole chemistry has been attracted by 3(5)-nitropyrazoles that contain no substituents at the C-4 position, due to the high reactivity of the C-4 atom in electrophilic substitution reactions, such as nitration.[3,15] As already mentioned above, a well-known method for the preparation of 3(5)-nitropyrazoles is the rearrangement of *N*-nitropyrazoles by thermolysis of dilute solutions in high-boiling solvents. The *N*-nitropyrazole **6** necessary for accomplishing this reaction was previously obtained by us in 94% yield by *N*-nitration of pyrazole **5** with acetyl nitrate.[9] When studying the thermolysis of 5−10% solutions of nitropyrazole **6**, it was found that the use of benzonitrile, anisole, or *o*-dichlorobenzene as solvents at 160−180°C, that is, following the conditions used for isomerization of 1,3-dinitropyrazole to 3,5-dinitropyrazole,[17] led to complete decomposition of the nitropyrazole **6**. However, the use of tetrachloroethene as solvent at 120°C temperature not only allowed to obtain a high yield of the target 3(5)-nitropyrazole **7** (Scheme 2), but also to isolate this compound from the reaction mixture by a simple filtration.

The same approaches to the synthesis of isomeric mononitro derivatives were used for obtaining the 4- and 3(5)-nitro derivatives of type **B** heteronuclear system. The key compound for these syntheses was *C*,*N*-unsubstituted 5-(1*H*-pyrazol-3(5)-yl)tetrazole (**9**) (in the 1*H*- or 2*H*-form). Its synthesis from 3(5)-cyanopyrazole (**8**) by the action of NaN_3–$ZnBr_2$ in DMF at 170°C under the conditions of microwave irradiation has been described in an earlier publication.[18] However, the only reported characterization of pyrazolyltetrazole **9** was by its ^{1}H NMR spectrum. Our studies have shown that the synthesis of compound **9** from cyanopyrazole **8** can be accomplished under milder conditions. Thus, the treatment of nitrile **8** with [$Et_3NH^+N_3^-$] system in

refluxing toluene[19] (that is, at 110°C) allowed to obtain compound **9** in 79% yield (Scheme 3).

Scheme 3



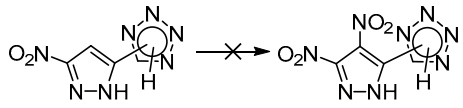
i: NaN_3, $Et_3N{\cdot}HCl$, PhH, 110°C, 10 h;
ii: H_2SO_4–HNO_3–H_2O, 20:3:1, rt, 24 h;
iii: 100% HNO_3, Ac_2O, CF_3CO_2H, 5–10°C, 2 h;
iv: $C_2H_4Cl_2$, 120°C, 4 h; 140°C, 10 h;
v: NaN_3, $Et_3N{\cdot}HCl$, PhH, 110°C, 8 h

When studying the nitration of pyrazole **9**, it was found that using the conditions developed by us for the synthesis of compound **1** was just as effective in this case. At room temperature, the reaction was complete in 1 day with the formation of 4-nitro derivative **2** in 82% yield (Scheme 3). At the same time, the attempt to perform *N*-nitration of pyrazole **9** with acetyl nitrate under various conditions[9] in order to obtain the respective *N*-nitropyrazole did not produce the expected results – complete degradation of the reaction mixture occurred, accompanied by vigorous evolution of gases. A possible reason for this was the presence of an unsubstituted nitrogen atom in the tetrazole ring of compound **9**, which under *N*-nitration conditions could lead to the formation of an unstable "*N*-nitrotetrazole".

Thus, we chose to base our synthesis of 3(5)-nitro derivative of type **B** on an approach that was previously described for the preparation of its 4-nitro isomer (Scheme 1),[14] where the key step in the formation of 5-(pyrazolyl)tetrazole system was the (3+2) cycloaddition of HN_3 to cyano-pyrazole that already contained a nitro group. The necessary starting material 5(3)-cyano-3(5)-nitropyrazole (**11**) was obtained in this study by *N*-nitration of nitrile **8**, followed by thermal isomerization of 3-cyano-1-nitro-pyrazole (**10**) (Scheme 3), with ~50% overall yield of the product. The synthesis of the target 5-(3(5)-nitro-1*H*-pyrazol-5(3)-yl)tetrazole (**12**) was accomplished in the same way as the preparation of its analog, the pyrazole **9**, which lacked a nitro group (Scheme 3). Thus, on the basis of pyrazole ring nitration in combination with rearrangement of *N*-nitro derivatives we have developed effective methods for the synthesis of all possible *C*-mononitro derivatives of 1- and 5-(pyrazol-3(5)-yl)-tetrazoles belonging to types **A** and **B**.

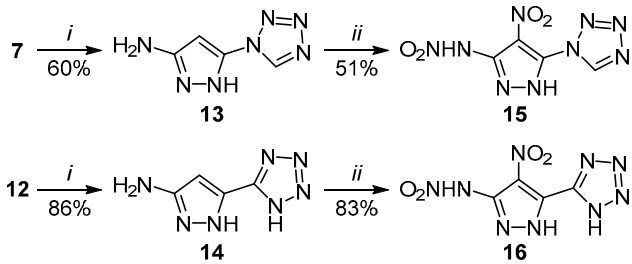
As already mentioned above, the presence of an unsubstituted C-4 carbon atom in 3(5)-nitro derivatives **7** and **12** theoretically permits the introduction of another nitro group by using acidic nitration. However, the presence of two strongly electron-withdrawing substituents (a nitro group and tetrazole ring) at the pyrazole ring led to a significant deactivation of it with respect to nitrating reagents. Our attempts to introduce a second nitro group at position 4 (Scheme 4) were unsuccessful. The compounds were left unchanged in the reaction mixture under mild conditions (HNO_3, KNO_3–H_2SO_4, HNO_3–H_3PO_4, 20–50°C), while decomposition occurred under forcing conditions (KNO_3–H_2SO_4, HNO_3–H_2SO_4, 90–110°C).

