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Synthesis of 4,4'-dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-diamine

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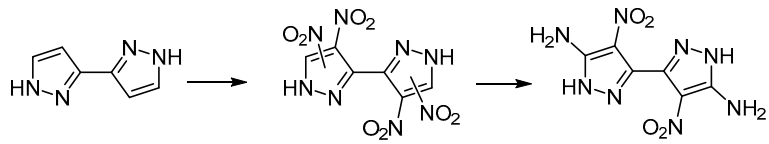


All of the synthetically accessible symmetric tetranitro-3,3'-bipyrazoles were prepared. On their basis, a method was developed for the synthesis of 4,4'-dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-diamine and its nitration was studied.

Keywords: bipyrazole, diaminodinitrobipyrazole, tetranitrobipyrazole, *cine*-substitution, nitration, nucleophilic substitution.

In recent decades there has been a significant increase of interest toward the chemistry of high-energy compounds. One of the promising directions in this area of study has been the synthesis and characterization of polynitrogen heterocycles as the basis for the design of new, safe and environmentally benign energetic materials. Nitro derivatives of pyrazole have been recognized as desirable templates for the creation of promising energetic compounds due to the suitable combination of high energy content, sensitivity, and thermal stability.[1–3] Furthermore, while earlier studies were typically focused on monocyclic pyrazole derivatives, currently there is an increase in the number of studies devoted to pyrazole-containing bi- and polycyclic systems.[4–6] Among energetic nitropyrazole derivatives, aminonitropyrazoles are of significant interest. The presence of an amino group not only improves the thermal stability and in many cases also the density of such compounds, but also provides opportunities for the introduction of additional energetic functional groups.[7]

In the series of *N*-unsubstituted monocyclic pyrazoles, all of the possible *C*-mono- and dinitro derivatives containing a C–NH_2 group were obtained, some of which (4-amino-3,5-dinitropyrazole (LLM-116), 5-amino-3,4-dinitropyrazole) are of interest as energetic compounds with low impact and friction sensitivity.[1,2c,8] At the same time, there are no literature precedents for the synthesis of their bicyclic analogs – *C*-aminonitropyrazoles, consisting of several pyrazole rings linked by a C–C bond.

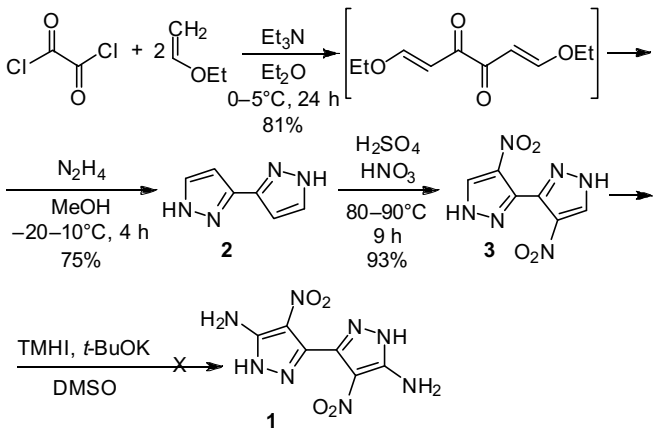
In a continuation of our efforts toward the synthesis and reactivity studies of *C*- and *N*-(hetaryl)nitropyrazoles,[4,9] the current report describes the synthesis of one such representative, 4,4'-dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-diamine (**1**) (Scheme 1). In our opinion and on the basis of available data on the chemistry of nitropyrazoles,[10] the following methods were deemed to be most suitable for the introduction of amino group in a pyrazole ring: vicarious nucleophilic substitution of hydrogen atom, *cine*-substitution of an *N*-nitro group, Hofmann rearrangement of amide group, reduction of a nitro group, and nucleophilic *ipso*-substitution of a nitro group.

We started our study from vicarious nucleophilic substitution of hydrogen atom. Such direct introduction of amino group at the *ortho* position relative to the nitro group in aromatic systems has been quite well described.[11] The starting compound selected for implementing this strategy was unsubstituted 3,3'-bipyrazole (**2**), which was synthesized in two steps according to a published procedure from oxalyl chloride and ethyl vinyl ether (Scheme 1).[12] Direct acidic nitration of bipyrazole **2** by heating in a mixture of concentrated sulfuric and nitric acids resulted in the introduction of two nitro groups at positions 4 of both pyrazole rings. Complete conversion of the starting bipyrazole was achieved in 9 h, with 93% yield of the product.

However, it was found that vicarious nucleophilic substitution was not successful for the introduction of

amino group in bipyrazole **3**. The employed conditions, which were previously effective for the amination of 3,4-dinitropyrazole,[7b] namely, treatment of bipyrazole **3** with trimethylhydrazinium iodide (TMHI) in the presence of *t*-BuOK as a base, did not result in the formation of diamino derivative **1** (Scheme 1).

