Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 752–762. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 819–829.

Adamanthylazoles: VII.[1] Acid-catalyzed Adamanthylation of C–C- and C–N-Linked Azopyrazoles

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Received November 13, 2002

Abstract — Acid-catalyzed N-adamanthylation of C–C-linked pyrazolyl- and tetrazolylpyrazoles in H_3PO_4–AcOH (4 : 1) or H_2SO_4 involves, depending on conditions, one or both rings. The mutual effect of the rings is weak. C–N-Linked azolylpyrazoles are a conjugated system, and the formation of N-adamanthyl derivatives is strongly affected by the second azolyl ring.

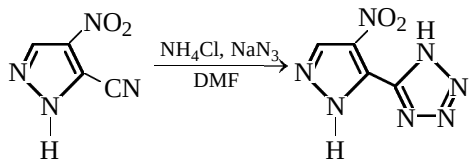
It was earlier shown that the acid-catalyzed alkylation of pyrazoles with adamanthanol (**I**) involves exclusively the unprotonated form of the former. The reaction direction is largely dependent on the basicity of the pyrazol: In the H_3PO_4–AcOH (4 : 1; here and hereinfter, weight ratio) system that is the most favorable for adamantylation, the reaction can be effected with pyrazoles whose pK_{BH^+} is no higher than 0.57 [2].

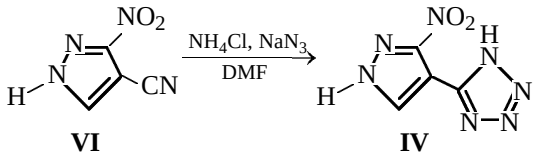
In the present work we have studied adamanthylation of C–C- and C–N-linked azolylpyrazoles in acid medium.

The effect of functional substituents on the basicity of the pyrazole ring is well described by a correlation equation and is rather predictable [1]. However, the basicity of azolylpyrazoles is unknown, and the nature of interaction of two heteroaromatic rings linked to each other is not always amenable to unambiguous treatment. Nevertheless, we admitted that with azolylpyrazoles containing an azolyl group which is more basic compared with pyrazolyl, protonation of the latter would favor adamanthylation by the pyrazole ring.

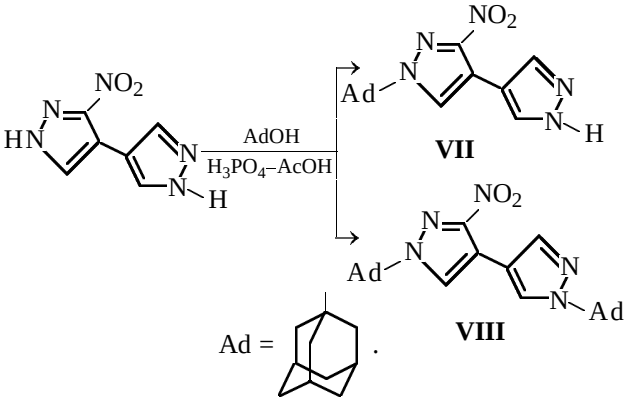
First we dwelt on C–C-linked azolylpyrazoles: 4-nitro-3-(pyrazol-4-yl)pyrazole (**II**), 4-nitro-3-(tetrazol-5-yl)-pyrazole (**III**), and 3-nitro-4-(tetrazol-5-yl)-pyrazole (**IV**). Compounds **III** and **IV** were prepared by the reactions of 3-cyano-4-nitro- (**V**) and 4-cyano-3-nitropyrazoles (**VI**), respectively, with sodium azide in DMF [2]. The reactivity of the cyano groups in **V** and **VI** is strongly dependent on their position in the ring: Compound **III** is formed easier and in a higher yield than compound **IV**.

The reaction of 4-nitro-3-(pyrazole-4-yl)pyrazole (**II**) with adamanthanol (**I**) was performed in a 4 : 1 H_3PO_4–AcOH mixture at 60°C. As a result, 1-(adamanthan-1-yl)-4-nitro-3-(pyrazole-4-yl)pyrazole (**VII**) was obtained (yield 55%).





With double the quantity of adamanthanol (**I**) and at a longer reaction time, 1-(adamanthan-1-yl)-3-[1-(adamanthan-1-yl)pyrazole-4-yl]-4-nitropyrazole (**VIII**) was obtained (yield 60%). Since pyrazole is not adamanthylated in such conditions [2], we can relate the latter result to an effect of the nitro group on the second, unsubstituted ring of compound **II**.



[1] For communication VI, see [1].

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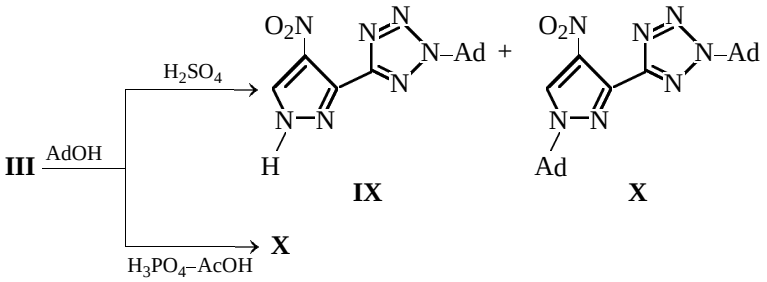
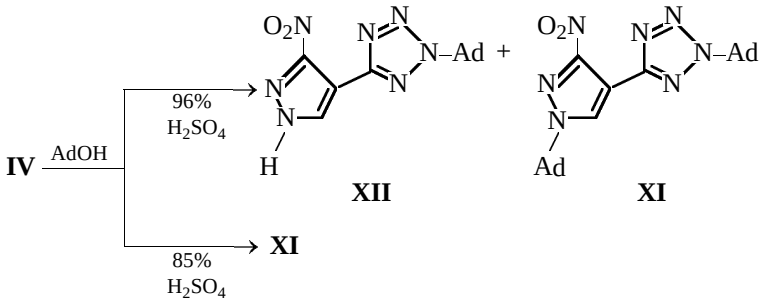
4-Nitro-3-(tetrazol-5-yl)pyrazole (**III**), too, is readily adamanthylated. Since tetrazoles readily react with adamanthanol (**I**) in sulfuric acid [3], in 96% sulfuric acid at 20°C we obtained 3-[2-(adamanthan-1-yl)tetrazol-5-yl]-4-nitropyrazole (**IX**). The pyrazole ring is protonated in these conditions and is not involved in reaction [1]. In the H_3PO_4–AcOH (4 : 1) medium, where the pyrazole ring is not protonated, the reaction with adamanthanol at 60°C gave 1-(adamanthan-1-yl)-3-[2-(adamanthan-1-yl)-tetrazol-5-yl]-4-nitropyrazole (**X**) in 65% yield (in sulfuric acid, compound **X** is formed in trace amounts).



