Nitropyrazoles

13.* Synthesis and reactivity of 1-methyl-3,5-dinitropyrazole-4-carbonitrile. Site of nucleophilic displacement of the nitro group in 4-R-1-methyl-3,5-dinitropyrazoles

A. A. Zaitsev,[a] T. I. Cherkasova,[a] I. L. Dalinger,[a] V. V. Kachala,[a] Yu. A. Strelenko,[a] I. V. Fedyanin,[b] V. N. Solkan,[a] T. K. Shkineva,[a] G. P. Popova,[a] and S. A. Shevelev[a]★

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation*
Fax: +7 (499) 135 5328. E-mail: shevelev@mail.ioc.ac.ru
[b]*N. A. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation*

A method for the synthesis of 1-methyl-3,5-dinitropyrazole-4-carbonitrile from 1,4-dimethyl-3,5-dinitropyrazole was developed. Nucleophilic substitution in 1,4-dimethyl-3,5-dinitropyrazole, 1-methyl-3,5-dinitropyrazole-4-carboxamide, and 1-methyl-3,5-dinitropyrazole-4-carbonitrile involves solely the 5-NO_2-group in the ring. 1-Methyl-3,5-dinitropyrazole-4-carbonitrile reacts with thioglycolic acid phenylamide and potassium carbonate to give 4-amino-1-methyl-3-nitro-*N*-phenyl-1*H*-thieno[2,3-*c*]pyrazole-5-carboxamide. The use of glycolic acid phenylamide instead of thioglycolic acid *N*-phenylamide under analogous conditions resulted in 5-anilino-1-methyl-3-nitro-1*H*-pyrazole-4-carbonitrile. An explanation for the regiospecificity of the nucleophilic substitution of the 5-NO_2 group in 4-R-1-methyl-3,5-dinitropyrazoles is given.

Key words: nitropyrazoles, dinitropyrazoles, nucleophilic substitution, thieno[2,3-*c*]pyrazoles, Smiles rearrangement.

This study, like the previous one,[1] is aimed at the development of new methods for preparation of polyfunctional and fused pyrazole-containing systems based on 4-R-3,5-dinitropyrazoles. In the previous work, the product of condensation of 1,4-dimethyl-3,5-dinitropyrazole (**1**) with DMF dimethylacetal at the 4-CH_3 group was used to prepare derivatives able to form fused aromatic heterocycles, namely, pyrazoloisoxazole and pyrazolopyrazole, upon intramolecular nucleophilic displacement of the nitro group.

The purpose of this work is the synthesis and study of transformations of 1-methyl-3,5-dinitropyrazole-4-carbonitrile (**2**) as a multipurpose building block in the 3,5-dinitropyrazole series. As expected, the presence of the strong electron-withdrawing cyano group in position 4 should appreciably increase the mobility of the nitro group in nucleophilic substitution; in addition, when the NO_2 group is replaced by a nucleophile with an active methylene fragment, subsequent intramolecular cyclization involving the cyano group is possible.

Nitrile **2** was synthesized from dinitropyrazole **1** by two methods (Scheme 1). According to the first method, isonitrosoaldehyde **3**, which we prepared previously[1] in two steps from dinitropyrazole **1**, was converted in one step into the desired nitrile **2** by treatment with trifluoroacetic anhydride and 4-dimethylaminopyridine according to a reported procedure.[2] In the second method, oxidation of dinitropyrazole **1** afforded carboxylic acid **4**, which was esterified to give ester **5**. By treatment with aqueous ammonia, ester **5** was converted into amide **6**, which was treated with phosphorus pentoxide to give nitrile **2**.

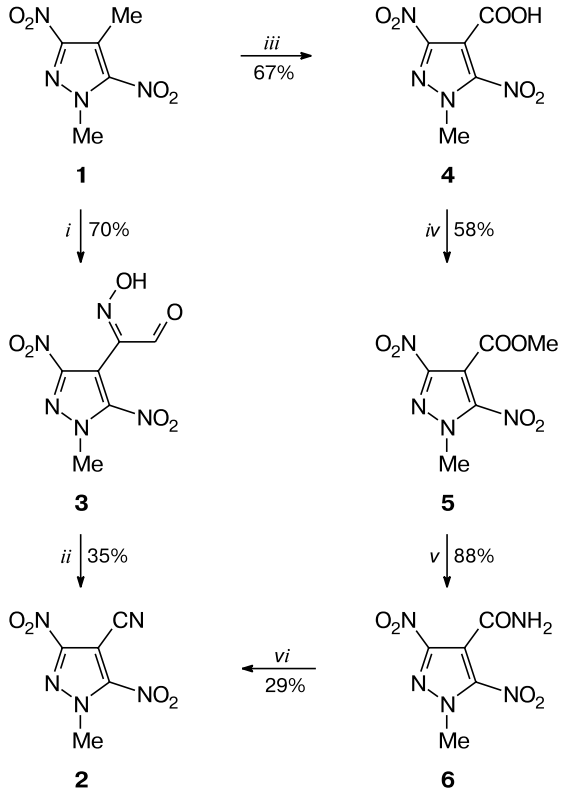
The first method for the synthesis of nitrile **2** is preferred, as the overall yield of the product is higher in this case (25% rather than 10%) and, moreover, it comprises fewer steps (three rather than four). Subsequently, we used this method to accumulate the required amount of nitrile **2**.

The crystal structure of compound **2** was studied by X-ray diffraction analysis. Figure 1 shows the general view of the molecule of **2** according to X-ray diffraction data. The nitro groups in compound **2** lie almost in the same plane as the pyrazole ring. The greatest rotation angle is 5.10°. Analysis of the crystal packing of **2** shows the presence of a large number of shortened intermolecular contacts, most of which involve the oxygen atoms of nitro groups. In the crystal packing of **2**, one can distinguish an O...π contact O(2)...N(2) (3.001(2) Å), an N...π contact

* For Part 12, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2004—2014, October, 2007.

Scheme 1



Reagents and conditions: *i*. Two steps (see Ref. 1); *ii*. TFAA, DMAP, MeCN, Δ; *iii*. $Na_2Cr_2O_7$, H_2SO_4, 40 °C; *iv*. MeOH, $SOCl_2$, Δ; *v*. $NH_3 \cdot H_2O$; *vi*. P_2O_5, $ClCH_2CH_2Cl$, Δ.

N(5)...N(1) (1.905(2) Å) between the cyano group and the ring π-system, and also contacts between the nitro groups O(1)...N(4) (2.801(2) Å) and between the nitro-group oxygen and the cyano-group carbon O(1)...C(2) 3.122(2) (Å). The mutual arrangement of the interacting fragments is different ranging from perpendicular to parallel.

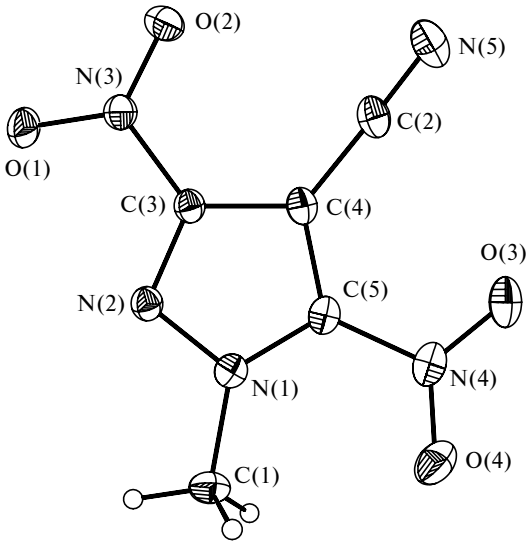
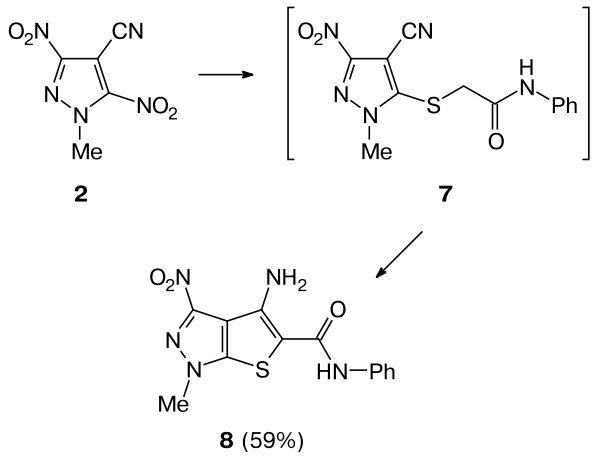


Fig. 1. General view of compound **2** according to X-ray diffraction data. Nonhydrogen atoms are presented by probability ellipsoids of thermal vibrations (p = 50%).