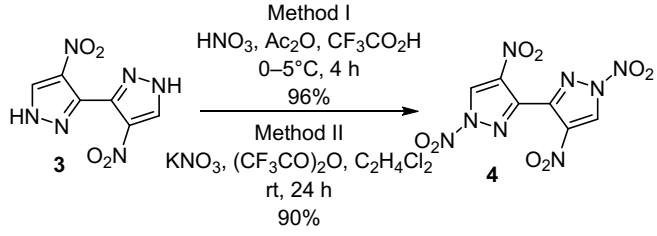
Scheme 1



Nucleophilic *cine*-substitution of *N*-nitro group in 1,4-dinitropyrazoles has been widely used for the introduction of not only amino groups, but also for other substituents at position 5(3) of the pyrazole ring.[6c,13,14] Thus, for example, 5-amino-3-methyl-4-nitropyrazole was formed by the action of ammonia on 3-methyl-1,4-dinitropyrazole.[13]

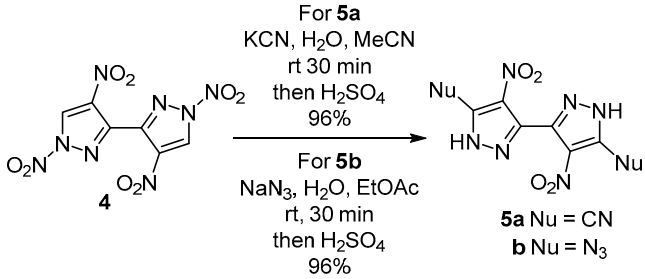
Two methods were used for the preparation of *N*-nitrobipyrazole **4**. The most common method, which we successfully used in the case of bicyclic pyrazolylazoles,[9d] involves the treatment of the starting bipyrazole **3** with acetyl nitrate in trifluoroacetic acid (Scheme 2, method I). This procedure provided a high yield of the only symmetrical isomer **4** containing *N*-nitro groups at the maximum possible distance from both the *C*-nitro group and the second pyrazole ring. Such structure of bicyclic *N*-nitropyrazole allows it to participate in *cine*-substitution reaction. The *N*-nitration of bipyrazole **3** under nonacidic conditions was performed with potassium or ammonium nitrates in the presence of $(CF_3CO)_2O$, using CH_2Cl_2 or 1,2-dichloroethane as solvent. The reaction at room temperature was complete in 1 day and also provided compound **4** as the sole product in a good yield (Scheme 2, method II).

Scheme 2



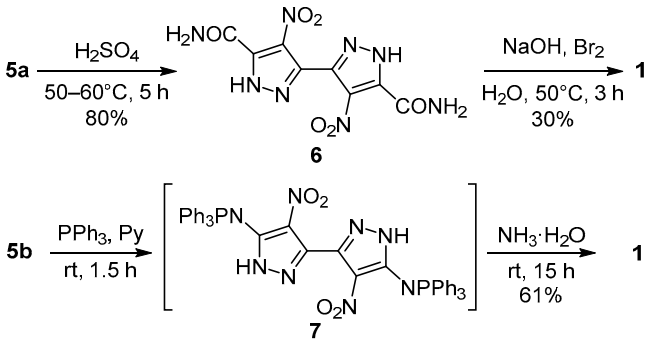
However, the treatment of *N*-dinitrobipyrazole **4** with ammonia in various solvents (EtOH, MeOH, $CHCl_3$, CH_2Cl_2) and over a wide range of temperature (from –30 to +20°C) led only to its decomposition. Therefore, another method was proposed for the preparation of diamino derivative **1**, which also was analogous to a literature precedent:[15] *cine*-substitution of *N*-nitro group with a suitable nucleophile and conversion of the introduced functional group to an amino group. We found that *N*-dinitrobipyrazole **4** in the presence of anionic C- and N-nucleophiles under mild conditions underwent a *cine*-substitution reaction, providing 5,5'-disubstituted derivatives **5a**,**b** in high yields (Scheme 3).