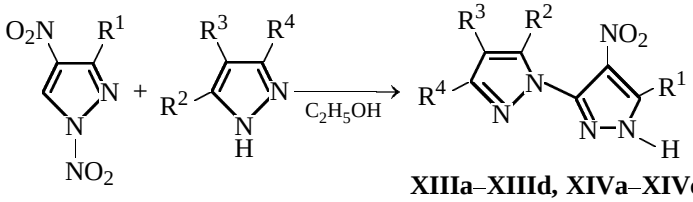
In tetrazolylpyrazole (**IV**), the 3-NO_2 group strongly reduces the basicity of the pyrazole ring, and compound **IV** in 85% sulfuric acid is adamanthylated by both rings to form 1-(adamanthan-1-yl)-4-[2-(adamanthan-1-yl)tetrazol-5-yl]-3-nitropyrazole (**XI**). In 96% sulfuric acid, the pyrazole ring is already protonated, and the reaction involves the tetrazole ring only and gives rise to 4-[2-(adamanthan-1-yl)tetrazol-5-yl]-3-nitropyrazole (**XII**). Compound **XI** in these conditions is formed in trace amounts only.



The resulting data show that each azolyl ring in C–C-linked azolylpyrazoles **II**–**IV** is adamanthylated depending on its nature, whereas the effect of the second ring is weak.

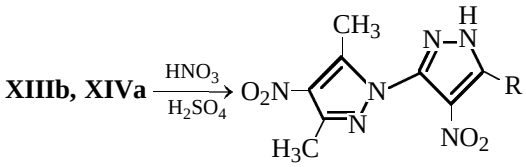
C–N-Linked 3-(azol-1-yl)pyrazoles were synthesized by *cine* substitution [4].

In this way we obtained 5-methyl-4-nitro-3-(pyrazol-1-yl)pyrazole (**XIIIa**), 3-(3,5-dimethylpyrazol-1-yl)-5-methyl-4-nitropyrazole (**XIIIb**), 3-(4-chloropyrazol-1-yl)-5-methyl-4-nitropyrazole (**XIIIc**), 3-(4-bromo-3,5-dimethylpyrazol-1-yl)-5-methyl-4-nitropyrazole (**XIIId**), 3-(3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (**XIVa**), 3-(4-chloropyrazol-1-yl)-4-nitropyrazole (**XIVb**), and 3-(4-bromo-3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (**XIVc**).



XIII, $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$ (**a**); $R^2 = R^4 = CH_3$, $R^3 = H$ (**b**), Br (**c**); $R^2 = R^4 = H$, $R^3 = Cl$ (**d**). **XIV**, $R^1 = H$; $R^2 = R^4 = CH_3$; $R^3 = H$ (**a**), Br (**c**); $R^2 = R^4 = H$, $R^3 = Cl$ (**b**).

Nitration with a mixture of sulfuric and nitric acids of compounds **XIIIb** and **XIVa** gave 3-(3,5-dimethyl-4-nitropyrazol-1-yl)-5-methyl-4-nitropyrazole (**XIIIe**), and 3-(3,5-dimethyl-4-nitropyrazol-1-yl)-4-nitropyrazole (**XIVd**), respectively.

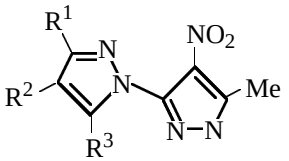


XIIIe, XIVd

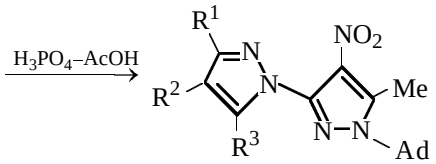
4-Nitro-3-(1,2,4-triazol-4-yl)pyrazole (**XVa**) was prepared by cyclization of 3-amino-4-nitropyrazole with diformylhydrazine [5], and 5-methyl-4-nitro-3-(1,2,4-triazol-1-yl)pyrazole (**XVb**) was prepared by *cine* substitution.

Azolylpyrazoles **XIIIa**, **XIIIb**, and **XVb** are adamanthylated not so unambiguously as C–C-linked azolylazoles **II**–**IV**. 4-Nitropyrazoles in the 4:1 H_3PO_4–AcOH system are readily adamanthylated at 60°C [1], whereas pyrazolylpyrazoles **XIIIa** and **XIIIb** and compound **XVb**, contrary to expectations, fail to react with adamanthanol (**I**) under these conditions. This fact can be explained in terms of protonation of the NH-containing pyrazole ring. Apparently, (azol-1-yl)pyrazoles **XIIIa** and **XIIIb** involve united conjugation systems, which favors effective transmission of the electronic effect of the azolyl substituent via nitrogen to the pyrazole ring and, thus renders the latter much more basic.

However, such an electron density distribution in 3-(azol-1-yl)pyrazoles is quite sensitive to substituents and an electron-acceptor substituent in the azolyl ring will suffice for successful adamanthylation. Evidence for this conclusion was provided by the adamanthylation of compounds **XIIIc**–**XIIIe** in the 4:1 H_3PO_4–AcOH system to obtain 1-(adamanthan-1-yl)-5-methyl-4-nitro-3-(4-bromo-3,5-dimethylpyrazol-1-yl)pyrazole (**XVId**), 1-(adamanthan-1-yl)-3-(4-chloropyrazol-1-yl)-5-methyl-4-nitropyrazole (**XVIc**), and 1-(adamanthan-1-yl)-3-(3,5-dimethyl-4-nitropyrazol-1-yl)-5-methyl-4-nitro-3-pyrazole (**XVIe**), respectively.



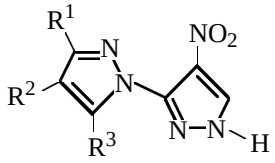
XIIIc–**XIIIe**



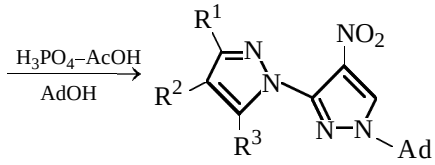
XVIc–**XVIe**

$R^1 = R^3 = H$, $R^2 = Cl$ (**c**); $R^1 = R^2 = Me$, $R^3 = Br$ (**d**), NO_2 (**e**).