Scheme 4



During the search for other routes toward obtaining dinitro derivatives of heterosystems **A** and **B**, it was decided to decrease the electron-withdrawing nature of the pyrazole ring by reducing the 3(5)-nitro group. The treatment of nitro derivatives **7** and **12** with hydrazine in the presence of iron salts[20] allowed to obtain the desired amines **13** and **14** (Scheme 5). The introduction of an amino group in the pyrazole ring radically changed its reactivity. The nitration of compounds **13** and **14** under mild conditions (HNO_3–CF_3CO_2H, 5–10°C) allowed to simultaneously introduce two nitro groups: one at position 4 of pyrazole ring, the other at the amino group (Scheme 5). The yield of nitration products in these reactions depended on the type of bond between the heterocycles in the molecule. In the case when the tetrazole ring was bonded to the pyrazole ring by a C–N bond, and thus served as the more electron-withdrawing substituent, the nitronitramine **15** was obtained in 51% yield. At the same time, for compound **14**, where the tetrazole ring was linked by a C–C bond and thus exerted a weaker electron-withdrawing influence, nitration was more effective, leading to the dinitro product **16** in 83% yield.

Scheme 5



i: N_2H_4, $FeCl_3{\cdot}6H_2O$, C, EtOH, H_2O, 70°C, 9 h;
ii: 100% HNO_3, CF_3CO_2H, 5–10°C, 2 h

The presence of an unsubstituted endocyclic nitrogen atom in the pyrazole ring presented additional opportunities for its functionalization by treatment with electrophilic reagents. One of the important directions for *N*-functionalization of nitropyrazole ring was *N*-amination, enabling the preparation of compounds with an additional

highly reactive *N*-amino group, which has been used widely in organic synthesis[4,21,22] and, in particular, for the preparation of high-energy materials.[23–26] These reactions are usually performed in alkaline media and involve the generation of a nucleophilic anion from the respective NH-pyrazole. However, such anions have ambident nature, which can result in obtaining a mixture of regioisomeric products. It is important to study the regioselectivity of such reactions for planning targeted synthesis of compounds with the desired set of characteristics. In the majority of examples described so far the *N*-amination of mono- and dinitropyrazoles led to a preferred formation of one isomer.[4,22,26,27] The direction of the reaction in these cases was determined by the nitro group – the attack occurred at the ring nitrogen atom that was most distant from the nitro group.

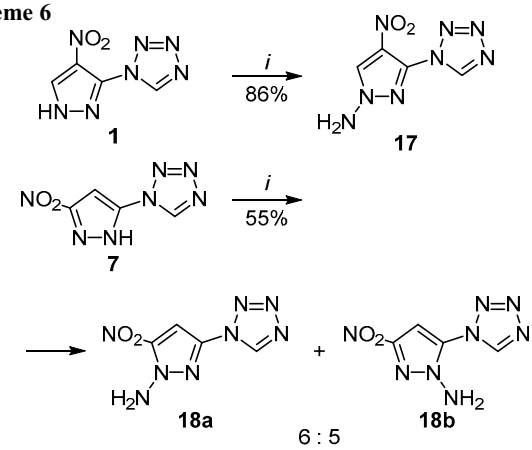
We have recently demonstrated that the presence of such electron-withdrawing substituent as furazanyl system at position 5(3) of 4- and 3(5)-nitropyrazoles preserves the dominant orienting influence of nitro group on *N*-amination. Nevertheless, a considerable amount of the minor regioisomer was still formed in the reactions, caused by the orienting influence of the furazanyl substituent.[12] In a continuation of this work, we studied the *N*-amination of 4-nitro- and 3(5)-nitro derivatives of 1-(1*H*-pyrazol-3(5)-yl)-1*H*-tetrazoles **1** and **7**. The reaction was performed under conditions that were analogous to those previously used for the *N*-amination of (1*H*-pyrazol-3(5)-yl)furazanes,[12] which was convenient for the comparison of results.

It was found that the *N*-amination of 4-nitropyrazole **1** with hydroxylamine-*O*-sulfonic acid for 6 h in aqueous phosphate buffer solution prepared from NaOH and KH_2PO_4 gave a high yield of amine **17** as the only product (Scheme 6). The 4-nitro group and 3(5)-tetrazole substituent in the pyrazole ring in this case exerted a synergistic influence on the reaction: a single isomer was formed that contained an *N*-substituent furthest removed both from the nitro group and the tetrazole ring. The directing influence by the *N*-tetrazole ring was substantially stronger, while in the case of furazanyl substituent there was 20% of isomer formed with the amino group located near the furazane substituent. According to these results, the *N*-tetrazole substituent had a comparable orienting effect to 3(5)-nitro group in 3(5),4-dinitropyrazole, the *N*-amination of which also led to a single isomer.[22,26]

Indeed, the calculated charge (details presented below) on the nitropyrazole ring, characterizing the degree of electron-withdrawing effect due to the substituent R in 3(5)-R-4-nitropyrazoles (where R = H, NO_2, CN, 4-furazanyl, 1-tetrazolyl) pointed to the fact that the effect of *N*-tetrazole substituent is nearly the same as the effect of nitro group and substantially stronger than the effect of furazanyl substituent. The electron-withdrawing effects of the substituents can be arranged in the following order (with the charge indicated in parentheses): H (–0.102) < 4-furazanyl (–0.022) < CN (+0.146) < NO_2 (+0.433) < 1-tetrazolyl (+0.467).