Scheme 3



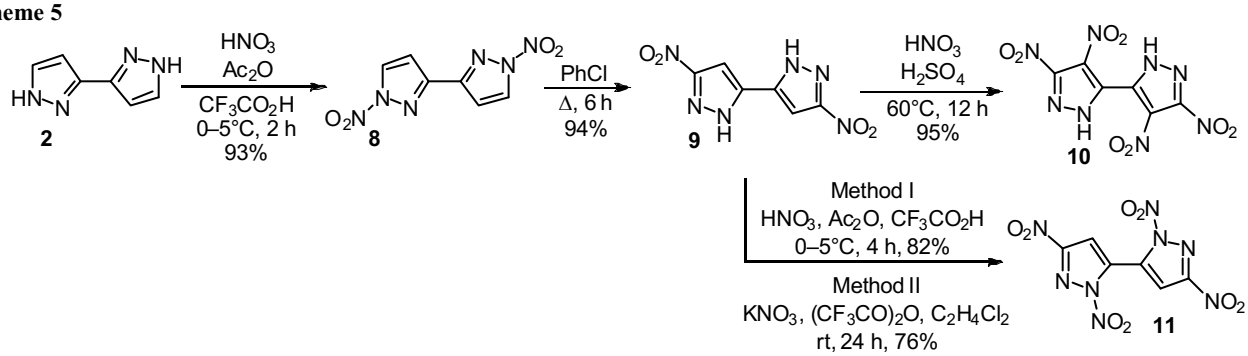
Acidic hydrolysis of the cyano groups in bipyrazole **5a** with mild heating for 5 h in concentrated sulfuric acid gave good yield of amide **6** (Scheme 4). We further studied the Hofmann rearrangement of amide **6**. The target amine **1** was obtained in a satisfactory yield by treatment of amide **6** with aqueous sodium hypobromite, that is, under the conditions previously developed by us for the preparation of monocyclic aminonitro- and aminodinitropyrazoles.[3d,16] There are also literature reports on transformations of azidopyrazoles to aminopyrazoles.[15,17] Diazide **5b** was treated with triphenylphosphine under the conditions of Staudinger reaction,[18] while phosphazine intermediate **7** hydrolyzed without isolation using aqueous ammonia solution, which led to the formation of the desired diamine **1** in a moderate yield.

Scheme 4



Another generally reliable method for the introduction of amino groups in a pyrazole ring is the transformation of nitro groups, which can be accomplished by two routes: nitro group reduction[10a] or its nucleophilic substitution.[10a,19] Suitable starting compounds include tetranitrobipyrazole **10**, which was first synthesized by our group.[20] Its synthesis was recently reproduced in 32% overall yield.[7a] By optimizing the synthetic procedure for the preparation of bipyrazole **10**, we improved its overall yield to 83%

Scheme 5

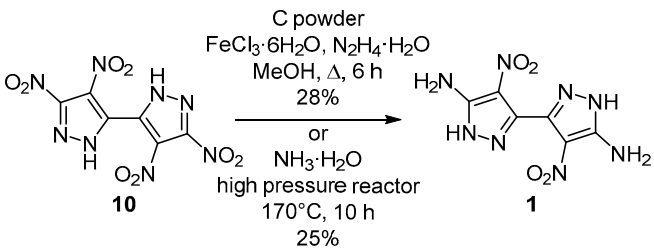


(Scheme 5). According to spectrophotometric data (H_2O, 20°C), tetranitrobipyrazole **10** is a relatively strong dibasic NH acid with pKa_1 1.80 and pKa_2 4.70 (for 3,4-dinitropyrazole p*K*a 5.48[21]).

It should be noted that the ability of *N*-nitropyrazoles to act as exogenous NO donors was discovered relatively recently.[22] At the same time, only a few pyrazoles are known that simultaneously contain two N–NO_2 groups. In order to expand the synthetic access to this uncommon type of *N*-nitropyrazoles, the possibilities for *N*-nitration were studied for an isomer of bipyrazole **3** – 5,5'-dinitro-2*H*,2'*H*-3,3'-bipyrazole (**9**). It was shown that, despite the presence of a bulky nitropyrazole substituent at position 3 and similarly to the case of 3-azolyl-5-nitropyrazoles,[9e] the direction of *N*-nitration was determined by the C-nitro group, and only symmetrical isomer **11** was formed (Scheme 5).

Selective reduction of nitro groups at the position C-5 of bipyrazole **10** was achieved by using hydrazine on activated carbon in the presence of $FeCl_3$ as a catalyst[23] (Scheme 6). The process was complicated by the occurrence of side reactions and poor solubility of product **1**, which may explain its mediocre yield.