Adamanthylation of 3-(pyrazol-1-yl)pyrazoles **XIVb**–**XIVd** is to a certain extent hindered by the methyl group α to the pyrazole NH group: When it is replaced by hydrogen, the yields of compounds **XVIIa**, **XVIIb**, and **XVIId** increase almost two times compared with compounds **XIVb**–**XIVd** under the same conditions.



XIVa–**XIVd**



XVIIa–**XVIId**

$R^1 = R^3 = Me$, $R^2 = H$ (**a**); $R^1 = R^3 = H$, $R^2 = Cl$ (**b**); $R^1 = R^3 = Me$, $R^2 = Br$ (**c**); $R^1 = R^3 = Me$, $R^2 = NO_2$ (**d**).

Attempted reaction with adamanthanol (**I**) of (1,2,4-triazol-4-yl)pyrazole (**XVa**) proved unsuccessful.

The results of the present work, on the other hand, highlight the role of protonation in acid-catalyzed adamanthylation of azoles and, on the other, the intricate and ambiguous nature of conjugation effects and protolytic reactions in C–N-linked azolylpyrazoles.

The structure of compounds **VII**–**XI** was proved by ROESY [6] and HMQR [7] spectra. The ^1H NMR spectra of compounds **XVIa**–**XVIc** and **XVIIa**–**XVIId** gave no unambiguous evidence for the position of the adamanthyl fragment. The structure was elucidated by X-ray diffraction on an example of compounds **XI** and **XVId** (Tables 1–6, Figs. 1, 2).

EXPERIMENTAL

The ^1H NMR spectra were measured on a Bruker AM-300 spectrometer (300.13 MHz) in $CDCl_3$ at 30°C. The 2D spectra were obtained using the HMQR technique [7]. Thin-layer chromatography was performed on Silufol UV-254 plates, development in

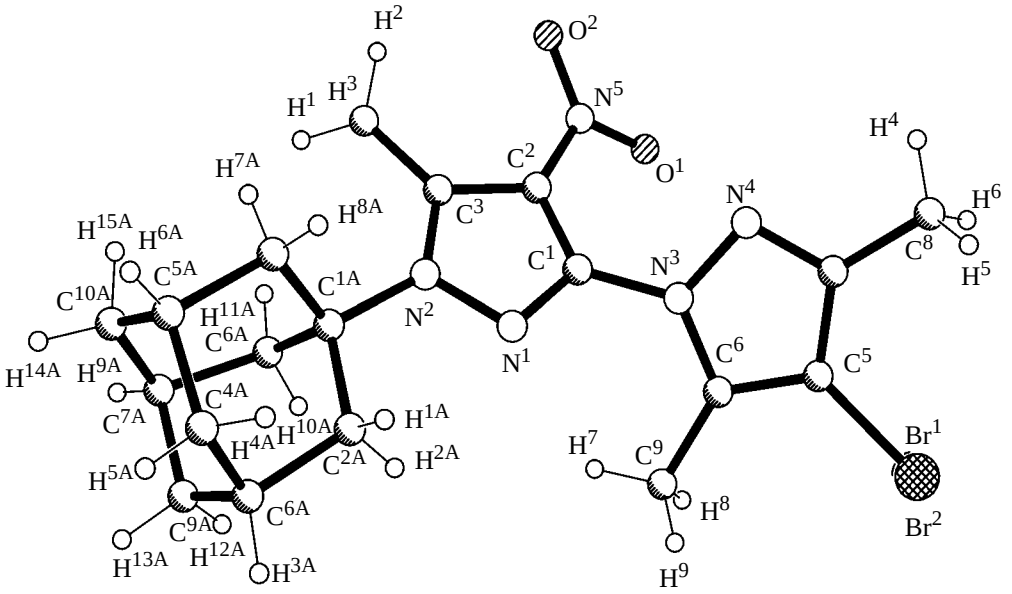


Fig. 1. Molecular structure of 1-(adamanthan-1-yl)-3-(4-bromo-3,5-dimethylpyrazol-1-yl)-5-methyl-4-nitropyrazole (**XVId**).

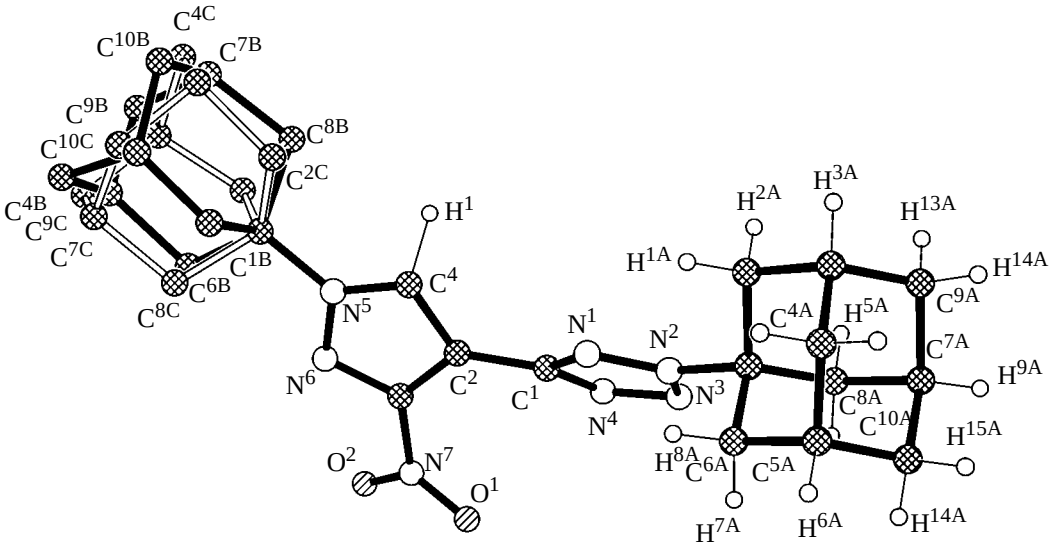


Fig. 2. Molecular structure of 1-(adamanthan-1-yl)-4-[2-(adamanthan-1-yl)tetrazol-5-yl]-3-nitropyrazole (**XI**).

iodine vapor or UV light. Elemental analysis was performed on a Hewlett–Packard B-185 analyzer.