Nucleophilic displacement of the nitro group was studied for nitrile **2** and, for comparison, for amide **6** and dinitropyrazole **1**.

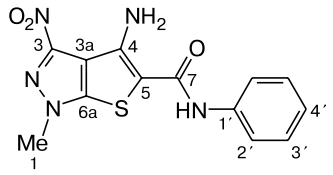
Nitrile **2** reacts with thioglycolic acid *N*-phenylamide in the presence of two equivalents of potassium carbonate in boiling acetonitrile to give substituted thieno[2,3-*c*]pyrazole **8** (Scheme 2). Evidently, nitrile **7** resulting from displacement of the 5-NO_2 group cyclizes *in situ* at the CN group to give bicyclic compound **8**.

Scheme 2

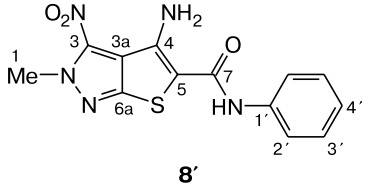


Reagents and conditions: $HSCH_2CONHPh$, K_2CO_3, MeCN, Δ.

Nucleophilic substitution in compound **2** can involve both 5- and 3-nitro groups in the pyrazole ring; this is expected to give isomeric bicyclic compounds **8** and **8′**, respectively.



8



8′

The fact that compound we synthesized has structure **8** rather than **8′** was proved by HMBC 2D NMR

spectroscopy (correlation by long-range (through two and three bonds) $^{1}H—^{13}C$ spin-spin coupling constants).

The signal of the C(3) atom was assigned by comparing the ^{13}C NMR spectra recorded at room temperature and at 70 °C. As the temperature increases, the solution viscosity decreases, resulting in retardation of ^{14}N quadrupole nuclear relaxation in the nitro group, which is manifested as pronounced narrowing of the NO_2-group signal in the ^{14}N NMR spectrum with increase in temperature (Fig. 2). In this case, it is possible to observe residual $^{14}N—^{13}C$ spin-spin coupling manifested as a noticeable broadening of the signal of the C(3) carbon directly bound to NO_2 (Fig. 3).

It can be seen from the HMBC NMR spectrum (Fig. 4) that a long-range $^{1}H—^{13}C$ coupling constant with the methyl-group protons is observed for C(6a) carbon atom; hence, this atom is separated from the methyl group by a fewer number of bonds; thus, the reaction product has structure **8** rather than alternative structure **8´**.

We studied the behavior of nitrile **2** in nucleophilic substitution with the glycolic acid and ethyl ester *N*-phenylamide. The reaction of nitrile **2** with these reagents in the presence of K_2CO_3 in acetonitrile at room temperature gives 5-substituted products **9** and **10** (Scheme 3).

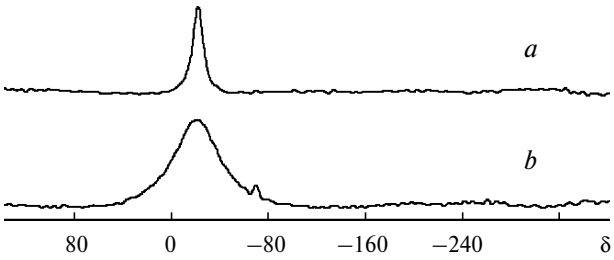


Fig. 2. ^{14}N NMR spectrum of compound **8** at 343 (*a*) and 295 K (*b*).

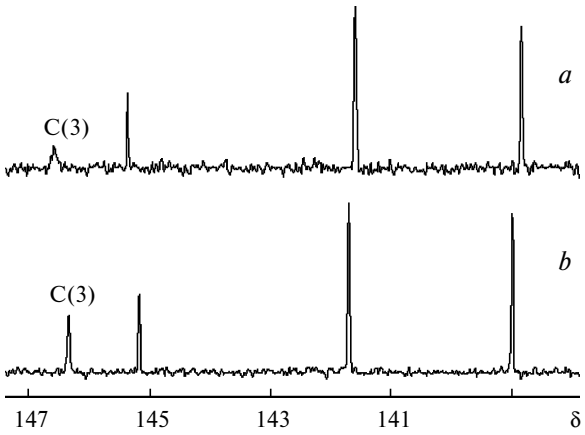


Fig. 3. Fragment of the ^{13}C NMR spectrum of compound **8** at 343 (*a*) and 295 K (*b*).

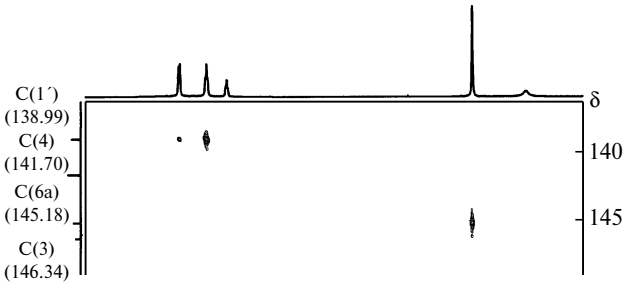
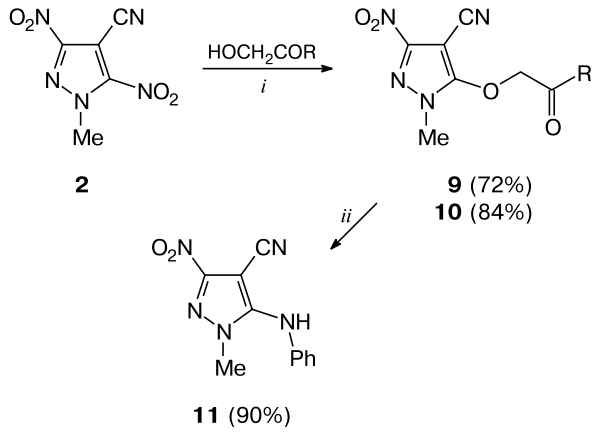


Fig. 4. Fragment of the HMBC 2D correlation NMR spectrum of compound **8**.

Scheme 3



Reagents and conditions: *i*. K_2CO_3 (1 equiv.), MeCN; *ii*. R = NHPh, K_2CO_3 (1 equiv.), MeCN, Δ.

The substitution direction at position 5 of the pyrazole ring was proved for the case of compound **9**, and the position of substituents in **10** was postulated by analogy with **9**. The position of the OCH_2COOEt group in the pyrazole ring in compound **9** was established on the basis of analysis of HMBC 2D correlation spectrum from long-range $^{1}H—^{13}C$ spin-spin coupling constants. In this spectrum (Fig. 5), long-range $^{1}H—^{13}C$ spin-spin coupling constants with the methyl group protons and with OCH_2 protons are found for the same carbon atom (the signal at δ 156.06), which is possible only if the OCH_2COOEt group is in position 5 of the pyrazole ring, while the NO_2 group is in position 3, but not *vice versa*. This is fully consistent with our earlier data.[1,3]

Treatment of compounds **9** and **10** with one more equivalent of potassium carbonate in acetonitrile gives different results. Compound **9** does not change on refluxing, whereas **10** is converted into 5-phenylamino-substituted product **11**. The possible mechanism of formation of compound **11** (so-called Smiles rearrangement[4]) is presented in Scheme 4.