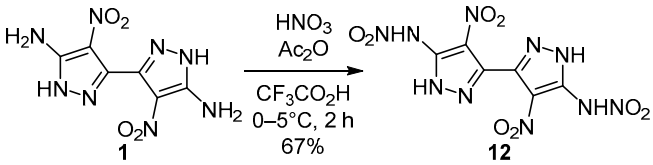
Scheme 6



We have previously studied in detail the nucleophilic substitution of nitro group in monocyclic nitropyrazoles. In particular, in the case of *N*-unsubstituted 3(5),4-dinitropyrazoles, a bicyclic analog of which is tetranitrobipyrazole **10**, the reaction proceeded in anionic form with the formation of 3(5)-substituted products.[24] At the same time, the presence of a strongly electron-withdrawing substituent at position 3 (namely, the dinitropyrazole moiety) could alter the direction of nucleophilic substitution, as it was observed for 3,4,5-trinitropyrazole, where the nitro groups at position 4 were substituted.[19a,b] We found that the nucleophilic substitution of nitro group with an amino group in compound **10** proceeded under sufficiently forcing conditions (autoclave, 170°C) and resulted in selective substitution of both nitro groups at positions 5 and formation of the desired diamine **1** (Scheme 6). The mediocre yields of this product can be explained by the occurrence of polymerization as a side reaction, as indicated by the partial resinification, while diaminopyrazole **1** could only be isolated by column chromatography.

Nitramino derivatives of pyrazoles are known to be of interest as high-energy compounds.[1c] For this reason, we studied the possibilities for accomplishing *N*-nitration of aminobipyrazole **1**, which has several potential reactive sites for nitration: C-amino groups and endocyclic nitrogen atoms. We showed that aminobipyrazole **1** can be smoothly nitrated at the C-amino groups with acetyl nitrate in trifluoroacetic acid, giving a good yield of tetranitrodiamine **12** (Scheme 7). Such a change in the direction of reaction, compared to the nitration of compounds **3** and **9**, was associated with the presence of C-nitro group next to the amino group, and has been previously reported both for the nitration of monocyclic aminonitropyrazoles,[3d] as well as for the nitration of azolyl-substituted aminonitropyrazoles.[9a,b]

Scheme 7



The structures of the obtained compounds were established on the basis of mass spectrometry, IR and UV spectroscopy, as well as ^1H and ^{13}C NMR data. The assignment of pyrazole ring signals, including the determination of N-nitro group position, was performed on the basis of well-known trends in ^1H and ^{13}C NMR signals of pyrazoles, which we have previously described in our studies of nitropyrazoles.[3,4,15,19,24] According to these precedents,[10a] the chemical shifts of ^1H NMR signals for *N*-unsubstituted pyrazoles or their derivatives containing electron-withdrawing *N*-substituents are usually in the following order: δ(H-5) > δ(H-3) > δ(H-4). At the same time, the chemical shifts of ^{13}C NMR signals are in the following order: δ(C(3)=N(sp^2)) > δ(C(5)–N(sp^3)) > > δ(C-4). The broadened signals of carbon nuclei in these spectra are most commonly associated with ^{13}C–^{14}N quadrupole

interaction and correspond to the carbon atoms bearing a nitro group, which additionally supports their assignment.

Thus, we have obtained 4,4'-dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-diamine for the first time. Several methods for its synthesis were developed on the basis of either *cine*-substitution of *N*-nitro group in 1,1',4,4'-tetranitro-1*H*,1'*H*-3,3'-bipyrazole, as well as modification of C-nitro group in 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole. Bicyclic nitropyrazoles containing N-nitro- and C-nitramino moieties were also obtained for the first time.

Experimental

IR spectra were recorded on a Bruker Alpha spectrometer in KBr pellets. UV spectrum was recorded on a Specord UV-VIS spectrometer. ^{1}H, ^{13}C, and ^{14}N NMR spectra were acquired on a Bruker AM-300 instrument (300, 75, and 22 MHz, respectively) in DMSO-d_6 (unless indicated otherwise) at 299 K. The chemical shifts of ^{1}H and ^{13}C nuclei are reported relative to TMS, for ^{14}N nuclei – relative to $MeNO_2$. Mass spectra were recorded on a Finnigan MAT Incos 50 mass spectrometer with direct introduction of the samples (EI ionization, 70 eV). High-resolution mass spectra (electrospray ionization) were recorded on a Bruker microOTOF II instrument. Elemental analysis was performed on a PerkinElmer Series II 2400 instrument. Melting points were determined according to the Kofler method on a Boetius hot stage (heating rate 4°C/min) and were not corrected. The reaction progress and purity of the obtained compounds were controlled by TLC method on Merck Silicagel 60 F-254 plates.