X-ray diffraction analysis was performed on an Enraf–Nonius CAD-4 automatic diffractometer (graphite monochromator, MoK_α radiation, θ scanning, θ_{max} 27°). The calculations were performed using the SHELX 93 program package [8].

Crystals of compound **XVId**, monoclinic, *a* 14.654(4), *b* 10.544(9), *c* 13.905(3) A; β 112.06(4)°, *V* 1991(2) Å^3, *M* 434.34, d_{calc} 1.45 g/cm^3, μ_{Mo} 2.09 mm^{-1}, *F*(000) 896.0, space group $P2_1/c$, *Z* 4. The crystals are stable in air but slowly decompose under X-ray irradiation. A total of 2291 reflections were measured, of which 1679 with $I > 2$ were used in structure solution and refinement. The refinement revealed strong oscillations of the bromine and adamanthane carbon atoms with respect to their gravity centers. The bromine atom oscillates so strongly that it may be safely suggested that it is statistically disordered over two positions. Their occupancies were refined isotropically with fixed thermal parameters. The following confidence parameters were obtained: *R* 0.076, R_W 0.204, and *Goof* 1.079. The atomic coordinates and thermal parameters are listed in Table 1.

Table 1. Atomic coordinates and thermal corrections B_{eq} for compound **XVId**

Atom	*x*	*y*	*z*	B_{eq}
Br^{1*}	0.3858(4)	0.1104(7)	0.0373(4)	8.5(2)
Br^2	0.3840(5)	0.1187(6)	0.0341(4)	9.5(2)
O^1	0.0656(5)	0.2908(7)	–0.3618(5)	7.0(2)
O^2	0.0449(5)	0.2191(8)	–0.5029(6)	8.0(2)
N^1	0.1940(4)	0.0239(6)	–0.5161(4)	4.2(1)
N^2	0.2423(5)	0.0134(7)	–0.4112(5)	5.0(1)
N^3	0.2165(5)	0.0869(7)	–0.2627(5)	4.6(1)
N^4	0.1454(5)	0.0640(8)	–0.2246(5)	5.3(2)
N^5	0.0378(6)	0.2195(8)	–0.4374(6)	5.5(2)
C^1	0.1892(6)	0.0822(9)	–0.3726(6)	5.0(2)
C^2	0.1095(5)	0.1346(8)	–0.4482(6)	4.1(1)
C^3	0.1126(6)	0.0949(8)	–0.5426(5)	4.1(1)
C^4	0.1915(7)	0.0679(8)	–0.1228(6)	4.9(2)
C^5	0.2901(6)	0.0977(8)	–0.0974(6)	4.9(2)
C^6	0.3059(6)	0.1094(8)	–0.1887(6)	4.9(2)
C^7	0.0436(6)	0.129(1)	–0.6488(6)	5.8(2)
C^8	0.1382(8)	0.040(1)	–0.0531(7)	7.1(2)
C^9	0.3965(7)	0.139(1)	–0.2088(7)	6.5(2)
C^{1A}	0.2411(5)	–0.0406(8)	–0.5832(6)	4.3(2)
C^{2A}	0.334(1)	–0.103(2)	–0.518(1)	14.2(7)
C^{3A}	0.392(1)	–0.154(1)	–0.584(1)	9.4(4)
C^{4A}	0.327(1)	–0.259(1)	–0.633(2)	12.0(6)
C^{5A}	0.2285(9)	–0.216(2)	–0.711(1)	11.0(5)
C^{6A}	0.177(1)	–0.139(2)	–0.648(1)	12.7(6)
C^{7A}	0.302(1)	–0.018(1)	–0.729(2)	10.4(5)
C^{8A}	0.268(1)	0.053(1)	–0.647(1)	11.4(5)
C^{9A}	0.399(1)	–0.060(2)	–0.659(1)	11.9(6)
C^{10A}	0.239(1)	–0.120(2)	–0.780(1)	10.6(5)
H^1	0.064	0.088	–0.699	
H^2	–0.021	0.101	–0.658	
H^3	0.043	0.219	–0.658	
H^4	0.070	0.022	–0.093	
H^5	0.168	–0.031	–0.010	
H^6	0.143	0.114	–0.011	
H^7	0.382	0.137	–0.282	
H^8	0.417	0.222	–0.182	
H^9	0.448	0.079	–0.174	
H^{1A}	0.322	–0.174	–0.482	
H^{2A}	0.372	–0.042	–0.468	
H^{3A}	0.458	–0.180	–0.543	
H^{4A}	0.315	–0.294	–0.575	
H^{5A}	0.358	–0.323	–0.660	
H^{6A}	0.193	–0.290	–0.745	
H^{7A}	0.122	–0.097	–0.699	
H^{8A}	0.152	–0.194	–0.608	
H^{9A}	0.307	0.039	–0.781	
H^{10A}	0.321	0.104	–0.602	
H^{11A}	0.213	0.107	–0.681	
H^{12A}	0.430	0.015	–0.622	
H^{13A}	0.437	–0.089	–0.698	
H^{14A}	0.254	–0.156	–0.835	
H^{15A}	0.173	–0.086	–0.809	

Table 2. Bond lengths in compound **XVId**

Bond	*d*, Å	Bond	*d*, Å
Br^1–Br^2	0.097(9)	Br^1–C^5	1.877(9)
Br^2–C^5	1.843(9)	N^1–N^2	1.366(8)
N^1–C^3	1.34(1)	N^1–C^1A	1.51(1)
N^2–C^1	1.32(1)	C^1–C^2	1.36(1)
C^1–N^3	1.43(1)	C^2–N^5	1.43(1)
C^2–C^3	1.40(1)	N^5–O^1	1.23(1)
N^5–O^2	1.21(1)	C^3–C^7	1.49(1)
C^7–H^1	0.96	C^7–H^2	0.96
C^7–H^3	0.96	N^3–N^4	1.36(1)
N^3–C^6	1.35(1)	N^4–C^4	1.32(1)
C^4–C^8	1.48(2)	C^4–C^5	1.39(1)
C^8–H^4	0.96	C^8–H^5	0.96
C^8–H^6	0.96	C^5–C^6	1.38(1)
C^6–C^9	1.49(1)	C^9–H^7	0.96
C^9–H^8	0.96	C^9–H^9	0.96
C^{1A}–C^{2A}	1.47(2)	C^{1A}–C^{6A}	1.46(2)
C^{1A}–C^{8A}	1.47(2)	C^{2A}–H^{1A}	0.96
C^{2A}–H^{2A}	0.96	C^{2A}–C^{3A}	1.55(2)
C^{3A}–H^{3A}	0.96	C^{3A}–C^{4A}	1.46(2)
C^{3A}–C^{9A}	1.47(2)	C^{4A}–H^{4A}	0.96
C^{4A}–H^{5A}	0.96	C^{4A}–C^{5A}	1.50(3)
C^{5A}–H^{6A}	0.96	C^{5A}–C^{6A}	1.58(2)
C^{5A}–C^{10A}	1.45(2)	C^{6A}–H^{7A}	0.96
C^{6A}–H^{8A}	0.96	C^{7A}–H^{9A}	0.96
C^{7A}–C^{8A}	1.59(3)	C^{7A}–C^{9A}	1.45(3)
C^{7A}–C^{10A}	1.42(3)	C^{8A}–H^{10A}	0.96
C^{8A}–H^{11A}	0.96	C^{9A}–H^{12A}	0.96
C^{9A}–H^{13A}	0.96	C^{10A}–H^{14A}	0.96
C^{10A}–H^{15A}	0.96		