Thus, the $—SCH_2COR$ adds to the C≡N bond in the corresponding pyrazole **7**; however, when the sulfur atom

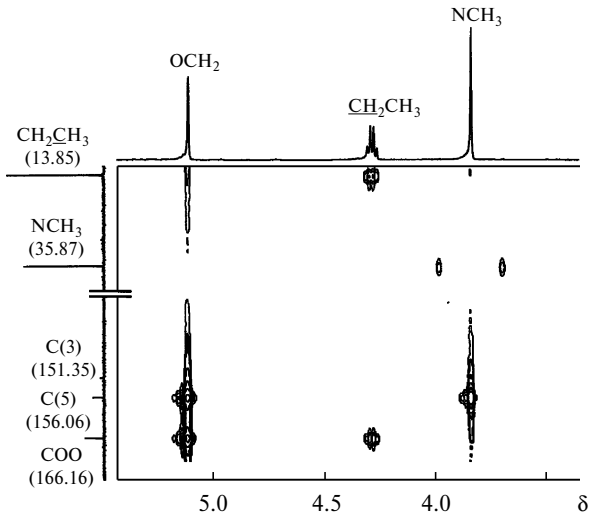
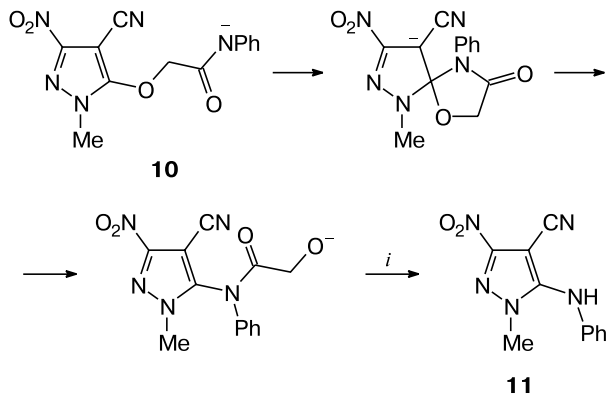


Fig. 5. Fragment of the HMBC 2D correlation NMR spectrum of compound **9**.

Scheme 4



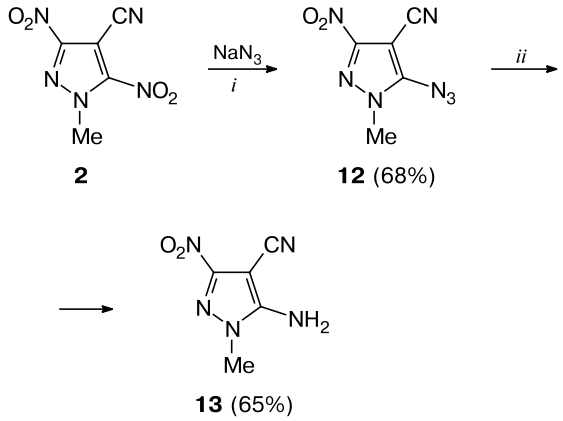
i. Hydrolysis.

has been replaced by oxygen, the activity of the methylene fragment is insufficient for this addition.

The reaction of compound **2** with sodium azide in acetonitrile gives the substitution product, azide **12**, which can be readily reduced to amine **13** with the nitro group left intact by a known procedure[5] (Scheme 5).

The fact that in compound **12**, the azido group is located in position 5 of the pyrazole ring was proved by HMBC 2D NMR correlation spectrum using long-range $^1H—^{13}C$ spin-spin coupling constants for compound **13**. In this spectrum, the long-range $^1H—^{13}C$ spin-spin coupling constants with the methyl group protons and with the NH_2 protons are found for the same carbon atom (the signal with δ 154.15), which is only possible if the NH_2 group is in position 5 of pyrazole ring. Moreover, the NOESY 2D correlation spectrum exhibits coupling between the NCH_3 and NH_2 protons, which is only possible

Scheme 5

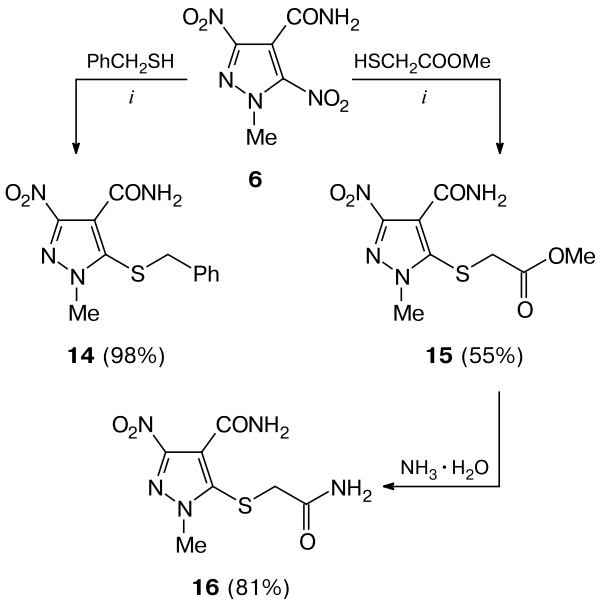


Reagents and conditions: *i*. MeCN, Δ; *ii*. $FeCl_3 \cdot 6H_2O$, $NaI \cdot 2H_2O$, MeCN.

provided that the NH_2 group occurs in position 5 of the pyrazole ring.

Amide **6** undergoes nucleophilic substitution of *S*-nucleophiles for the nitro group. Thus **6** reacts with benzylmercaptan and methyl thioglycolate in the presence of potassium carbonate in DMF at room temperature to give substitution products **14** and **15**. Ester **15** is converted into diamide **16** on treatment with aqueous ammonia (Scheme 6).

Scheme 6



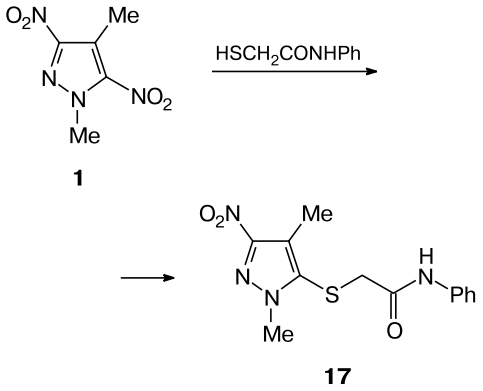
Reagents: *i*. K_2CO_3 (1 equiv.), DMF.

The positions of substituents in compound **15** were proved by analysis of the HMBC 2D NMR correlation

spectrum using long-range $^{1}H—^{13}C$ spin-spin coupling constants in the same way as this was done for compound **9**. In this spectrum, long-range $^{1}H—^{13}C$ spin-spin coupling constants with the methyl group protons and with the SCH_2 group protons are found for the same carbon atom (the signal with δ 134.82). No similar analysis was carried out for compound **14**; its structure was postulated by analogy with **15** and with other compounds that we mentioned in a previous publication.[1]

On treatment of dinitropyrazole **1** with thioglycolic acid *N*-phenylamide in the presence of potassium carbonate, the nitro group in position 5 is substituted to give product **17** (Scheme 7). The position of the $SCH_2CONHPh$ group in the pyrazole ring was established by analysis of HMBC 2D NMR correlation spectrum using long-range $^{1}H—^{13}C$ spin-spin coupling constants as this was done for **9** and **15**. In this spectrum, long-range $^{1}H—^{13}C$ spin-spin coupling constants with the methyl group protons and with the SCH_2 group protons are found for the same carbon atom (the signal with δ 134.31). In addition the NOESY 2D correlation spectrum shows coupling between the NCH_3 and SCH_2 protons, which is only possible provided that the $SCH_2CONHPh$ group is located in position 5 of the pyrazole ring.

Scheme 7



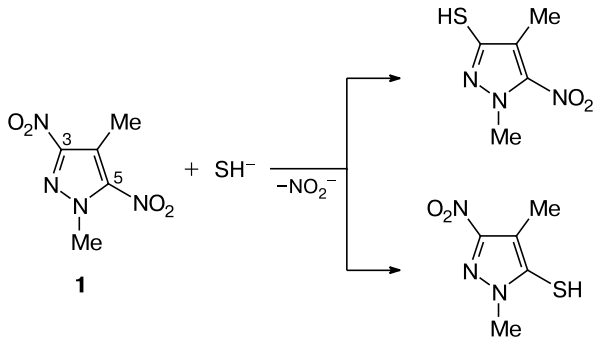
Reagents and conditions: K_2CO_3 (1 equiv.), MeCN or NMP, Δ; MeCN, 28%; NMP, 41%.