The starting 3,3'-bipyrazole (**2**) was obtained according to a published procedure.[11]

4,4'-Dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-diamine (1). Preparation from azide **5b**. Ph_3P (1.24 g, 4.73 mmol) was added with stirring to a solution of azide **5b** (0.48 g, 1.57 mmol) in pyridine (7 ml) at 20–25°C. The reaction mixture was stirred for 1.5 h, then treated by dropise addition of 20% aqueous ammonia solution (5 ml) and maintained for 15 h. The reaction mixture was poured into H_2O (25 ml), washed with PhH (3×50 ml), then with Et_2O (3×50 ml). The aqueous layer was acidified with concentrated HCl to pH 1–2. The obtained precipitate was filtered off, yielding the first crop of the product. The filtrate was extracted with EtOAc (3×50 ml). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed by evaporation at reduced pressure, yielding the second crop of the product. The precipitates were combined and purified by silica gel flash column chromatography (eluent $CHCl_3$–MeOH, 3:1), R_f 0.25. Yield 0.24 g (61%), light-yellow powder, mp >360°C. IR spectrum, ν, cm^{-1}: 3426 (m), 3145 (m), 1662 (s), 1634 (m), 1449 (s), 1366 (s), 1201 (s), 1133 (m), 949 (w), 830 (m), 770 (m), 739 (w). ^{1}H NMR spectrum, δ, ppm: 12.49 (2H, br. s, NH pyrazole); 7.31 (2H, s, NH_2). ^{13}C NMR spectrum, δ, ppm: 147.7 (C-3); 138.9 (C-5); 116.8 (C-4). ^{14}N NMR spectrum, δ, ppm: –18.10 (NO_2). Found, *m*/*z*: 255.0585 $[M+H]^+$. $C_6H_7N_8O_4$. Calculated, *m*/*z*: 255.0585.

Preparation from amide **6**. A solution of NaOH (12 g, 0.3 mol) in H_2O (100 ml) was cooled to 0–5°C and treated by dropwise addition of Br_2 (3.1 ml, 60 mmol), then amide **6** (7.75 g, 25 mmol) was added in several portions and the reaction mixture was stirred at 0–5°C for 40 min. The temperature was increased to 55–60°C and maintained for 3 h. The reaction mixture then was cooled to 10°C and acidified with concentrated HCl to pH 2–3. The obtained precipitate was filtered off, providing the first crop of the product. The filtrate was extracted with EtOAc (3×50 ml). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed by evaporation at reduced pressure, providing the second crop of the product. Both crops were combined and separated by silica gel column chromatography (eluent $CHCl_3$–MeOH, 3:1), R_f 0.25. Yield 1.93 g (30%), light cream-colored powder, mp >360°C.

Preparation from bipyrazole **10**. Bipyrazole **10** (1.0 g, 3.2 mmol) was added at room temperature to a solution of hydrazine hydrate (0.48 ml, 9.6 mmol) in MeOH (30 ml), followed by the addition of $FeCl_3 \cdot 6H_2O$ (0.02 g, 0.08 mmol) and activated carbon (0.16 g, 13.2 mmol). The reaction mixture was heated to reflux and maintained at reflux temperature for 15 h. The precipitate was filtered off, washed with EtOH (3×40 ml) and the organic fractions were combined. The solvent was removed by distillation at reduced pressure, giving oil that was acidified with 2 M hydrochloric acid solution to pH 1–2. The reaction mixture was extracted with EtOAc (5×50 ml), the organic layer was dried over anhydrous Na_2SO_4, the solvent was removed by evaporation at reduced pressure. The residue was separated by silica gel column chromatography (eluent $CHCl_3$–MeOH, 3:1), R_f 0.25. Yield 0.23 g (28%), light-yellow powder, mp >360°C.

Preparation from bipyrazole **10**. An autoclave was charged with bipyrazole **10** (1 g, 3.2 mmol) and 20% aqueous ammonia solution (115 ml), then heated at 170°C for 10 h. The reaction mixture was cooled, acidified with 50% H_2SO_4 solution to pH 1–2, and extracted with EtOAc (5×50 ml). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed by evaporation at reduced pressure and the residue was separated by silica gel flash chromatography (eluent $CHCl_3$–MeOH, 3:1), R_f 0.25. Yield 0.20 g (25%), light-yellow powder, mp >360°C.

4,4'-Dinitro-1*H*,1'*H*-3,3'-bipyrazole (3). Bipyrazole **2** (8.0 g, 0.06 mol) was added to 92% H_2SO_4 (80 ml)[11] and the mixture was then treated by dropwise addition of HNO_3 (ρ 1.50 g/cm^3, 34.6 ml). The reaction mixture was gradually heated to 80–90°C and further stirred for 9 h at this temperature. Then the reaction mixture was cooled to 20°C, poured into ice water (600 ml), the obtained precipitate was filtered off, washed with ice water, and air-dried. Yield 12.5 g (93%), white powder, mp >360°C (H_2O–EtOH, 1:1). IR spectrum, ν, cm^{-1}: 3134 (s), 3033 (m), 2954 (m), 2907 (m), 2865 (m), 2823 (w), 1525 (w), 1394 (w), 1323 (w), 1197 (w), 1047 (m), 913 (w), 848 (w), 757 (s), 608 (w). ^{1}H NMR spectrum, δ, ppm: 14.35 (2H, br. s, NH); 8.98 (2H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 135.6 (br. s, C-4); 133.8 (C-3); 132.3 (C-5). ^{14}N NMR spectrum, δ, ppm: –18.89 (NO_2). Mass spectrum, *m*/*z* (I_{rel}, %): 224 $[M]^+$ (100). Found, %: C 32.54; H 2.06; N 37.10. $C_6H_4N_6O_4$. Calculated, %: C 32.15; H 1.80; N 37.50.