The C–N-linked pyrazole rings of the bipyrazole fragment are almost planar (the mean deviations of atoms from the plane are 0.004 and 0.009 Å in the nitromethylpyrazole and dimethylbromopyrazole rings, respectively); the dihedral angle between the planes is 48.4°. Such a mutual position of the heterorings is explained by the presence of *ortho*-substituents with respect to the exocyclic C–N bond. The exocyclic C–N bond (1.43 Å) is closer in length to the ordinary bond C_{sp^2}–N_{sp^3} than to the ordinary bond C_{sp^2}–N_{sp^2} (1.416 and 1.355 Å, respectively [9]), implying lack of conjugation between the pyrazole rings. The nitro group is turned with respect to the heteroring plane by 31.4°, and its parameters are normal values [9]. The orientation of the adamanthane fragment with respect to the pyrazole ring can be characterized by the $N^2N^1C^{1A}C^{2A}$ torsion angle (–1.2°). Its C–C bond lengths vary within 1.45–1.59 Å. Regardless of the strong scatter in individual values, the mean C–C bond length in the adamanthane fragment (1.50 Å) is

Table 3. Bond angles in compound **XVId**

Angle	ω, deg	Angle	ω, deg
$N^2N^1C^3$	113.0(6)	$N^2N^1C^{1A}$	116.6(6)
$C^3N^1C^{1A}$	130.3(6)	$N^1N^2C^1$	104.0(7)
$N^2C^1C^2$	112.1(8)	$N^2C^1N^3$	119.0(8)
$C^2C^1N^3$	128.8(8)	$C^1C^2N^5$	128.6(8)
$C^1C^2C^3$	106.4(7)	$N^5C^2C^3$	124.9(7)
$C^2N^5O^1$	116.9(8)	$C^2N^5O^2$	119.1(8)
$O^1N^5O^2$	124.0(8)	$N^1C^3C^2$	104.4(7)
$N^1C^3C^7$	127.7(7)	$C^2C^3C^7$	127.8(7)
$C^3C^7H^1$	110	$C^3C^7H^2$	109
$C^3C^7H^3$	110	$H^1C^7H^2$	109
$H^1C^7H^3$	109	$H^2C^7H^3$	109
$C^1N^3N^4$	117.7(7)	$C^1N^3C^6$	128.6(7)
$N^4N^3C^6$	113.7(7)	$N^3N^4C^4$	104.8(7)
$N^4C^4C^8$	120.8(8)	$N^4C^4C^5$	110.1(8)
$C^8C^4C^5$	129.1(9)	$C^4C^8H^4$	110
$C^4C^8H^5$	110	$C^4C^8H^6$	108
$H^4C^8H^5$	109	$H^4C^8H^6$	109
$H^5C^8H^6$	109		
$Br^1C^5C^4$	125.9(7)	$Br^1C^5C^6$	126.2(7)
$Br^2C^5C^4$	126.7(7)	$Br^2C^5C^6$	125.5(7)
$C^4C^5C^6$	107.8(8)	$N^3C^6C^5$	103.6(7)
$N^3C^6C^9$	125.0(8)	$C^5C^6C^9$	131.5(8)
$C^6C^9H^7$	110	$C^6C^9H^8$	107
$C^6C^9H^9$	111	$H^7C^9H^8$	109
$H^7C^9H^9$	109	$H^8C^9H^9$	109
$N^1C^{1A}C^{2A}$	110.6(9)	$N^1C^{1A}C^{6A}$	111.0(9)
$N^1C^{1A}C^{8A}$	111.0(8)	$C^{2A}C^{1A}C^{6A}$	107(1)
$C^{2A}C^{1A}C^{8A}$	106(1)	$C^{6A}C^{1A}C^{8A}$	111(1)
$C^{1A}C^{2A}H^{1A}$	111	$C^{1A}C^{2A}H^{2A}$	108
$C^{1A}C^{2A}C^{3A}$	112(1)	$H^{1A}C^{2A}H^{2A}$	108
$H^{1A}C^{2A}C^{3A}$	106	$H^{2A}C^{2A}C^{3A}$	111
$C^{2A}C^{3A}H^{3A}$	114	$C^{2A}C^{3A}C^{4A}$	98(1)
$C^{2A}C^{3A}C^{9A}$	112(1)	$H^{3A}C^{3A}C^{4A}$	114
$H^{3A}C^{3A}C^{9A}$	107	$C^{4A}C^{3A}C^{9A}$	112(1)
$C^{3A}C^{4A}H^{4A}$	101	$C^{3A}C^{4A}H^{5A}$	113(2)
$C^{3A}C^{4A}C^{5A}$	113(1)	$H^{4A}C^{4A}H^{5A}$	108
$H^{4A}C^{4A}C^{5A}$	107(2)	$H^{5A}C^{4A}C^{5A}$	114
$C^{4A}C^{5A}H^{6A}$	108	$C^{4A}C^{5A}C^{6A}$	107(1)
$C^{4A}C^{5A}C^{10A}$	112(1)	$H^{6A}C^{5A}C^{6A}$	114
$H^{6A}C^{5A}C^{10A}$	115(2)	$C^{6A}C^{5A}C^{10A}$	102(1)
$C^{1A}C^{6A}C^{5A}$	112(1)	$C^{1A}C^{6A}H^{7A}$	107
$C^{1A}C^{6A}H^{8A}$	111	$C^{5A}C^{6A}H^{7A}$	105
$C^{5A}C^{6A}H^{8A}$	112	$H^{7A}C^{6A}H^{8A}$	109
$H^{9A}C^{7A}C^{8A}$	112	$H^{9A}C^{7A}C^{9A}$	112
$H^{9A}C^{7A}C^{10A}$	108	$C^{8A}C^{7A}C^{9A}$	99(1)
$C^{8A}C^{7A}C^{10A}$	113(1)	$C^{9A}C^{7A}C^{10A}$	113(2)
$C^{1A}C^{8A}C^{7A}$	110(1)	$C^{1A}C^{8A}H^{10A}$	109
$C^{1A}C^{8A}H^{11A}$	109	$C^{7A}C^{8A}H^{10A}$	109
$C^{7A}C^{8A}H^{11A}$	111	$H^{10A}C^{8A}H^{11A}$	108
$C^{3A}C^{9A}C^{7A}$	112(2)	$C^{3A}C^{9A}H^{12A}$	108
$C^{3A}C^{9A}H^{13A}$	113	$C^{7A}C^{9A}H^{12A}$	105
$C^{7A}C^{9A}H^{13A}$	110	$H^{12A}C^{9A}H^{13A}$	107
$C^{5A}C^{10A}C^{7A}$	114(2)	$C^{5A}C^{10A}H^{14A}$	112
$C^{5A}C^{10A}H^{15A}$	102	$C^{7A}C^{10A}H^{14A}$	113
$C^{7A}C^{10A}H^{15A}$	107	$H^{14A}C^{10A}H^{15A}$	108