The *N*-amination of 3(5)-nitropyrazole **7** proceeded differently (Scheme 6). The presence of two strongly

Scheme 6



i: KH_2PO_4, NaOH, H_2NOSO_3H, H_2O, 60°C, 6–21 h

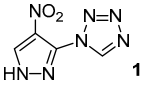
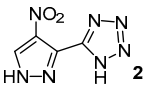
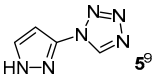
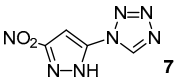
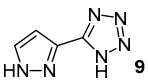
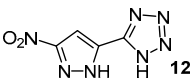
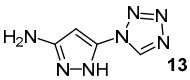
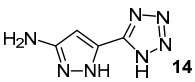
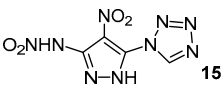
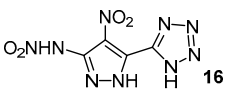
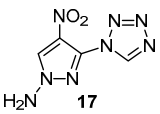
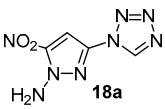
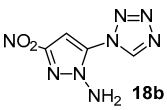
electron-withdrawing substituents adjacent to the ring nitrogen atoms resulted in a lower nucleophilicity of the respective anion, which caused the yield of the amination product **18** to decrease to 55%, compared to yield of the analogous product **17** (86%), even when extending the reaction time to 21 h. Furthermore, the competing and similarly strong orienting effects of the nitro group and the tetrazole ring led to the formation of a regioisomeric mixture **18a**/**18b** with the prevalence of 5-nitroisomer **18a**, which was in agreement with the considerations described above. Such a direction of *N*-amination in the series of nitropyrazoles with the formation of more than 50% of 5-nitroisomer in the reaction products was established for the first time in this study. It should be noted that, in the case of 3(5)-furazanyl substituent, the reaction product contained less than 25% of the 5-nitro isomer.[12]

The structures of all pyrazolyltetrazoles were confirmed by spectral methods (Table 1). The assignment of ^{1}H NMR signals was based on the known trend in pyrazole series, where the signals of protons bonded to the pyrazole ring are typically in the order of δ(H-5) > δ(H-3) > δ(H-4).[3] The assignment of ^{13}C NMR signals was based on the fact that the carbon atom bearing the nitro group gave a significantly broadened signal due to the ^{13}C–^{14}N quadrupole relaxation, while the most intense among the aromatic carbon signals was that of the tertiary carbon atom. In the series of *N*-unsubstituted derivatives **1**, **2**, **7**, **12**–**16**, which were capable of tautomerization, the assignment of ^{13}C NMR signals relied on the known trend of δ(C-3) > δ(C-5) > δ(C-4).[3]

The obtained data allow to identify several rules with regard to ^{13}C NMR spectra of 1-(pyrazolyl)- and 5-(pyrazolyl)tetrazoles, which are useful for the structural characterization of new compounds belonging to this class. Thus, the presence of a 1-tetrazole substituent at position 3(5) of the pyrazole ring leads to a downfield shift of the signal due to the pyrazole ring carbon atom bearing this substituent, and the downfield shift is stronger by 3–8 ppm, compared to that caused by the presence of a 5-tetrazole substituent. This indicates a more pronounced electron-withdrawing effect of the C–N-bonded tetrazole ring on the electron density distribution in pyrazole.

The introduction of a nitro group in pyrazole ring caused a downfield shift of the signal for the carbon atom bearing

Table 1. Spectral characteristics of 1-[1*H*-pyrazol-3(5)-yl]- and 5-[1*H*-pyrazol-3(5)-yl]-1*H*-tetrazole derivatives (DMSO-d_6)

Compound	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ, ppm				^{14}N NMR spectrum, δ, ppm (NO_2)
		C-3	C-4	C-5	C tetrazole	
 **1**	9.25 (1H, s, H-5); 10.05 (1H, s, H tetrazole); 14.80 (1H, br. s, NH)	135.6	128.0 (br. s)	132.5	145.4	−22.6
 **2**	9.15 (1H, s, H-5); 14.69 (1H, br. s, NH)	132.3	133.5 (br. s)	132.0	148.0	−20.8
 **5**$^{\ominus}$	6.79 (1H, s, H-4); 8.05 (1H, s, H-5); 9.98 (1H, s, H tetrazole)	142.8	97.8	131.6	142.2	–
 **7**	7.70 (1H, s, H-4); 10.10 (1H, s, H tetrazole)	152.0 (br. s)	96.6	139.6	143.4	−27.4
 **9**	6.89 (1H, s, H-4); 8.01 (1H, s, H-5); 13.58 (1H, br. s, NH); 16.82 (1H, br. s, NH)	137.1	104.9	130.9	150.2	–
 **12**	7.50 (1H, s, H-4); 13.28 (1H, br. s, NH)	156.0 (br. s)	101.9	131.8	149.1	–16.5
 **13**	5.55 (2H, s, NH_2); 5.70 (1H, s, H-4); 9.85 (1H, s, H tetrazole); 12.00 (1H, br. s, NH)	150.0	80.0	142.5	141.6	–
 **14**	5.50 (2H, br. s, NH_2); 5.87 (1H, s, H-4); 12.20 (1H, br. s, NH)	150.5	87.3	136.3	150.1	–
 **15**	10.00 (s, H tetrazole)	143.4	116.8 (br. s)	136.1	145.8	−20.2
 **16**	–	140.0	125.5 (br. s)	130.4	147.4	−28.2
 **17**	7.30 (2H, s, NH_2); 9.04 (1H, s, H-5); 10.02 (1H, s, H tetrazole)	131.9	126.0 (br. s)	131.2	145.4	−24.6
 **18a**	7.44 (2H, s, NH_2); 7.74 (1H, s, H-4); 10.07 (1H, s, H tetrazole)	135.9	97.3	142.4 (br. s)	142.8	−30.1
 **18b**	7.13 (2H, s, NH_2); 7.71 (1H, s, H-4); 9.98 (1H, s, H tetrazole)	149.8 (br. s)	99.2	131.6	145.3	−24.8

this nitro group. This downfield shift was ~28–30 ppm for the C-4 atom of pyrazole ring and somewhat less (19–20 ppm) for the C-3 atom, corresponding to the typical trends in monocyclic nitropyrazoles.[3] The replacement of 3(5)-nitro group with an amino group practically did not affect the chemical shift of the carbon atom bearing these groups, but led to an upfield shift of the adjacent C-4 carbon signal by 14–16 ppm.