Note that nucleophilic displacement of the nitro group in dinitropyrazole **1** takes place under much more drastic conditions than in **2** or **6** where substitution of S-nucleophiles proceeds at room temperature in acetonitrile or DMF (see above). In the case of compound **1**, the reaction in acetonitrile requires long-term refluxing (~80 °C) and complete conversion is not attained even after three days. Complete conversion can be attained in 5 h at 100 °C in *N*-methylpyrrolidone; however, in this case, the formation of compound **17** is accompanied by substantial resinification.

The attempts to involve dinitropyrazole **1** into nucleophilic substitution with O- and N-nucleophiles (glycolic acid *N*-phenylamide, phenol, ethyl sarcosinate, 3,5-dimethyl-4-nitropyrazole, sodium azide) in *N*-methylpyrrolidone failed: no substitution product was formed even at 150 °C.

As follows from the data of this and our previous studies,[1,3] both on treatment with anionic nucleophiles and in intramolecular cyclization, only the 5-NO_2 group in 4-R-1-methyl-3,5-dinitropyrazoles is substituted, *i.e.*, both inter- and intramolecular nucleophilic displacement of nitro groups is regiospecific. We investigated the reasons for such pronounced difference between the reactivities of 3- and 5-NO_2 groups in N-substituted pyrazoles by quantum chemistry using the model reaction of 1,4-dimethyl-3,5-dinitropyrazole **1** with HS^- as the nucleophile (Scheme 8).

Scheme 8



The calculation was carried out by density functional theory (B3LYP) in the σ-31+G* basis set with full geometry optimization for two transition states corresponding to nucleophilic displacement of nitro groups in positions 3 and 5 of dinitropyrazole **1**.

Note that we did not detect anionic *ipso*-σ-complexes, which are usually involved in aromatic nucleophilic substitution, on the potential energy surface of the joint molecular system [**1** + HS^-]. Thus, all calculated characteristics refer to direct nucleophilic displacement of 3- or 5-NO_2 groups. It cannot be ruled out that this reaction is a one-step synchronous bimolecular substitution; with some structural features of the substrate, this is still possible in the aromatic series.[6]

To confirm that the values found for transition states (TS) correspond to nucleophilic substitution of HS group for the nitro group, we carried out internal reaction coordinate (IRC) calculations and showed that they connect the reactant and product valleys on the potential energy surface of the joint molecular system [**1** + HS^-]. In addition, the polarizable continuum model (PCM) was used to calculate the electrostatic contribution to the free energy of solvation (ΔG) in a highly polar solvent (ε = 78).

Table 1. Activation parameters of the nucleophilic substitution of HS^- for 3- and 5-NO_2 in dinitropyrazole **1** (kcal mol^{-1})

Medium	$\Delta G^{\#}_5$	$\Delta G^{\#}_3$	$\Delta G^{\#}_3 - \Delta G^{\#}_5$	$\Delta H^{\#}_5$	$\Delta H^{\#}_3$	$\Delta H^{\#}_3 - \Delta H^{\#}_5$
Gas phase	2.6	12	9.4	–6	3.2	9.2
Highly polar solvent ($\varepsilon = 78$)	28.8	36.7	7.9	20.3	27.9	7.6

The calculation results were used to calculate the free activation energies ($\Delta G^{\#}$) and activation enthalpies ($\Delta H^{\#}$) for reactions carried out both in the gas phase and in a highly polar solvent (Table 1).

As can be seen from the data of Table 1, free activation energy $\Delta G^{\#}$ of nucleophilic substitution both in the gas phase and in a highly polar solvent is lower for the 5-NO_2 group than for the 3-NO_2 group by 9.4 and 7.9 kcal mol^{-1}, respectively, which corresponds to a difference in the nitro group displacement rates by four to five orders of magnitude in the temperature range of 20—100 °C. This extremely pronounced difference in the displacement rates is responsible for the regiospecific pattern of nucleophilic displacement of the 5-NO_2 group, *i.e.*, the formation of only one of the two possible isomers.

It is noteworthy that the difference between the activation enthalpies $\Delta H^{\#}_3 - \Delta H^{\#}_5$ at positions 3 and 5 is nearly the same as for the free activation energies $\Delta G^{\#}_3 - \Delta G^{\#}_5$ (see Table 1). This implies that the steric effect of the methyl group in position 1 does not affect the substitution rate at position 5. This result corresponds to the general trend according to which in heteroaromatic series, the steric hindrance of nucleophilic substitution caused by primary and secondary alkyl groups or phenyl groups is insignificant.[7a] Moreover, calculation of dinitropyrazole **1** geometry by the above method shows that the 3- and 5-NO_2 groups are almost coplanar with the pyrazole ring, *i.e.*, no significant steric interaction between the methyl groups and nitro groups is present. The same result was obtained by X-ray diffraction study of compound **1**. Thus comparison of the torsion angles (Fig. 6 and Table 2) indicates that the maximum torsion angle of the 5-NO_2 group is 7.03°. This is consistent with the data of quantum chemical calculations of the geometry of compound **1**.

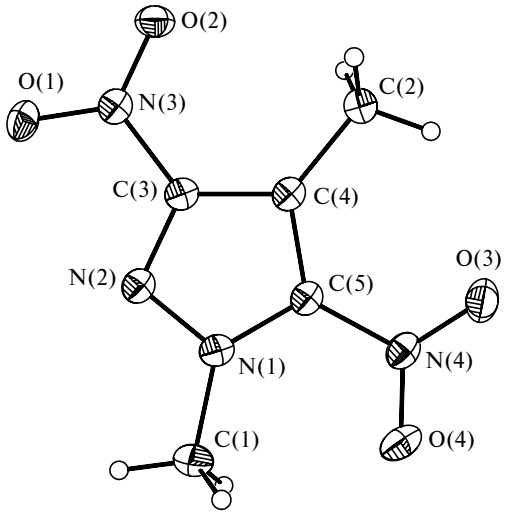


Fig. 6. General view of compound **1** according to X-ray diffraction data. Nonhydrogen atoms are presented by probability ellipsoids of thermal vibrations ($p = 50\%$). The bond lengths and angles are given in Table 4 and the torsion angles are in Table 2.

This raises the question of what factor ensures the regiospecificity of nucleophilic displacement of the nitro group in position 5 of the ring. It is usually considered that the electrostatic factor plays the crucial role in heteroaromatic nucleophilic substitution, *i.e.*, nucleophilic substitution reactions are directed most often at electron-deficient atoms of the heterocycle.[7b] However, a number of exceptions to this rule are known.[7b] In the case of dinitropyrazole **1**, the electrostatic factor is still most likely to govern the substitution site. Indeed, even in the parent pyrazole (with a fixed position of the NH proton), according to the simple MOH calculation, the positive π-charge is twice higher in position 5 than in position 3: +0.051 and +0.025, respectively (in position 4, the π-charge is –0.107).[7c] This electron density distribution is due to the fact that pyrazole is a slightly π-excessive heterocycle and, therefore, the π-balance state is significantly affected by the "pyrrole" nitrogen atom.[7c] As regards dinitropyrazole **1**, the calculation of Mulliken full atomic charges (Table 3) shows that the charges on C(3) and C(5) atoms are appreciably different, which, in our opinion, is responsible for the pronounced difference in

Table 2. Torsion angles (deg) characterizing rotation of the NO_2 group relative to the pyrazole ring in compounds **1** and **2**

Compound	**1**	**2**
O(2)—N(3)—C(3)—N(2)	178.57(12)	174.90(8)
O(1)—N(3)—C(3)—N(2)	–0.80(19)	–3.93(13)
O(2)—N(3)—C(3)—C(4)	–1.9(2)	–3.64(13)
O(1)—N(3)—C(3)—C(4)	178.71(13)	177.53(8)
O(3)—N(4)—C(5)—N(1)	–173.89(12)	177.14(8)
O(4)—N(4)—C(5)—N(1)	7.03(19)	–2.92(13)
O(3)—N(4)—C(5)—C(4)	5.6(2)	–2.45(13)
O(4)—N(4)—C(5)—C(4)	–173.44(13)	177.49(8)

Table 3. Mulliken full atomic charges of 1,4-dimethyl-3,5-dinitropyrazole **1**

Atom	Charge	Atom	Charge
C(1)	−0.156730	N(3)	0.156404
C(2)	−0.240873	N(4)	0.142687
C(3)	0.456971	O(1)	−0.244846
C(4)	−0.307725	O(2)	−0.279653
C(5)	0.568642	O(3)	−0.258880
N(1)	−0.318748	O(4)	−0.277976
N(2)	−0.188331		

the free activation energies of nucleophilic substitution at C(3) and C(5) and, hence, for the regiospecific displacement of the nitro group at C(5).