Table 4. Atomic coordinates and thermal corrections B_{eq} for compound **XI**

Atom	*x*	*y*	*z*	B_{iso}, B_{eq}
O^1	1.107(1)	0.396(1)	0.192(1)	6.9(5)
O^2	0.984(1)	0.393(1)	0.027(2)	6.9(5)
N^1	1.084(1)	0.344(1)	0.530(2)	3.9(4)
N^2	1.137(1)	0.409(1)	0.591(1)	4.2(4)
N^3	1.138(1)	0.486(2)	0.528(2)	5.8(5)
N^4	1.076(1)	0.470(2)	0.421(2)	5.5(5)
N^5	0.848(1)	0.257(1)	0.225(2)	4.0(4)
N^6	0.882(1)	0.290(1)	0.138(1)	3.9(4)
N^7	1.023(2)	0.380(1)	0.134(2)	4.7(4)
C^1	1.045(2)	0.382(2)	0.422(2)	3.6(4)
C^2	0.976(2)	0.335(1)	0.326(2)	3.7(5)
C^3	0.962(1)	0.338(1)	0.200(2)	3.5(4)
C^4	0.900(1)	0.280(2)	0.335(2)	3.8(5)
C^{1A}	1.198(1)	0.402(1)	0.719(2)	3.7(4)
C^{2A}	1.133(1)	0.364(2)	0.789(2)	4.8(5)
C^{3A}	1.197(2)	0.347(2)	0.922(2)	6.4(6)
C^{4A}	1.277(2)	0.280(2)	0.923(2)	7.5(7)
C^{5A}	1.339(2)	0.312(2)	0.850(2)	6.5(7)
C^{6A}	1.276(2)	0.329(2)	0.721(2)	5.1(5)
C^{7A}	1.312(2)	0.473(2)	0.902(2)	6.7(6)
C^{8A}	1.245(2)	0.489(2)	0.770(2)	6.4(6)
C^{9A}	1.243(2)	0.438(2)	0.970(2)	7.2(7)
C^{10A}	1.389(1)	0.400(2)	0.899(2)	6.7(6)
C^{1B}	0.760(1)	0.197(1)	0.194(1)	4.0(4)
C^{2B}	0.774(2)	0.092(2)	0.234(2)	6(1)
C^{3B}	0.685(2)	0.032(2)	0.216(2)	7(2)
C^{4B}	0.635(2)	0.024(2)	0.077(2)	7(1)
C^{5B}	0.623(2)	0.123(2)	0.026(2)	4(1)
C^{6B}	0.724(2)	0.190(2)	0.052(2)	3.4(8)
C^{7B}	0.581(2)	0.177(2)	0.204(2)	4(1)
C^{8B}	0.677(2)	0.246(2)	0.242(2)	4.5(9)
C^{9B}	0.599(2)	0.074(2)	0.248(2)	11(2)
C^{10B}	0.535(2)	0.175(2)	0.056(2)	10(2)
C^{2C}	0.738(2)	0.152(2)	0.305(2)	5(1)
C^{3C}	0.632(2)	0.105(2)	0.267(2)	3.3(8)
C^{4C}	0.547(2)	0.166(2)	0.180(2)	12(2)
C^{5C}	0.574(2)	0.187(2)	0.067(2)	6(1)
C^{6C}	0.666(2)	0.256(2)	0.114(2)	9(2)
C^{7C}	0.677(2)	0.057(2)	0.072(2)	5(1)
C^{8C}	0.771(2)	0.122(2)	0.104(2)	10(2)
C^{9C}	0.667(2)	0.025(2)	0.197(2)	8(2)
C^{10C}	0.601(2)	0.118(2)	–0.017(2)	11(2)
H^1	0.863(1)	0.268(2)	0.418(2)	
H^{1A}	1.102(1)	0.308(2)	0.754(2)	
H^{2A}	1.082(1)	0.409(2)	0.788(2)	
H^{3A}	1.157(2)	0.325(2)	0.969(2)	
H^{4A}	1.247(2)	0.223(2)	0.891(2)	
H^{5A}	1.316(2)	0.270(2)	1.005(2)	
H^{6A}	1.389(2)	0.267(2)	0.851(2)	
H^{7A}	1.317(2)	0.352(2)	0.675(2)	
H^{8A}	1.246(2)	0.273(2)	0.685(2)	
H^{9A}	1.343(2)	0.532(2)	0.941(2)	
H^{10A}	1.194(2)	0.532(2)	0.771(2)	
H^{11A}	1.282(2)	0.514(2)	0.720(2)	
H^{12A}	1.279(2)	0.432(2)	1.054(2)	
H^{13A}	1.192(2)	0.483(2)	0.964(2)	
H^{14A}	1.4246(7)	0.4213(6)	0.8460(8)	
H^{15A}	1.4351(7)	0.3923(6)	0.9776(8)	