The introduction of a nitro group at the C-4 carbon atom and NH_2 group in 3(5)-aminopyrazoles **13**, **14** caused a strong downfield shift of the C-4 carbon signal by 36–38 ppm in the spectra of the respective products **15**, **16** and a simultaneous upfield shift by 6–11 ppm for the signal of carbon atom bearing the $NHNO_2$ group. Analogous spectral features were observed by us in the series of monocyclic nitropyrazoles: $\Delta|\delta(\underline{C}NH_2) - \delta(\underline{C}NHNO_2)| = 9–13$ ppm.[28]

The interpretation of NMR signals and structural characterization of the *N*-amino derivatives **17**, **18a**,**b** was based on the trend that we previously identified in the case of the analogous *N*-amino derivatives of 3(5)-furazanyl-

nitropyrazoles,[12] according to which Δ|δ(C-3) – δ(C-5)| is about 1 ppm for 4-nitro regioisomers with distant C- and N-substituents. However, this difference in the case of 3(5)-nitro regioisomers was smaller by 10–12 ppm, compared to *N*-amino derivatives with adjacent C- and N-substituents. The applicability of this rule for compounds **18b** was confirmed by using ^{1}H–^{1}H NOESY 2D NMR experiments, which showed a correlation between the H-5 hydrogen atom of the tetrazole ring (δ 9.98 ppm) and the hydrogen atoms of *N*-amino group, pointing to their spatial proximity (Fig. 2). Such a correlation was absent in the other isomer of this pair, compound **18a**.

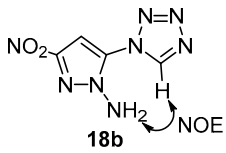


Figure 2. Scheme of correlations in ^{1}H–^{1}H NOESY spectrum of compound **18b**.

The structures of compounds **1** and **17** were also unequivocally proved by X-ray structural analysis. For both of the compounds, the symmetrically independent part of crystallographic unit cell contained a single molecule, the general views of which are presented in Figure 3. The nitro group in the molecule of compound **1** was coplanar with the pyrazole ring, while the tetrazole ring was rotated by 49°. The distribution of bond lengths within the pyrazole ring indicated preferred delocalization of the electron density distribution between the N(1) atom and the nitro group (Table 2). When changing from compound **1** to its amino derivative **17**, the nitro group did not change its orientation. The amino group was rotated perpendicularly to the ring, as in the previously studied *N*-amino-heterocycles.[12,21,25,26,29] The bond length distribution in the pyrazole ring of compounds **1** and **17** changed insignificantly: the delocalization between the N(1) atom and nitro group was somewhat weaker, and the C(2)–C(3) bond was shorter. The latter fact may be related to the different orientation of the tetrazole ring, which was rotated perpendicularly to the pyrazole ring in compound **17**. Such a rotation was apparently caused by the crystal packing and probably could not be attributed to the steric effect of the amino group.

In order to explain the observed orientation of the tetrazole ring, we performed conformational analysis of a molecule of compound **1** by varying the torsion angle C(2)–C(3)–N(3)–C(4) from 0 to 180° (the symmetrically independent range for this angle) with a step of 10°. These and the following calculations were carried out at the M052X/aug-cc-pvdz level of approximation that we previously used with success for the calculation of the spatial structure of nitrogen-containing heterocycles and polynitro compounds.[30] The analysis of intramolecular contacts, their energy and charge distribution was performed within the framework of the Bader's topological theory.[31]

The dependence of conformational energy on the value of C(2)–C(3)–N(3)–C(4) angle is presented in Figure 4.

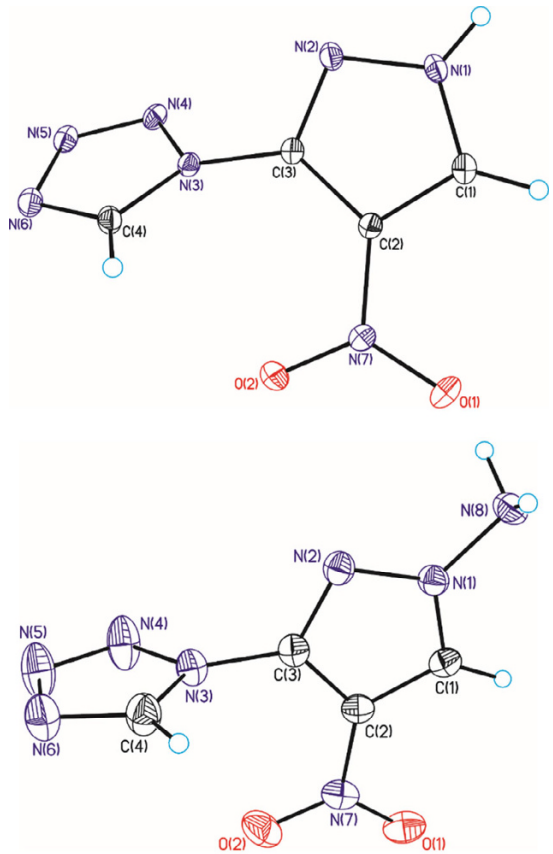


Figure 3. The molecular structures of compounds **1** (top) and **17** (bottom) with atoms represented by thermal vibration ellipsoids of 50% probability.