Preparation of *N*-nitro derivatives 4, 8, and 11 (General procedure). Method I. Bipyrazole **3**, **2**, or **9** (16 mmol) was added to CF_3CO_2H (16 ml) at 0°C, followed by dropwise addition of HNO_3 (ρ 1.50 g/cm^3, 3.9 ml) and acetic anhydride (10.92 ml). The reaction mixture was stirred for 4 h at 0–5°C and then poured into ice water (150 ml). The obtained precipitate was filtered off, washed with ice water, and air-dried. The filtrate was extracted with CH_2Cl_2 (3×25 ml), and the organic layer was dried over anhydrous $CaCl_2$. The solvent was removed by evaporation at reduced pressure, providing the second crop of the product, after which both crops were combined.

Method II. Potassium nitrate (1.79 g, 18 mmol) was added to a suspension of bipyrazole **3** or **9** (1.00 g, 3 mmol) in 1,2-dichloroethane (100 ml) at 20–25°C, followed by dropwise addition of $(CF_3CO)_2O$ (14 ml). The reaction mixture was furher stirred at 20–25°C for 24 h and then poured into water (75 ml). The organic layer was separated, the aqueous phase was extracted with EtOAc (2×35 ml). The organic fractions were combined and the solvent was removed by evaporation at reduced pressure.

1,1',4,4'-Tetranitro-1*H*,1'*H*-3,3'-bipyrazole (4). Yield 4.71 g (96%, method I), 4.41 g (90%, method II), white powder, decomp. temp. 187–188°C ($CHCl_3$), 192–194°C. IR spectrum, ν, cm^{-1}: 3160 (s), 3147 (s), 1627 (s), 1525 (m), 1394 (m), 1367 (s), 1302 (s), 1280 (s), 1264 (s), 1185 (s), 1092 (s), 1035 (s), 963 (m), 902 (w), 823 (s), 771 (s), 736 (m). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.95 (2H, s, H-5). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 135.5 (C-3); 134.3 (br. s, C-4); 131.9 (d, *J* = 200.2, C-5). ^{14}N NMR spectrum, δ, ppm: –65.28 (NNO_2); –22.15 (CNO_2). Found, %: C 23.13; H 0.89; N 36.06. $C_6H_2N_8O_8$. Calculated, %: C 22.94; H 0.64; N 35.67.

1,1'-Dinitro-1*H*,1'*H*-3,3'-bipyrazole (8). Yield 3.32 g (93%, method I), white powder, mp 184°C (decomp., $CHCl_3$). IR spectrum, ν, cm^{-1}: 3162 (s), 3146 (s), 1629 (s), 1503 (m), 1384 (m), 1365 (s), 1303 (s), 1281 (s), 1263 (s), 1187 (s), 1091 (s), 1033 (s), 964 (m), 904 (w), 821 (s), 772 (s), 734 (m). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.92 (2H, d, *J* = 2.3, H-5); 7.18 (2H, d, *J* = 2.3, H-4). ^{13}C NMR spectrum, δ, ppm: 143.9 (C-3); 128.6 (C-5); 107.5 (C-4). Found, %: C 32.52; H 1.86; N 37.68. $C_6H_4N_6O_4$. Calculated, %: C 32.15; H 1.80; N 37.50.

2,2',5,5'-Tetranitro-2*H*,2'*H*-3,3'-bipyrazole (11). Yield 4.02 g (82%, method I), 3.73 g (76%, method II), white powder, mp 165–167°C (decomp., $CHCl_3$). IR spectrum, ν, cm^{-1}: 3178 (s), 3154 (s), 2982 (m), 1611 (s), 1518 (m), 1401 (m), 1377 (s), 1363 (s), 1315 (s), 1287 (s), 1259 (s), 1237 (m), 1175 (s), 1103 (s), 1045 (s), 959 (m), 836 (s). ^{1}H NMR spectrum, δ, ppm: 7.85 (2H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 150.8 (br. s, C-5); 128.0 (C-3); 110.0 (C-4). ^{14}N NMR spectrum, δ, ppm: –24.13 (CNO_2); –61.06 (NNO_2). Found, %: C 23.18; H 0.81; N 35.95. $C_6H_2N_8O_8$. Calculated, %: C 22.94; H 0.64; N 35.67.