Table 5. Bond lengths in compound **XI**

Bond	*d*, Å	Bond	*d*, Å
N^1–N^2	1.29(3)	N^1–C^1	1.33(3)
N^2–N^3	1.34(3)	N^2–C^{1A}	1.49(3)
N^3–N^4	1.32(3)	N^4–C^1	1.35(3)
C^1–C^2	1.43(3)	C^2–C^3	1.42(3)
C^2–C^4	1.37(3)	C^3–N^6	1.34(3)
C^3–N^7	1.45(3)	C^4–H^1	1.24
C^4–N^5	1.32(3)	N^5–N^6	1.34(2)
N^5–C^{1B}	1.48(2)	N^7–O^1	1.22(3)
N^7–O^2	1.22(3)	C^{1A}–C^{2A}	1.51(3)
C^{1A}–C^{6A}	1.52(3)	C^{1A}–C^{8A}	1.47(3)
C^{2A}–H^{1A}	0.96	C^{2A}–H^{2A}	0.96
C^{2A}–C^{3A}	1.56(3)	C^{3A}–H^{3A}	0.96
C^{3A}–C^{4A}	1.48(4)	C^{3A}–C^{9A}	1.50(4)
C^{4A}–H^{4A}	0.96	C^{4A}–H^{5A}	0.96
C^{4A}–C^{5A}	1.48(4)	C^{5A}–H^{6A}	0.96
C^{5A}–C^{6A}	1.53(3)	C^{5A}–C^{10A}	1.49(3)
C^{6A}–H^{7A}	0.96	C^{6A}–H^{8A}	0.96
C^{7A}–H^{9A}	0.96	C^{7A}–C^{8A}	1.58(3)
C^{7A}–C^{9A}	1.52(4)	C^{7A}–C^{10A}	1.53(3)
C^{8A}–H^{10A}	0.96	C^{8A}–H^{11A}	0.96
C^{9A}–H^{12A}	0.96	C^{9A}–H^{13A}	0.96
C^{10A}–H^{14A}	0.96	C^{10A}–H^{15A}	0.96
C^{1B}–C^{2B}	1.58(1)	C^{1B}–C^{6B}	1.59(1)
C^{1B}–C^{8B}	1.61(1)	C^{1B}–C^{2C}	1.57(1)
C^{1B}–C^{6C}	1.63(1)	C^{1B}–C^{8C}	1.55(1)
C^{2B}–C^{3B}	1.49(1)	C^{3B}–C^{4B}	1.57(1)
C^{3B}–C^{9B}	1.52(1)	C^{4B}–C^{5B}	1.54(1)
C^{5B}–C^{6B}	1.69(1)	C^{5B}–C^{10B}	1.58(1)
C^{7B}–C^{8B}	1.64(1)	C^{7B}–C^{9B}	1.58(1)
C^{7B}–C^{10B}	1.65(1)	C^{2C}–C^{3C}	1.59(1)
C^{3C}–C^{4C}	1.59(1)	C^{3C}–C^{9C}	1.58(1)
C^{4C}–C^{5C}	1.52(1)	C^{5C}–C^{6C}	1.60(1)
C^{5C}–C^{10C}	1.53(1)	C^{7C}–C^{8C}	1.59(1)
C^{7C}–C^{9C}	1.58(1)	C^{7C}–C^{10C}	1.54(1)

close to that in the free adamanthane (1.52 Å [10]). The bond lengths and angles are listed in Table 2, and the structure of this compound is shown in Fig. 1.

Crystals of compound **XI**, monoclinic, *a* 14.219(5), *b* 14.482(7), *c* 11.657(5) Å; β 107.12(5)°, *V* 2294(2) $Å^3$, *M* 449.6, d_{calc} 1.302 g/cm^3, μ_{Mo} 0.087 mm^{-1}, *F*(000) 960.0, space group $P2_1/c$, *Z* 4. A total of 3167 reflections were measured, 1045 of which with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure of compound **XI** was solved by the direct method and refined by full-matrix least-squares calculations with allowance for the anisotropy of thermal oscillations of non-hydrogen atoms. The refinement revealed that carbon atoms of one of the adamanthane fragments are statistically disordered over two positions. Their occupancies were calculated with fixed thermal parameters and set invariant in further refinement. The positional and thermal parameters of disordered atoms were refined isotropically. The pyrazole hydrogen atom was located by difference synthesis. The positions of hydrogens in the nondisordered adamanthane fragment were calculated geometrically with allowance for crystal chemical data. The hydrogen atoms were included in the refinement with fixed positional and thermal parameters (*B* 3.948 and 6.316 $Å^2$ for H^1 and H^{1A}–H^{15A}, respectively). The final confidence factors are as follows: *R* 0.125, R_W 0.356, and *Goof* 0.959. The high confidence factors are explained by the mosaic nature of the crystal, fast intensity decay with increasing sinθ/λ, as well as the presence of a disordered adamanthane carcass. The atomic coordinates and thermal parameters are listed in Table 1 and the bond lengths and angles, in Table 2.

The almost planar heterorings of the pyrazolyltetrazole fragment (Fig. 2) (the mean deviations of atoms from the plane are 0.015 and 0.005 A for the tetrazole and pyrazole rings, respectively) are turned with respect to each other by 39.2°. The geometric parameters of the azoles (Table 5) are close to normal values [9]. The exocyclic C–C bond (1.43 Å) is slightly shorter that the ordinary C_{sp^2}–C_{sp^2} bond (1.478 and 1.455 Å for unconjugated and conjugated bonds, respectively [9]). The nitro group is turned with respect to the pyrazole ring by 20.8°, and its parameters are close to normal values [9].

The orientation of the adamanthane fragments with respect to the tetrazole and pyrazole rings can be characterized by the torsion angles listed in Table 3. The C–C bond lengths in them vary within a rather wide range, the strongest scatter observed in the disordered adamanthane carcass. The mean bond lengths in the ordered and disordered adamanthane fragments are 1.51 and 1.58 Å, respectively (1.52 Å in adamanthane [10]).

All intermolecular contacts in both compounds have van der Waals values.