Only when the angle approached 180°, there was some increase of conformational energy (caused by steric effects), while the energy differences in the range of 0–160° did not exceed 1.5 kcal/mol, which was on the order of intermolecular interaction energy. To explain the preference for a non-planar conformation both in the crystal structure and in isolated molecule, a full geometry optimization was performed without restrictions at the variable torsion angle. Topological analysis showed that the non-planar structure was stabilized by the non-bonded *n*–π* interaction between the nitro group and tetrazole ring (Supplementary information file). It can be concluded that in the case of compound **1** the crystal structure was mostly determined by intramolecular forces, while the crystal

Table 2. Bond lengths (Å) in the pyrazole ring and the relative orientation of rings (in degrees) in molecules **1** and **17**

Bond or angle	Compound **1**	Compound **17**
C(3)–N(3)	1.410(2)	1.412(2)
N(1)–C(1)	1.333(2)	1.336(2)
C(1)–C(2)	1.383(2)	1.377(2)
C(2)–C(3)	1.411(2)	1.405(2)
C(3)–N(2)	1.323(2)	1.324(2)
N(1)–N(2)	1.359(2)	1.359(2)
C(2)–C(3)–N(3)–C(4)	49.0(2)	–91.1(2)

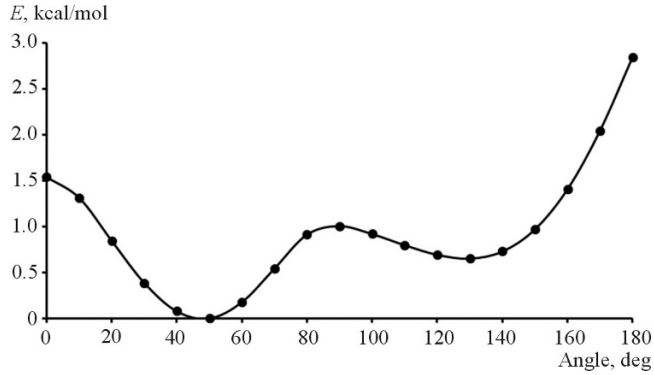


Figure 4. The dependence of relative conformational energy (*E*) on the value of C(2)–C(3)–N(3)–C(4) torsion angle in compound **1**.

structure of compound **17** largely depended on the crystal packing effects.

Finally, it should be noted that this study has resulted in the development of new, effective methods for the synthesis of *N*-unsubstituted isomeric 1-(nitro-1*H*-pyrazol-3(5)-yl)-1*H*-tetrazoles and 5-(nitro-1*H*-pyrazol-3(5)-yl)-tetrazoles, based on *C*- and *N*-nitration of pyrazole ring. As a result of studying the *N*-amination of 4- and 3(5)-nitro derivatives, we established for the first time the strong orienting influence of an electron-withdrawing 3(5)-substituent in the pyrazole ring, which was comparable to the effect of a nitro group. The trends of NMR chemical shifts characteristic for regioisomeric nitro derivatives have been identified, and can be used in the future for establishing the structure of more complex compounds.

Experimental

IR spectra were recorded on a Bruker ALPHA spectrometer for KBr pellets. ^{13}C NMR spectrum of compound **15** was acquired on a Bruker AV-600 instrument at 150 MHz frequency, 2D ^{1}H–^{1}H NOESY NMR spectra of compounds **18a**,**b** were acquired on a Bruker DRX-500 instrument (500 MHz). The rest of ^{1}H, ^{13}C, and ^{14}N NMR spectra were acquired on a Bruker AM-300 instrument (300, 75, and 21 MHz, respectively) in DMSO-d_6 at 25°C. The chemical shifts of ^{1}H and ^{13}C atoms are reported relative to TMS, for ^{14}N atoms – relative to $MeNO_2$ (δ 0.0 ppm). Mass spectra were recorded on a Finnigan MAT Incos 50 instrument (direct introduction of sample, EI, 70 eV). High-resolution mass spectra with electrospray ionization were recorded on a Bruker MicroOTOFII instrument. Elemental analysis was performed on a Perkin Elmer Series II 2400 instrument. Melting points and the onset decomposition temperatures for compounds **1**, **2**, **7**, **12**, **15**, and **16** were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on a NETZSCH STA 449 F3 Jupiter apparatus at the heating rate of 5°/min (see the Supplementary information file). Melting points of the rest of the compounds were determined by Kofler method on a Boetius hot stage (at 4°/min heating rate) and were not corrected. The progress of the reactions and purity of the obtained compounds were controlled by TLC on Merck Silicagel 60 F_{254} plates. The starting 1-(1*H*-pyrazol-3(5)-yl)-1*H*-tetrazole (**5**) and 1-(1-nitro-1*H*-pyrazol-3(5)-yl)-1*H*-tetrazole (**6**) were obtained according to our previously developed procedure,[9] 3(5)-cyanopyrazole (**8**) – according to a published procedure.[18]

Synthesis of compounds 1 and 2 by nitration of the respective pyrazolyltetrazoles 5 and 9 (General method). The appropriate pyrazolyltetrazole **5** or **9** (2.00 g, 15 mmol) was added to a mixture of 92% H_2SO_4 (10 ml), concd HNO_3 (1.5 ml), and H_2O (0.6 ml) at 5–10°C. In the case of compound **1** the reaction mixture was stirred for 5 h at 5–10°C, while in the case of compound **2** it was stirred for 24 h at room temperature. The reaction mixture was poured into ice water (50 ml), the precipitate that formed was filtered off, washed with cold water, and air-dried.