Analysis of the crystal packing of compounds **1** (see Fig. 6) and **2** shows the presence of a large number of shortened intermolecular contacts, most involving oxygen of the nitro groups. In crystal **1**, one can distinguish a shortened intermolecular O...π contact O(1)...N(1) (3.011(2) Å) and a pair contact between the nitro groups in positions 5 and 3 with N(3)...O(4) and O(2)...N(4) distances equal to 2.925(2) and 3.006(2) Å. Generally, neither in structure **1** nor in structure **2**, a predominant type of contacts can be distinguished on the basis of geometric data alone.

Until now, the crystal structures for only two 3,5-dinitropyrazoles have been known, namely, 4-amino-3,5-dinitropyrazole (**18**) and its solvate with DMSO[8] (the Cambridge Crystallographic Data Centre codes are UFUXOI and UFUXUO) and 3,3′,5,5′-tetranitro-4,4′-bipyrazole[9] (**19**) (this structure is missing from the Cambridge Crystallographic Data Centre).* Table 4 compares the bond lengths and angles for compounds **1** and **2**, **18** and **19**, and for unsubstituted pyrazole (**20**).

The presence of two electron-withdrawing nitro groups in positions 3 and 5 results in a substantial change in the bond lengths in the ring compared to unsubstituted pyrazole (see Table 4). The C(4)—C(5) and C(5)—N(1) bonds are shorter than the corresponding bonds in pyrazole by, on average, 0.02 Å, and C(3)—C(4), by 0.03 Å. Meanwhile, the nature of substituents in positions 1 and 4 has little influence on the geometric parameters of the ring: in compounds **1** and **2** and in 4-amino-3,5-dinitropyrazole (**18**), the greatest difference between bond lengths is 0.01 Å for the N(1)—N(2) and N(1)—C(5) bonds. The planes of the nitro groups are nearly parallel to the pyrazole ring, the greatest torsion being observed for the nitro group at C(5) in molecule **1** (7.03°). Note that the C—NO_2 bond lengths in compounds **1** and **2** are equal for positions 3 and 5 and also do not depend on substituents in the ring.

* T. K. Shkineva, V. M. Vinogradov, I. L. Dalinger, S. A. Shevelev, and V. S. Kuz′min, unpublished results.

Experimental

^{1}H NMR were recorded on Bruker AC-200, Bruker WM-250, Bruker AC-300, and Bruker-500 at 295K (unless another temperature is indicated). ^{1}H and ^{13}C chemical shifts are referred to $SiMe_4$ and ^{14}N chemical shifts are referred to CH_3NO_2. IR spectra were measured on a Specord M-80 in KBr pellets. Mass spectra were recorded on a Kratos MS-30 instrument. The reactions were monitored and the compound purity was checked by TLC on Silufol UV-254 plates. Elemental analysis was carried out on a Perkin Elmer Series II 2400 instrument.

X-Ray diffraction studies of compounds 1 and 2 were carried out on a Bruker APEX II automated diffractometer (Mo-Kα radiation, graphite monochromator, ω-scan mode). The structures were solved by the direct method and refined by the least squares method in the full matrix anisotropic approximation on F^2_{hkl}. The hydrogen atoms of the methyl groups were located from difference Fourier syntheses and refined by the riding model. All calculations were carried out using the SHELXTL PLUS program package. X-Ray diffraction experiment details and crystal lattice parameters are summarized in Table 5.

1-Methyl-3,5-dinitropyrazole-4-carbonitrile (2). Method *A*. Synthesis of nitrile 2 from 2-hydroxyimino-2-(1-methyl-3,5-dinitropyrazol-4-yl)acetaldehyde (3). 4-Dimethylaminopyridine (2.650 g, 21.7 mmol) was added at 0—5 °C to a solution of hydroxyimino(1-methyl-3,5-dinitropyrazole-4-yl)acetaldehyde (**3**) (3.000 g, 12.3 mmol) in acetonitrile (100 mL), and the mixture was stirred for 10 min. Then trifluoroacetic anhydride (1.80 mL, 12.7 mmol) was added dropwise at the same temperature. The mixture was heated for 2 h at 50—60 °C. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (elution with chloroform) to give 0.862 g of product **2** (35%).

Method *B*. Preparation of nitrile 2 from 1-methyl-3,5-dinitropyrazole-4-carboxamide (6). Phosphorus(v) oxide (1.180 g, 8.3 mmol) was added in small portions with stirring to a suspension of amide **6** (0.300 g, 1.4 mmol) in anhydrous 1,2-dichloroethane at 5—10 °C. The mixture was kept for 3 h at room temperature and then refluxed for 30 h. The inorganic precipitate was filtered off, and dichloroethane was evaporated *in vacuo* to give 0.080 g of product **2** (29%).

Nitrile **2**, m.p. 187—190 °C. Found (%): C, 30.87; H, 1.57; N, 35.27. $C_5H_3N_5O_4$. Calculated (%): C, 30.47; H, 1.53; N, 35.53. ^{1}H NMR ($(CD_3)_2SO$), δ: 4.31 (s, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 151.29 (C(3)); 148.01 (C(5)); 108.44 (CN); 87.65 (C(4)); 43.07 (Me). IR, ν/cm^{-1}: 2264 (C≡N); 1540 (NO_2); 1336 (NO_2). MS, *m/z*: 197 $[M]^+$.

The crystal lattice parameters of nitrile **2** are given in Table 5, bond lengths and angles are in Table 4, and torsion angles are in Table 3.

1-Methyl-3,5-dinitropyrazole-4-carboxylic acid (4). The salt $Na_2Cr_2O_7 \cdot 2H_2O$ (48.00 g, 161 mmol) was added in small portions with vigorous stirring at temperature of 30—40 °C to a solution of dinitropyrazole **1** (15.00 g, 81 mmol) in concentrated sulfuric acid (225 mL). The mixture was kept at this temperature for 4 h and at room temperature for 16 h, poured on ice, extracted with ethyl acetate, and dried with $MgSO_4$, The solvent was removed *in vacuo*. The residue was recrystallized from toluene to give 11.60 g (67%) of product **4**, m.p. 159—160 °C (from toluene). Found (%): C, 28.06; H, 1.94; N, 25.44. $C_5H_4N_4O_6$.

Table 4. Selected bond lengths and angles in compounds **1** and **2** and 4-amino-3,5-dinitropyrazole (**18**)[8], 3,3′,5,5′-tetranitro-4,4′-bipyrazole (**19**),[9] and pyrazole (**20**)[10] according to X-ray diffraction data