4,4'-Dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-dicarbonitrile (5a). A solution of bipyrazole **4** (1.29 g, 4.1 mmol) in MeCN (30 ml) was added slowly to a solution of KCN (1.6 g, 24.6 mmol) in water (20 ml) at 20°C. The reaction mixture was stirred at the same temperature for 30 min and acidified while stirring with 20% H_2SO_4 solution to pH 1–2. The obtained precipitate (K_2SO_4) was removed by filtration and discarded, the solvent was removed from the organic layer by evaporation at reduced pressure, and the residue was extracted with Et_2O (3×80 ml). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed by evaporation at reduced pressure, and the solid residue was air-dried. Yield 1.09 g (96%), white powder, mp 269–270°C (EtOH). IR spectrum, ν, cm^{-1}: 3561 (m), 3453 (m), 3238 (w), 2268 (m), 1574 (m), 1529 (s), 1475 (s), 1414 (m), 1370 (s), 1355 (s), 1210 (w), 1125 (m), 1064 (w), 960 (m), 833 (m), 712 (w). ^{13}C NMR spectrum, δ, ppm: 135.0 (C-3); 130.3 (C-5); 121.1 (C-4), 111.1 (CN). ^{14}N NMR spectrum, δ, ppm: –28.08 (NO_2). Found, *m*/*z*: 273.0128 [M–H]$^-$. $C_8HN_8O_4$. Calculated, *m*/*z*: 273.0126. Found, %: C 35.21; H 0.76; N 41.07. $C_8H_2N_8O_4$. Calculated, %: C 35.05; H 0.74; N 40.87.

5,5'-Diazido-4,4'-dinitro-1*H*,1'*H*-3,3'-bipyrazole (5b). A solution of NaN_3 (3.65 g, 56.1 mmol) in water (25 ml) was stirred at room temperature and treated by dropwise addition of bipyrazole **4** (1.47 g, 22.6 mmol) solution in EtOAc (25 ml). The reaction mixture was stirred at the same temperature for 30 min, then acidified with 20% H_2SO_4 solution to pH 1–2. The workup was analogous to the procedure for the preparation of compound **5a**. Yield 1.37 g (96%), white crystals, mp 93–95°C (EtOH). IR spectrum, ν, cm^{-1}: 2874 (w), 2153 (s), 2130 (m), 1580 (s), 1521 (s), 1443 (s), 1376 (s), 1224 (s), 955 (m), 831 (m), 790 (w). Found, *m*/*z*: 305.0258 [M–H]$^-$. $C_8HN_{12}O_4$. Calculated, *m*/*z*: 305.0249. Found, %: C 24.00; H 0.53; N 53.87. $C_6H_2N_{12}O_4$. Calculated, %: C 23.54; H 0.66; N 54.90.

4,4'-Dinitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-dicarboxamide (6). Bipyrazole **5a** (2.74 g, 10 mmol) was added to concentrated H_2SO_4 (10 ml) and the mixture was stirred for 5 h at 50–60°C. The reaction mixture was then cooled, poured into ice water (30 ml), the obtained precipitate was filtered off, washed with ice water, and air-dried. The filtrate was extracted with EtOAc (4×50 ml), the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation at reduced pressure, providing the second crop of product. Both crops were combined and crystallized from H_2O. Yield 2.49 g (80%), white crystals, mp 299–300°C. IR spectrum, ν, cm^{-1}: 3411 (m), 3285 (w), 3232 (w), 1665 (s), 1621 (m), 1595 (m), 1525 (vs), 1467 (s), 1435 (m), 1392 (m), 1338 (m), 1296 (m), 1145 (w), 890 (w), 839 (m), 625 (m). ^{1}H NMR spectrum, δ, ppm: 14.97 (2H, br. s, NH); 8.39 (2H, br. s, $CONH_2$); 8.14 (2H, br. s, $CONH_2$). ^{13}C NMR spectrum, δ, ppm: 159.8 (CO); 140.2 (br. s, C-3); 134.0 (br. s, C-4); 130.4 (C-5). ^{14}N NMR spectrum, δ, ppm: –29.25 (NO_2). Found, *m*/*z*: 309.0335 [M–H]$^-$. $C_8H_5N_8O_6$. Calculated, *m*/*z*: 309.0338. Found, %: C 31.29; H 2.13; N 36.50. $C_8H_6N_8O_6$. Calculated, %: C 30.98; H 1.95; N 36.13.