1-(4-Nitro-1*H*-pyrazol-3(5)-yl)-1*H*-tetrazole (1). Yield 2.42 g (91%), light-yellow plates, decomp. temp. 199°C (EtOH–H_2O, 1:1) (mp 208–209°C).[9]

5-(4-Nitro-1*H*-pyrazol-3(5)-yl)tetrazole (2). Yield 2.19 g (82%), white powder, decomp. temp. 240°C (EtOH) (mp 239–240°C[14]). Mass spectrum, *m*/*z*: 181 $[M]^+$, 153 $[M–N_2]^+$. Found, %: C 26.67; H 1.63; N 54.09. $C_4H_3N_7O_2$. Calculated, %: C 26.53; H 1.67; N 54.14.

1-(5(3)-Nitro-1*H*-pyrazol-3(5)-yl)-1*H*-tetrazole (7). Pyrazole **6** (10.8 g, 59.7 mmol) was added to tetrachloroethene (600 ml); the mixture was heated to 120°C and maintained at this temperature for 10 h. The reaction mixture was cooled, the precipitate that formed was filtered off and dissolved in water (100 ml) containing $NaHCO_3$ (10 g), and the undissolved residue of pyrazole **6** was removed by filtration. The aqueous solution was acidified with concd HCl to pH 1, extracted with Et_2O (4×100 ml) and the organic layer was dried over Na_2SO_4. The solvent was removed at reduced pressure to ~100 ml. The precipitate that formed was filtered off and air-dried. Yield 8.2 g (76%), yellow powder, decomp. temp. 179°C (EtOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 3126 (m), 2799 (w), 2748 (w), 1551 (s), 1505 (s), 1493 (s), 1459 (m), 1398 (s), 1369 (w), 1350 (s), 1214 (m), 1088 (m), 946 (m), 816 (m). Mass spectrum, *m*/*z*: 182 $[M+H]^+$. Found, %: C 26.62; H 1.61; N 54.21. $C_4H_3N_7O_2$. Calculated, %: C 26.53; H 1.67; N 54.14.

1-Nitro-1*H*-pyrazole-3-carbonitrile (10). A solution of 3(5)-cyanopyrazole (**8**) (0.93 g, 0.01 mol) in TFA (10 ml) was cooled to 5−10°C and treated by dropwise addition of HNO_3 (1.68 ml, 0.04 mol, ρ 1.50 g/cm^3) and acetic anhydride (3.8 ml, 0.04 mol). The reaction mixture was stirred at this temperature for 2 h and then poured into ice water (100 ml). The precipitate that formed was filtered off and washed with cold water. The filtrate was extracted with CH_2Cl_2 (3×50 ml), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, providing the second crop of the product. Both precipitates were combined and recrystallized from $CHCl_3$. Yield 1.10 g (80%), white powder, mp 107–109°C. IR spectrum, ν, cm^{-1}: 3167 (w), 3154 (w), 3138 (m), 2251 (w), 1639 (s), 1337 (w), 1296 (s), 1263 (s), 1132 (s), 1045 (m), 826 (m), 775 (m). ^{1}H NMR spectrum, δ, ppm: 9.01 (1H, s, H-5); 7.38 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 128.5 (C-3); 124.6 (C-5); 113.4 (C-4); 112.4 (CN). ^{14}N NMR

spectrum, δ, ppm: −62.17 ($N\underline{N}O_2$). Mass spectrum, *m*/*z*: 138 $[M]^+$. Found, %: C 34.84; H 1.30; N 40.55. $C_4H_2N_4O_2$. Calculated, %: C 34.79; H 1.46; N 40.57.

3(5)-Nitro-1*H*-pyrazol-5(3)-carbonitrile (11). Pyrazole **10** (5.0 g, 36 mmol) was added to tetrachloroethane (50 ml), the mixture was heated to 120°C and maintained at this temperature for 4 h, then the temperature was elevated to 140°C, and the mixture was refluxed for 10 h. The reaction mixture was cooled, the precipitate that formed was filtered off, recrystallized from water with activated carbon, and air-dried. Yield 3.2 g (64%), mp 151–153°C (H_2O). IR spectrum, ν, cm^{-1}: 3244 (vs), 3165 (m), 2255 (w), 1571 (s), 1550 (s), 1467 (w), 1401 (m), 1340 (s), 1280 (m), 992 (m), 834 (w), 758 (m). ^1H NMR spectrum, δ, ppm: 8.01 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 154.4 (br. s, C-3); 117.6 (C-5); 110.4 (CN); 109.8 (C-4). ^{14}N NMR spectrum, δ, ppm: −23.50 (NO_2). Mass spectrum, *m*/*z*: 138 $[M]^+$. Found, %: C 34.78; H 1.36; N 40.80. $C_4H_2N_4O_2$. Calculated, %: C 34.79; H 1.46; N 40.57.

Synthesis of compounds 9 and 12 from the respective cyanopyrazoles 8 and 11 (General method). A mixture of cyanopyrazole **8** or **11** (0.05 mol), NaN_3 (4.23 g, 0.065 mol), triethylamine hydrochloride (8.94 g, 0.065 mol), and toluene (150 ml) was refluxed for 10 h in the case of compound **9** or 8 h in the case of compound **12**. The reaction mixture was cooled, stirred, and diluted with H_2O (200–500 ml) until complete dissolution of the precipitate. The aqueous layer was separated and acidified with HCl to pH 1–2. The precipitate that formed was filtered off, washed with cold water, and air-dried. In the case of compound **12**, the filtrate was additionally extracted with EtOAc (3×50 ml), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, providing a second crop of the product. Both precipitates were combined and air-dried.