Parameter	1	2	18	19	20
Bond			*d*/Å		
N(1)—N(2)	1.329(2)	1.339(1)	1.325(4)	1.327 1.335	1.343
N(2)—C(3)	1.330(2)	1.324(1)	1.346(4)	1.331 1.332	1.322
C(3)—C(4)	1.405(2)	1.400(1)	1.409(4)	1.396 1.398	1.369
C(4)—C(5)	1.386(2)	1.387(1)	1.390(4)	1.369 1.381	1.361
C(5)—N(1)	1.365(2)	1.352(1)	1.381(4)	1.348 1.343	1.335
N(1)—C(1)	1.466(2)	1.473(1)			
C(3)—N(3)	1.441(2)	1.447(1)	1.424(4)	1.446 1.427	
C(5)—N(4)	1.441(2)	1.445(1)	1.398(4)	1.428 1.434	
C(4)—C(2)	1.486(2)	1.422(1)		1.471*	
C(2)—N(5)		1.145(1)			
Angle			ω/deg		
N(1)—N(2)—C(3)	104.3(1)	104.97(7)	104.4(3)	104.65 104.14	103.80
N(2)—C(3)—C(4)	115.2(1)	113.59(8)	114.4(3)	113.58 113.81	112.25
C(3)—C(4)—C(5)	99.7(1)	101.64(7)	100.9(3)	101.20 101.33	105.00
C(4)—C(5)—N(1)	110.3(1)	109.04(8)	109.1(3)	110.00 109.36	106.62
C(5)—N(1)—N(2)	110.4(1)	110.76(7)	111.2(3)	110.56 111.36	112.32
N(2)—N(1)—C(1)	117.5(1)	118.23(8)			
C(5)—N(1)—C(1)	131.9(1)	131.01(8)			
C(3)—C(4)—C(2)	129.2(1)	129.01(8)		129.57 130.87	
C(5)—C(4)—C(2)	131.1(1)	129.34(8)		129.06 127.79	
N(2)—C(3)—N(3)	117.6(1)	119.92(8)	118.8(3)	118.53 118.98	
C(4)—C(3)—N(3)	127.2(1)	126.48(8)	126.8(3)	127.88 127.20	
C(4)—C(5)—N(4)	128.2(1)	126.52(8)	129.1(3)	129.88 130.65	
N(1)—C(5)—N(4)	121.5(1)	124.45(8)	121.8(3)	120.11 119.98	

* C(4)—C(4′) bond length.

Calculated (%): C, 27.79; H, 1.87; N, 25.93. ^{1}H NMR ($(CD_3)_2SO$), δ: 4.26 (s, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 159.72 (COO); 147.22 (C(3)); 142.57 (C(5)); 110.59 (C(4)); 42.46 (Me). IR, ν/cm^{-1}: 3150 br (OH); 1732 (C=O); 1540 (NO_2); 1340 (NO_2). MS, *m*/*z*: 216 $[M]^+$.

Methyl 1-methyl-3,5-dinitropyrazole-4-carboxylate (5). Thionyl chloride (13.50 mL, 186 mmol) was added dropwise with stirring at 10—15 °C to a solution of acid **4** (3.900 g, 18.0 mmol) in methanol (50 mL) and the mixture was refluxed for 20 h. The solution was cooled and the precipitate was filtered off. The solvent was evaporated from the filtrate to a volume of 25 mL, the precipitate was filtered off, the filtrate was combined with the previous portion, and washed with cold (5—10 °C) methanol to give 2.405 g (58%) of product **5**, m.p. 122—124 °C. Found (%): C, 30.81; H, 2.88; N, 23.95. $C_6H_6N_4O_6$. Calculated (%): C, 31.31; H, 2.63; N, 24.35. ^{1}H NMR ($(CD_3)_2SO$), δ: 4.28 (s, 3 H, NMe); 3.97 (s, 3 H, OMe). ^{13}C NMR ($(CD_3)_2SO$), δ: 159.00 (COO); 147.33 (C(3)); 143.05 (C(5)); 108.51 (C(4));

Table 5. Crystal lattice parameters of compounds **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_5H_6N_4O_4$	$C_5H_3N_5O_4$
Molecular weight	186.14	197.12
T/K	100	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Z	4	4
a/Å	13.3402(15)	5.4800(3)
b/Å	6.2017(7)	8.8687(4)
c/Å	9.4656(11)	15.7014(8)
β/deg	106.429(2)	92.6940(10)
V/Å^3	751.13(15)	762.25(7)
d_{calc}/g cm^{-3}	1.646	1.718
$2\theta_{max}$/deg	56	60
The number of measured reflections	6737	8764
The number of independent reflections	1807	2227
R_{int}	0.0545	0.0363
The number of reflections with $I > 2\sigma(I)$	1413	1982
The number of refined parameters	120	128
R_1	0.0380	0.0322
wR_2	0.1012	0.0889
Residual electron density, e Å^{-3}(d_{min}/d_{max})	0.336/−0.194	0.426/−0.265

53.88 (OMe); 42.49 (NMe). IR, ν/cm^{-1}: 1748 (C=O); 1556 (NO_2); 1548 (NO_2); 1344 (NO_2). MS, m/z: 230 $[M]^+$.

1-Methyl-3,5-dinitropyrazole-4-carboxamide (6). A suspension of ester **5** (3.000 g, 13.0 mmol) in aqueous ammonia (150 mL) was stirred for 4 h at room temperature until the solid completely dissolved. The mixture was kept for 16 h and the precipitate was filtered off. The solvent was evaporated from the filtrate to a volume of 75 mL, the precipitate was filtered off, the filtrate was combined with the previous portion, washed with a small amount of ice water, and dried to give 2.458 g (88%) of product **6**, m.p. 192—194 °C. Found (%): C, 28.01; H, 2.32; N, 32.67. $C_5H_5N_5O_5$. Calculated (%): C, 27.92; H, 2.34; N, 32.56. ^{1}H NMR ($(CD_3)_2SO$), δ: 8.03 (s, 1 H, NH_2); 7.94 (s, 1 H, NH_2); 4.27 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 158.97 (COO); 147.78 (C(3)); 142.62 (C(5)); 112.93 (C(4)); 42.29 (Me). IR, ν/cm^{-1}: 3428 (NH_2); 3320 (NH_2); 3268 (NH_2); 1684 (C=O); 1676 (C=O); 1552 (NO_2); 1544 (NO_2); 1344 (NO_2). MS, m/z: 215 $[M]^+$.

4-Amino-1-methyl-3-nitro-*N*-phenyl-1*H*-thieno[2,3-*c*]pyrazole-5-carboxamide (8). A mixture of nitrile **2** (0.200 g, 1.0 mmol), thioglycolic acid *N*-phenylamide (0.170 g, 1.0 mmol), and potassium carbonate (0.310 g, 2.2 mmol) in acetonitrile (20 mL) was refluxed for 4 h, cooled, poured into water, and acidified with HCl to pH 5—6, and the precipitate was filtered off, washed with water, and dried to give 0.190 g of product **8** (59%). M.p. 261—262 °C (from ethanol). Found (%): C, 49.25; H, 3.63; N, 21.93; S, 10.00. $C_{13}H_{11}N_5O_3S$. Calculated (%): C, 49.20; H, 3.49; N, 22.07; S, 10.11. ^{1}H NMR ($(CD_3)_2SO$), δ: 9.34 (s, 1 H, NH); 7.64 (d, 2 H, *o*-Ph, J = 7.5 Hz); 7.30 (t, 2 H, *m*-Ph, J = 7.5 Hz); 7.06 (t, 1 H, *p*-Ph, J = 7.5 Hz); 7.03 (s, 2 H, NH_2); 4.03 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 163.62 (CO); 146.34 (C(3)); 145.18 (C(6a)); 141.70 (C(4)); 138.99 (*ipso*-Ph); 128.32 (*m*-Ph); 123.27 (*p*-Ph); 121.12 (*o*-Ph); 115.84 (C(5)); 99.40 (C(3a)); 39.26 (Me). ^{13}C NMR ($(CD_3)_2SO$), δ, 343 K: 163.58 (CO); 146.58 (C(3)); 145.37 (C(6a)); 141.60 (C(4)); 138.83 (*ipso*-Ph); 128.25 (*m*-Ph); 123.43 (*p*-Ph); 121.27 (*o*-Ph); 116.07 (C(5)); 100.26 (C(3a)); 39.22 (Me). ^{14}N NMR ($(CD_3)_2SO$), δ: −22.11 (NO_2). ^{14}N NMR ($(CD_3)_2SO$, 343 K), δ: −22.21. IR, ν/cm^{-1}: 3464, 3392, 3300 (NH_2 + NH); 1640 (C=O); 1512 (NO_2); 1364 (NO_2). MS, m/z: 317 $[M]^+$.