5,5'-Dinitro-2*H*,2'*H*-3,3'-bipyrazole (9). Bipyrazole **8** (10.3 g, 0.046 mol) was added to chlorobenzene (200 ml). The reaction mixture was refluxed for 6 h, cooled, the obtained precipitate was filtered off, washed with hexane, and air-dried. Yield 9.67 g (94%) light-brown powder, mp 373–374°C (EtOH). IR spectrum, ν, cm^{-1}: 3208 (m), 3140 (s), 3118 (m), 3052 (w), 2967 (m), 2873 (m), 1554 (s),

1542 (s), 1474 (w), 1429 (w), 1369 (s), 1313 (w), 1246 (m), 1071 (w), 1006 (s), 931 (w), 829 (s), 759 (m). ^{1}H NMR spectrum, δ, ppm: 14.67 (2H, br. s, NH); 7.49 (2H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 158.1 (br. s, C-5); 134.3 (C-3); 99.9 (C-4). ^{14}N NMR spectrum, δ, ppm: –20.39 (CNO_2). Found, %: C 32.25; H 1.67; N 37.80. $C_6H_4N_6O_4$. Calculated, %: C 32.15; H 1.80; N 37.50.

4,4',5,5'-Tetranitro-2*H*,2'*H*-3,3'-bipyrazole (10). Bipyrazole **9** (6.87 g, 0.03 mol) was added to concentrated H_2SO_4 (47 ml) then treated by dropwise addition of HNO_3 (ρ 1.50 g/cm^3, 6.2 ml). The reaction mixture was heated at 60°C for 12 h, cooled and poured into ice water (240 ml). The obtained precipitate was filtered off, washed with a small amount of ice water, and air-dried. The filtrate was extracted with Et_2O (3×50 ml) and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by evaporation at reduced pressure, providing the second crop of the product. 4,4',5,5'-Tetranitro-2*H*,2*H*'-3,3'-bipyrazole monohydrate was obtained in 9.67 g (95%) yield, colorless crystals, mp 187°C (H_2O, decomp. at 238°C). Anhydrous bipyrazole **10** was obtained in 9.14 g (95%) yield by maintaining the monohydrate over P_2O_5 at 120°C and reduced pressure for 10 h. IR spectrum, ν, cm^{-1}: 3616 (w), 3250 (m), 2701 (w), 2666 (w), 1570 (s), 1554 (s), 1530 (s), 1482 (s), 1425 (w), 1409 (w), 1365 (s), 1335 (s), 1107 (w), 1039 (w), 950 (w), 851 (w), 822 (m), 808 (m), 755 (w), 697 (w). UV spectrum, λ, nm (log ε): 212 (4.42) (H_2O); 306 (4.11) dianion (H_2O–NaOH). ^{1}H NMR spectrum, ($(CD_3)_2CO$), δ, ppm: 11.30 (2H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 149.8 (C-5); 132.2 (br. s, C-3); 125.1 (C-4). ^{14}N NMR spectrum, δ, ppm: –28.0 (CNO_2). Mass spectrum, *m*/*z* (I_{rel}, %): 314 $[M]^+$ (100). Found, %: C 23.09; H 0.84; N 35.17. $C_6H_2N_8O_8$. Calculated, %: C 22.94; H 0.64; N 35.67.

***N*,*N*',4,4'-Tetranitro-1*H*,1'*H*-[3,3'-bipyrazole]-5,5'-diamine (12).** A suspension of compound **1** (0.64 g, 2.5 mmol) in CF_3CO_2H (5 ml) was stirred at 0°C and treated by dropwise addition of HNO_3 (ρ 1.5 g/cm^3, 3.3 ml, 0.08 mol). The obtained solution was treated with Ac_2O (1 ml, 0.01 mol) and stirred for 2 h at 0–2°C. The obtained precipitate was filtered off, washed with H_2O, and air-dried. Yield 0.58 g (67%), white powder, mp 172°C (decomp., H_2O + CF_3CO_2H). IR spectrum, ν, cm^{-1}: 3152 (m), 3132 (w), 2940 (w); 1560 (s), 1440 (m), 1376 (s), 1354 (s), 1344 (s), 1296 (m), 1128 (m), 1018 (w), 960 (m), 904 (w), 834 (m). ^{13}C NMR spectrum, δ, ppm: 137.2 (C-3); 135.2 (br. s, C-5); 117.1 (C-4). ^{14}N NMR spectrum, δ, ppm: –26.23 (CNO_2); –40.25 ($NH\underline{N}O_2$); –206.74 ($\underline{N}HNO_2$). Found, %: C 21.12; H 1.23; N 40.99. $C_6H_4N_{10}O_8$. Calculated, %: C 20.94; H 1.17; N 40.70.

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