5-(1*H*-Pyrazol-3(5)-yl)tetrazole (9). Yield 5.37 g (79%), decomp. temp. 272–274°C (EtOH). IR spectrum, ν, cm^{-1}: 3379 (s), 3222 (s), 3125 (s), 2975 (m), 2870 (m), 2757 (m), 2637 (s), 2520 (m), 1871 (vs), 1614 (s), 1456 (s), 1347 (w), 1223 (m), 1196 (m), 1068 (s), 1034 (s), 942 (m), 922 (m), 782 (s), 750 (s), 709 (m), 608 (m). Mass spectrum, *m*/*z*: 136 $[M]^+$. Found, %: C 35.24; H 2.96; N 61.42. $C_4H_4N_6$. Calculated, %: C 35.30; H 2.96; N 61.74.

5-(3(5)-Nitro-1*H*-pyrazol-5(3)-yl)tetrazole (12). Yield 9.05 g (90%), decomp. temp. 233°C (EtOH). IR spectrum, ν, cm^{-1}: 3613 (m), 3475 (vs), 3135 (s), 3078 (s), 2879 (s), 2756 (m), 2003 (m), 1544 (s), 1477 (w), 1378 (s), 1350 (s), 1209 (w), 1024 (m), 1000 (m), 832 (w). Mass spectrum, *m*/*z*: 181 $[M]^+$. Found, %: C 26.64; H 1.69; N 54.22. $C_4H_3N_7O_2$. Calculated, %: C 26.53; H 1.67; N 54.14.

Synthesis of compounds 13 and 14 by reduction of pyrazolyltetrazoles 7 and 12 (General method). A mixture of nitro derivative **7** or **12** (5.43 g, 0.03 mol), hydrazine hydrate (5.8 ml, 0.12 mol), $FeCl_3·6H_2O$ (0.042 g), and activated carbon (0.53 g) in 1:1 EtOH–H_2O mixture (190 ml) was refluxed for 9 h. The activated carbon was removed from the reaction mixture by filtration, the filtrate was evaporated under vacuum. The obtained residue was dissolved in water and acidified with HCl to pH 3–4. The precipitate that formed was filtered off, washed with cold water, and air-dried.

1-(3(5)-Amino-1*H*-pyrazol-5(3)-yl)-1*H*-tetrazole (13). Yield 2.72 g (60%), decomp. temp. 215–216°C (EtOH–H_2O). IR spectrum, ν, cm^{-1}: 3387 (vs), 3349 (s), 3273 (s), 2302 (s), 2121 (s), 1661 (m), 1638 (s), 1613 (vs), 1599 (vs), 1548 (s), 1527 (s), 1454 (w), 1437 (w), 1211 (m), 1197 (w), 1095 (m), 1022 (w), 968 (w), 948 (m), 730 (m), 674 (m), 570 (w). Found, *m*/*z*: 152.0677 $[M+H]^+$. $C_4H_6N_7$. Calculated, *m*/*z*: 152.0679. Found, %: C 31.49; H 3.21; N 64.64. $C_4H_5N_7$. Calculated, %: C 31.79; H 3.33; N 64.88.

5-(3(5)-Amino-1*H*-pyrazol-5(3)-yl)tetrazole (14). Yield 3.90 g (86%), decomp. temp. 286–288°C (EtOH–H_2O). IR spectrum, ν, cm^{-1}: 3327 (vs), 3160 (vs), 2926 (vs), 2738 (vs), 1662 (s), 1611 (m), 1514 (w), 1450 (m), 1401 (w), 1365 (m), 1212 (w), 1003 (w), 803 (m), 677 (m). Mass spectrum, *m*/*z*: 151 $[M]^+$. Found, %: C 29.86; H 3.77; N 60.00. $C_4H_4N_7·2/3H_2O$. Calculated, %: C 29.45; H 3.91, N 60.10.

Synthesis of compounds 15 and 16 by nitration of aminopyrazoles 13 and 14 (General method). A solution of amine **13** or **14** (1.0 g, 5.1 mol) in TFA (15 ml) was cooled to 5–10°C and treated by dropwise addition of HNO_3 (ρ 1.50 g/cm^3, 1.5 ml). The mixture was maintained at 0–5°C for 2 h, the precipitate that formed was filtered off, washed with cold TFA (3 ml), and dried over P_2O_5 in vacuum.

1-(3(5)-Nitramino-4-nitro-1*H*-pyrazol-5(3)-yl)-1*H*-tetrazole (15). Yield 0.82 g (51%), cream colored powder, decomp. temp. 169°C (H_2O–TFA). IR spectrum, ν, cm^{-1}: 3230 (s), 3140 (s), 2665 (w), 1625 (vs), 1587 (vs), 1495 (s), 1455 (m), 1399 (m), 1338 (vs), 1289 (w), 1245 (vs), 1204 (m), 1175 (w), 1154 (m), 1105 (s), 1004 (s), 978 (w), 899 (w), 848 (m), 778 (w), 761 (m), 747 (w), 642 (w). Found, *m*/*z*: 242.0383 $[M+H]^+$. $C_4H_4N_9O_4$. Calculated, *m*/*z*: 242.0381. Found, %: C 19.43; H 1.08; N 52.02. $C_4H_3N_9O_4$. Calculated, %: C 19.92; H 1.25; N 52.28.