Ethyl (4-cyano-1-methyl-3-nitropyrazol-5-yl)oxyacetic acid (9). Potassium carbonate (0.140 g, 1.0 mmol) was added to a solution of nitrile **2** (0.200 g, 1.0 mmol) and ethyl glycolate (0.10 mL, 1.0 mmol) in acetonitrile (20 mL), and the mixture was refluxed for 1 h, cooled, poured into water (150 mL), and extracted with ethyl acetate (2×25 mL). The extract was washed with brine and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the resulting oily residue was chromatographed on silica gel (elution with chloroform) to give 0.185 g (72%) of product **9**, m.p. 90—92 °C. Found (%): C, 42.87; H, 4.16; N, 22.00. $C_{13}H_{11}N_5O_4$. Calculated (%): C, 42.52; H, 3.97; N, 22.04. ^{1}H NMR ($CDCl_3$), δ: 5.10 (s, 2 H, O$\underline{C}H_2$CO); 4.28 (q, 2 H, O$\underline{C}H_2CH_3$, J = 7.5 Hz); 3.82 (s, 3 H, NMe); 1.29 (t, 3 H, CMe, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 166.16 (COO); 156.06 (C(5)); 151.35 (C(3)); 109.54 (CN); 72.85 (C(4)); 68.54 (O$\underline{C}H_2$COO); 62.55 ($\underline{C}H_2CH_3$); 35.87 (NMe); 13.85 ($CH_2\underline{C}H_3$). IR, ν/cm^{-1}: 2244 (C≡N); 1756 (C=O); 1528 (NO_2); 1348 (NO_2). MS, m/z: 254 $[M]^+$.

2-(4-Cyano-1-methyl-3-nitropyrazol-5-yl)oxy-*N*-phenylacetamide (10). Potassium carbonate (0.140 g, 1.0 mmol) was added to a solution of nitrile **2** (0.200 g, 1.0 mmol) and glycolic acid *N*-phenylamide (0.153 g, 1.0 mmol) in acetonitrile (20 mL), and the mixture was refluxed for 1 h, cooled, poured into water (150 mL), acidified to pH 3—4, filtered, washed with cold water, and dried to give 0.257 g of product **10** (84%), m.p. 203—205 °C (from ethanol). Found (%): C, 51.58; H, 3.60;

N, 23.06. $C_9H_{10}N_4O_5$. Calculated (%): C, 51.83; H, 3.68; N, 23.25. ^{1}H NMR ($(CD_3)_2SO$), δ: 10.33 (s, 1 H, NH); 7.55 (d, 2 H, *o*-Ph, J = 10 Hz); 7.32 (t, 2 H, *m*-Ph, J = 7.5 Hz); 7.09 (t, 1 H, *p*-Ph, J = 7.5 Hz); 5.28 (s, 2 H, CH_2); 3.82 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 164.11 (CONH); 156.72 (C(5)); 150.92 (C(3)); 138.02 (*ipso*-Ph); 128.86 (*m*-Ph); 123.98 (*p*-Ph); 119.67 (*o*-Ph); 110.34 (CN); 72.46 (C(4)); 70.66 (OCH_2); 35.84 (Me). IR, ν/cm^{-1}: 3332 (NH); 3304 (NH); 2244 (C≡N); 1716 (C=O); 1524 (NO_2); 1344 (NO_2). MS, *m/z*: 301 $[M]^+$.

5-Anilino-1-methyl-3-nitropyrazole-4-carbonitrile (11). Potassium carbonate (0.025 g, 0.18 mmol) was added to a solution of product **10** (0.048 g, 0.16 mmol) in acetonitrile (10 mL) and the mixture was refluxed for 4 h, cooled, poured into water (100 mL), acidified with dilute HCl to pH 5—6, extracted with ethyl acetate (2×20 mL), and washed with brine. The solvent was removed *in vacuo* to give 0.035 g (90%) of product **11**, m.p. 235—236 °C. Found (%): C, 54.49; H, 4.01; N, 28.54. $C_{11}H_9N_5O_2$. Calculated (%): C, 54.32; H, 3.73; N, 28.79. ^{1}H NMR ($(CD_3)_2SO$), δ: 9.25 (s, 1 H, NH); 7.32 (t, 2 H, *m*-Ph, J = 7.5 Hz); 7.05 (m, 3 H, *o*-Ph + *p*-Ph); 3.80 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 152.01 (C(3)); 148.98 (C(5)); 139.66 (*ipso*-Ph); 129.20 (*m*-Ph); 123.01 (*p*-Ph); 118.81 (*o*-Ph); 110.63 (CN); 76.12 (C(4)); 37.09 (Me). IR, ν/cm^{-1}: NH (3364); 2232 (C≡N); 1536 (NO_2); 1348 (NO_2). MS, *m/z*: 243 $[M]^+$.

5-Azido-1-methyl-3-nitropyrazole-4-carbonitrile (12). Sodium azide (0.120 g, 1.8 mmol) was added to a solution of nitrile **2** (0.336 g, 1.7 mmol) in acetonitrile (35 mL), the mixture was refluxed for 10 min and cooled, and water (150 mL) was added. The aqueous solution together with the precipitate was extracted with ethyl acetate (2×35 mL), the extract was dried with Na_2SO_4, and the solvent was removed *in vacuo* to give 0.223 g of product **12** (68%), m.p. 131—133 °C. Found (%): C, 31.52; H, 1.55; N, 49.79. $C_5H_3N_7O_2$. Calculated (%): C, 31.10; H, 1.57; N, 50.77. ^{1}H NMR ($(CD_3)_2SO$), δ: 3.75 (s, Me). ^{13}C NMR ($(CD_3)_2SO$, δ: 151.69 (C(3)); 143.90 (C(5)); 109.42 (CN); 79.65 (C(4)); 36.80 (Me). IR, ν/cm^{-1}: 2244 (C≡N); 2148 (N_3); 1512 (NO_2); 1352 (NO_2). MS, *m/z*: 193 $[M]^+$.

5-Amino-1-methyl-3-nitropyrazole-4-carbonitrile (13). $NaI \cdot 2H_2O$ (1.013 g, 5.5 mmol) and then $FeCl_3 \cdot 6H_2O$ (0.246 g, 0.9 mmol) were added to a solution of azide **12** (0.117 g, 0.6 mmol) in acetonitrile (20 mL), the mixture was stirred for 15 min, and chloroform (50 mL) was added. The solution was washed with dilute solution of $Na_2S_2O_3$ and brine and dried with Na_2SO_4, and the solvent was removed *in vacuo* to give 0.066 g (65%) of product **13**, m.p. 218—220 °C. Found (%): C, 35.82; H, 3.19; N, 42.15. $C_5H_5N_5O_2$. Calculated (%): C, 35.93; H, 3.02; N, 41.90. ^{1}H NMR ($(CD_3)_2SO$), δ: 7.29 (s, NH_2); 3.65 (s, Me). ^{13}C NMR ($(CD_3)_2SO$, δ: 154.15 (C(5)); 151.89 (C(3)); 112.42 (CN); 68.74 (C(4)); 36.40 (Me). IR, ν/cm^{-1}: 3432 (NH_2); 3344 (NH_2); 3256 (NH_2); 3216 (NH_2); 2236 (C≡N); 1524 (NO_2); 1348 (NO_2). MS, *m/z*: 167 $[M]^+$.

5-Benzylthio-1-methyl-3-nitropyrazole-4-carboxamide (14). A solution of K_2CO_3 (0.580 g, 4.2 mmol) in water (1 mL) was added with stirring to a solution of amide **6** (0.500 g, 2.3 mmol) in DMF (7 mL), and then a solution of benzylmercaptan (0.280 g, 2.3 mmol) in DMF (3 mL) was added dropwise. The reaction mixture was stirred for 3 h, kept for 16 h, and poured in ice. The precipitate was filtered off, washed with several portions of ice water, and dried to give 0.665 g (98%) of product **14**, m.p. 194—197 °C. Found (%): C, 49.20; H, 4.44; N, 18.95; S, 11.00. $C_{12}H_{12}N_4O_3S$. Calculated (%): C, 49.31; H, 4.14; N, 19.17; S, 10.97. ^{1}H NMR ($(CD_3)_2SO$), δ: 7.91 (s, 1 H, NH_2); 7.82 (s, 1 H, NH_2); 7.34 (m, 3 H, Ph); 7.17 (m, 2 H, Ph); 4.17 (s, 2 H, CH_2); 3.40 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 162.25 ($CONH_2$); 149.92 (C(3)); 137.23 (*ipso*-Ph); 135.14 C((5)); 128.83, 128.71 (*o*-Ph + *m*-Ph); 127.71 (*p*-Ph); 120.91 (C(4)); 40.47 (Me); 37.28 (Me). IR, ν/cm^{-1}: 3400 (NH_2); 1688 (C=O); 1672 (C=O); 1528 (NO_2); 1364 (NO_2). MS, *m/z*: 292 $[M]^+$.