5-(3(5)-Nitramino-4-nitro-1*H*-pyrazol-5(3)-yl)tetrazole (16). Yield 1.32 g (83%), cream colored powder, decomp. temp. 170°C (H_2O–TFA). IR spectrum, ν, cm^{-1}: 3291 (m), 3119 (w), 2678 (w), 1602 (vs), 1520 (m), 1495 (m), 1448 (w), 1383 (m), 1347 (s), 1277 (s), 1159 (m), 1079 (m), 1019 (w), 1008 (w), 978 (w), 869 (w), 814 (w), 764 (w), 647 (w), 569 (m). Found, *m*/*z*: 240.0234 $[M–H]^+$. $C_4H_2N_9O_4$. Calculated, *m*/*z*: 240.0236.

Synthesis of compounds 17 and 18a,b by *N*-amination of pyrazolyltetrazoles 1 and 7 (General method). The appropriate pyrazole **1** or **7** (0.46 g, 2.56 mmol) was added to a mixture of NaOH (0.82 g, 0.02 mol) and K_2HPO_4 (1.40 g, 0.01 mol) in H_2O (13 ml). The obtained mixture was stirred for 10 min at 20°C, followed by the addition of hydroxylamine-*O*-sulfonic acid (0.87 g, 7.7 mmol). The mixture was heated to 60°C and stirred for 6 h in the case of compound **17** or for 21 h in the case of compounds **18**. The precipitate that formed was filtered off and washed with water. The filtrate was extracted with EtOAc (2×25 ml), the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure until the formation of a solid residue. Compound **17** was crystallized from CH_2Cl_2. In the case of compounds **18**,

the organic layer was additionlly washed with a saturated solution of $NaHCO_3$ in order to remove the unreacted pyrazole **7**. The obtained product (0.32 g, 55% yield) contained two isomers of the *N*-amino derivatives **18a** and **18b** in a 6:5 ratio. The obtained isomers were separated by silica gel column chromatography (eluent $CHCl_3$).

1-(1-Amino-4-nitro-1*H*-pyrazol-3-yl)-1*H*-tetrazole (17). Yield 0.50 g (86%), light-yellow prismatic crystals, mp 151–152°C (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 3318 (s), 3213 (m), 3143 (w), 3107 (m), 1643 (w), 1576 (s), 1531 (s), 1515 (s), 1480 (m), 1454 (m), 1394 (m), 1337 (s), 1274 (m), 1234 (m), 1194 (m), 1174 (m), 1092 (m), 1042 (w), 1015 (m), 882 (w), 829 (m), 757 (m), 677 (w), 620 (m), 441 (w). Found, *m/z*: 197.0532 $[M+H]^+$. $C_4H_5N_8O_2$. Calculated, *m/z*: 197.0535. Found, %: C 24.38; H 1.85; N 56.97. $C_4H_4N_8O_2$. Calculated, %: C 24.50; H 2.06; N 57.13.

1-(1-Amino-5-nitro-1*H*-pyrazol-3-yl)-1*H*-tetrazole (18a). Yield 0.17 g (29%), light-yellow needles, mp 122–123°C ($CHCl_3$–MeOH, 10:1). R_f 0.43 ($CHCl_3$–MeOH, 10:1). IR spectrum, ν, cm^{-1}: 3307 (s), 3144 (s), 2928 (m), 1729 (w), 1625 (w), 1542 (s), 1505 (s), 1356 (s), 1329 (s), 1265 (m), 1181 (w), 1125 (m), 1093 (m), 1072 (m), 1018 (w), 971 (w), 945 (w), 870 (w), 841 (m), 817 (m), 745 (w). Found, *m/z*: 219.0351 $[M+Na]^+$. $C_4H_4N_8NaO_2$. Calculated, *m/z*: 219.0350. Found, %: C 24.36; H 1.93; N 56.37. $C_4H_4N_8O_2$. Calculated, %: C 24.50; H 2.06; N 57.13.

1-(1-Amino-3-nitro-1*H*-pyrazol-5-yl)-1*H*-tetrazole (18b). Yield 0.15 g (26%), yellow rhombic crystals, mp 131–132°C ($CHCl_3$–MeOH, 10:1). R_f 0.49 ($CHCl_3$–MeOH, 10:1). IR spectrum, ν, cm^{-1}: 3314 (m), 3216 (w), 3153 (w), 2924 (w), 1647 (w), 1589 (m), 1543 (s), 1501 (m), 1461 (w), 1416 (m), 1364 (s), 1320 (m), 1199 (w), 1117 (m), 1088 (w), 994 (m), 869 (w), 829 (m), 810 (m), 754 (w), 735 (m), 637 (w). Found, *m/z*: 197.0535 $[M+H]^+$. $C_4H_5N_8O_2$. Calculated, *m/z*: 197.0530. Found, %: C 24.71; H 2.08; N 56.58. $C_4H_4N_8O_2$. Calculated, %: C 24.50; H 2.06, N 57.13.

Quantum-chemical calculations were performed with the Gaussian software,[32] the electron density topology calculations were performed with the AIMALL program.[33]

X-ray structural analysis of compounds **1** and **17** was performed on a Bruker Kappa APEX II CCD diffractometer (λ(Mo*K*α) 0.71073 Å, graphite monochromator, ω-scanning) at 100 K and 298 K. The structures were solved by direct method and refined by full-matrix method of least squares in anisotropic approximation for non-hydrogen atoms by F_{hkl}^2. The hydrogen atom positions were calculated from differential synthesis of electronic density and refined in isotropic approximation. The processing of starting matrices, solving and refinement of structures were performed with APEX2[34] and SHELXTL software suites.[35] The main crystallographic parameters are presented in Table SI1 (Supplementary information file).

The Supplementary information file containing the crystallographic data for compounds **1** and **17**, quantum-chemical calculations for compounds **1**, **17** and their analogs, as well as DCS/TGA data for compounds **1**, **2**, **7**, **12**, **15**, **16** is available from the journal website at http://link.springer.com/journal/10593.

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