Methyl (4-carbamoyl-1-methyl-3-nitropyrazol-5-yl)thioacetate (15). A solution of K_2CO_3 (0.330 g, 2.4 mmol) in water (1 mL) was added with stirring to a solution of amide **6** (0.300 g, 1.4 mmol) in DMF (5 mL). Then a solution of methyl thioglycolate (0.15 g, 1.4 mmol) in DMF (2 mL) was added dropwise. The reaction mixture was stirred for 3 h, kept for 16 h, and poured in ice. The precipitate was filtered off, washed with several portions of ice water, and recrystallized from water to give 0.210 g (55%) of product **15**, m.p. 133—135 °C (from water). Found (%): C, 34.89; H, 3.94; N, 20.09; S, 11.47. $C_8H_{10}N_4O_5S$. Calculated (%): C, 35.04; H, 3.68; N, 20.43; S, 11.69. ^{1}H NMR ($(CD_3)_2SO$), δ: 7.87 (s, 1 H, NH_2); 7.64 (s, 1 H, NH_2); 4.04 (s, 3 H, NMe); 3.94 (s, 2 H, CH_2); 3.63 (s, 3 H, OMe). ^{13}C NMR ($(CD_3)_2SO$), δ: 169.09 (COOMe); 161.85 ($CONH_2$); 150.01 (C(3)); 134.82 (C(5)); 120.19 (C(4)); 52.44 (OMe); 38.08 (NMe); 37.16 (CH_2). IR, ν/cm^{-1}: 3396 (NH_2); 3308 (NH_2); 3208 (NH_2); 1704 (C=O, $COOCH_3$); 1668 (C=O, $CONH_2$); 1532 (NO_2); 1328 (NO_2). MS, *m/z*: 243 $[M - OCH_3]^+$.

5-[(2-Amino-2-oxoethyl)thio]-1-methyl-3-nitropyrazole-4-carboxamide (16). Aqueous ammonia (20 mL) was added to product **15** (0.500 g, 1.8 mmol). The resulting solution was stirred for 4 h and kept for 16 h. The precipitate was filtered off and the solvent was removed *in vacuo*. The portions of the product were combined and recrystallized from water to give 0.383 g (81%) of product **16**, m.p. 202—204 °C. Found (%): C, 32.15; H, 3.73; N, 27.09; S, 12.21. $C_7H_9N_5O_4S$. Calculated (%): C, 32.43; H, 3.50; N, 27.01; S, 12.37. ^{1}H NMR ($(CD_3)_2SO$), δ: 7.93 (s, 1 H, NH_2); 7.70 (s, 1 H, NH_2); 7.53 (s, 1 H, NH_2); 7.15 (s, 1 H, NH_2); 4.03 (s, 3 H, NMe); 3.62 (s, 2 H, CH_2). ^{13}C NMR ($(CD_3)_2SO$), δ: 169.39 (CH_2CONH_2); 161.97 ($CONH_2$); 150.24 (C(3)); 135.45 (C(5)); 120.04 (C(4)); 39.03 (CH_2); 38.21 (Me). IR, ν/cm^{-1}: 3516 (NH_2); 3400 br (NH_2); 3388 br (NH_2); 3200 (NH_2); 1696 (C=O); 1672 (C=O); 1556 (NO_2); 1332 (NO_2). MS, *m/z*: 243 $[M - NH_2]^+$.

2-[(1,4-Dimethyl-3-nitropyrazol-5-yl)thio]-*N*-phenylacetamide (17). Thioglycolic acid *N*-phenylamide (0.460 g, 2.8 mmol) and potassium carbonate (0.390 g, 2.8 mmol) were added to a solution of 1,4-dimethyl-3,5-dinitropyrazole (**1**) (0.500 g, 2.7 mmol) in acetonitrile (30 mL) (or *N*-methylpyrrolidone) and the mixture was stirred at reflux (or heated at 100 °C) for 70 h (or 5 h). The mixture was cooled, poured in water, and acidified with HCl to pH 2—3. The precipitate was filtered off, washed with several portions of water, dried, and recrystallized from toluene to give 0.230 g (28%) (0.340 g (41%)) of product **17**, m.p. 172—175 °C (from toluene). Found (%): C, 50.83; H, 4.46; N, 17.97; S, 10.24. $C_{13}H_{14}N_4O_3S$. Calculated (%): C, 50.97; H, 4.61; N, 18.29; S, 10.47. ^{1}H NMR ($(CD_3)_2SO$), δ: 9.99 (s, 1 H, NH); 7.46 (d, 2 H, *o*-Ph, J = 7.5 Hz); 7.29 (t, 2 H, *m*-Ph, J = 7.5 Hz); 7.05 (t, 1 H, *p*-Ph, J = 7.5 Hz); 3.99 (s, 3 H, NMe); 3.56 (s, 2 H, CH_2); 2.27 (s, 3 H, CMe). ^{13}C NMR ($(CD_3)_2SO$), δ: 166.11 (CONH); 151.92 (C(3)); 138.54 (*ipso*-Ph); 134.31 (C(5)); 128.76 (*m*-Ph);

123.62 (*p*-Ph); 120.11 (C(4)); 119.10 (*o*-Ph); 38.99 (CH_2); 38.13 (NMe); 10.13 (CMe). IR, ν/cm^{-1}: 3248 (NH); 3200 (NH); 1652 (C=O); 1556 (NO_2); 1344 (NO_2). MS, *m/z*: 306 $[M]^+$.

This work was supported by the Russian Foundation for Basic Research (Project No. 04-03-33097).

Reference

1. A. A. Zaitsev, I. L. Dalinger, A. M. Starosotnikov, V. V. Kachala, Yu. A. Strelenko, T. K. Shkineva, and S. A. Shevelev, *Zh. Org. Khim.*, 2005, **41**, 1538 [*Russ. J. Org. Chem.*, 2005, **41**, 1507 (Engl. Transl.)].
2. R. S. Hosmane, A. Bhan, and M. E. Rauser, *J. Org. Chem.*, 1985, **50**, 5892.
3. I. L. Dalinger, A. A. Zaitsev, T. K. Shkineva, and S. A. Shevelev, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 553 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 580].
4. (a) B. T. Tozer and S. Smiles, *J. Chem. Soc.*, 1938, 2052; (b) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 365; (c) R. Bayles, M. C. Johnson, R. F. Maisey, and R. W. Turner, *Synthesis*, 1977, 31; (d) R. Bayles, M. C. Johnson, R. F. Maisey, and R. W. Turner, *Synthesis*, 1977, 33; (e) I. G. C. Coutts and M. R. Southcott, *J. Chem. Soc., Perkin Trans. 1*, 1990, 767.
5. A. Kamal, K. V. Ramana, H. B. Ankati, and A. V. Ramana, *Tetrahedron Lett.*, 2002, **43**, 6861.
6. M. N. Glukhovtsev, R. D. Buch, and S. Laiter, *J. Org. Chem.*, 1997, **62**, 4036.
7. A. F. Pozharskii, *Teoreticheskie osnovy khimii heterocycleov* [*Theoretical Grounds of the Heterocycle Chemistry*], Khimiya, Moscow, 1985, (a) p. 221—222; (b) p. 225 and further; (c) p. 70.
8. R. D. Schmidt, G. S. Lee, P. F. Pagoria, A. R. Mitchell, and R. Gilardi, *J. Heterocycl. Chem.*, 2001, **38**, 1227.
9. (a) I. L. Dalinger, T. K. Shkinyova, S. A. Shevelev, V. S. Kuz´min, E. A. Arnautova, and T. S. Pivina, *Energetic Materials — Technology, Manufacturing and Processing, 29th International Annual Conference of ICT*, 1998, 57.
10. T. la Cour and S. E. Rasmussen, *Acta Chem. Scand.*, 1973, **27**, 1845.

Received April 28, 2007;
in revised form 4, 2007