4-Nitro-3-(tetrazol-5-yl)pyrazole (III). Sodium azide, 3.9 g, and 3.21 g of ammonium chloride were added to a solution of 6.9 g of 3-cyano-4-nitropyrazole (**V**) in 150 ml of DMF. The mixture was heated at 110°C for 6 h, after which the precipitate was filtered off, the solution was concentrated to 30–40 ml and poured into 150 ml of water. The solution was acidified with HCl to pH 2–3. The precipitate that formed was filtered off and dried. Yield 6.33 g (70%),

Table 6. Bond angles in compound **XI**

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$N^2N^1C^1$	103(2)	$N^1N^2N^3$	114(2)	$C^{8A}C^{7A}C^{9A}$	105(2)	$C^{8A}C^{7A}C^{10A}$	108(2)
$N^1N^2C^1A$	125(2)	$N^3N^2C^{1A}$	121(2)	$C^{9A}C^{7A}C^{10A}$	111(2)	$C^{1A}C^{8A}C^{7A}$	110(2)
$N^2N^3N^4$	105(2)	$N^3N^4C^1$	106(2)	$C^{1A}C^{8A}H^{10A}$	108	$C^{1A}C^{8A}H^{11A}$	110(3)
$N^1C^1N^4$	111(2)	$N^1C^1C^2$	123(2)	$C^{7A}C^{8A}H^{10A}$	108	$C^{7A}C^{8A}H^{11A}$	112(3)
$N^4C^1C^2$	126(2)	$C^1C^2C^3$	130(2)	$H^{10A}C^{8A}H^{11A}$	108	$C^{3A}C^{9A}C^{7A}$	112(2)
$C^1C^2C^4$	126(2)	$C^3C^2C^4$	103(2)	$C^{3A}C^{9A}H^{12A}$	110	$C^{3A}C^{9A}H^{13A}$	109(3)
$C^2C^3N^6$	113(2)	$C^2C^3N^7$	130(2)	$C^{7A}C^{9A}H^{12A}$	109	$C^{7A}C^{9A}H^{13A}$	109(3)
$N^6C^3N^7$	117(2)	$C^2C^4H^1$	132(2)	$H^{12A}C^{9A}H^{13A}$	108	$C^{5A}C^{10A}C^{7A}$	110(2)
$C^2C^4N^5$	107(2)	$H^1C^4N^5$	119(2)	$C^{5A}C^{10A}H^{14A}$	107	$C^{5A}C^{10A}H^{15A}$	112(1)
$C^4N^5N^6$	115(2)	C^4N^5C1B	125(2)	$C^{7A}C^{10A}H^{14A}$	109	$C^{7A}C^{10A}H^{15A}$	111(1)
$N^6N^5C^{1B}$	120(1)	$C^3N^6N^5$	102(2)	$H^{14A}C^{10A}H^{15A}$	108	$N^5C^{1B}C^{2B}$	118(1)
$C^3N^7O^1$	116(2)	$C^3N^7O^2$	116(2)	$N^5C^{1B}C^{6B}$	106.7(9)	$N^5C^{1B}C^{8B}$	108.3(9)
$O^1N^7O^2$	128(2)	$N^2C^{1A}C^{2A}$	108(2)	$N^5C^{1B}C^{2C}$	114(1)	$N^5C^{1B}C^{6C}$	109.2(9)
$N^2C^{1A}C^{6A}$	106(2)	$N^2C^{1A}C^{8A}$	114(2)	$N^5C^{1B}C^{8C}$	109(1)	$C^{2B}C^{1B}C^{6B}$	102.7(7)
$C^{2A}C^{1A}C^{6A}$	108(2)	$C^{2A}C^{1A}C^{8A}$	112(2)	$C^{2B}C^{1B}C^{8B}$	110.7(7)	$C^{6B}C^{1B}C^{8B}$	110.2(7)
$C^{6A}C^{1A}C^{8A}$	110(2)	$C^{1A}C^{2A}H^{1A}$	110(2)	$C^{2C}C^{1B}C^{6C}$	110.8(7)	$C^{2C}C^{1B}C^{8C}$	110.7(8)
$C^{1A}C^{2A}H^{2A}$	109	$C^{1A}C^{2A}C^{3A}$	109(2)	$C^{6C}C^{1B}C^{8C}$	102.1(7)	$C^{2B}C^{3B}C^{4B}$	107.4(8)
$H^{1A}C^{2A}H^{2A}$	108	$H^{1A}C^{2A}C^{3A}$	110(2)	$C^{1B}C^{2B}C^{3B}$	119.4(8)	$C^{4B}C^{3B}C^{9B}$	97.6(7)
$H^{2A}C^{2A}C^{3A}$	110	$C^{2A}C^{3A}H^{3A}$	110(3)	$C^{2B}C^{3B}C^{9B}$	116.7(8)	$C^{4B}C^{5B}C^{6B}$	118.1(8)
$C^{2A}C^{3A}C^{4A}$	110(2)	$C^{2A}C^{3A}C^{9A}$	107(2)	$C^{3B}C^{4B}C^{5B}$	106.9(8)	$C^{6B}C^{5B}C^{10B}$	112.1(7)
$H^{3A}C^{3A}C^{4A}$	111	$H^{3A}C^{3A}C^{9A}$	110(3)	$C^{4B}C^{5B}C^{10B}$	111.4(8)	$C^{8B}C^{7B}C^{9B}$	116.2(8)
$C^{4A}C^{3A}C^{9A}$	109(2)	$C^{3A}C^{4A}H^{4A}$	109(3)	$C^{1B}C^{6B}C^{5B}$	102.9(7)	$C^{9B}C^{7B}C^{10B}$	107.1(7)
$C^{3A}C^{4A}H^{5A}$	110	$C^{3A}C^{4A}C^{5A}$	112(2)	$C^{8B}C^{7B}C^{10B}$	109.6(7)	$C^{3B}C^{9B}C^{7B}$	111.0(8)
$H^{4A}C^{4A}H^{5A}$	108	$H^{4A}C^{4A}C^{5A}$	108(3)	$C^{1B}C^{8B}C^{7B}$	106.4(7)	$C^{1B}C^{2C}C^{3C}$	110.8(8)
$H^{5A}C^{4A}C^{5A}$	110	$C^{4A}C^{5A}H^{6A}$	110(3)	$C^{5B}C^{10B}C^{7B}$	98.5(7)	$C^{2C}C^{3C}C^{9C}$	92.2(7)
$C^{4A}C^{5A}C^{6A}$	110(2)	$C^{4A}C^{5A}C^{10A}$	110(2)	$C^{2C}C^{3C}C^{4C}$	115.0(8)	$C^{3C}C^{4C}C^{5C}$	108.8(8)
$H^{6A}C^{5A}C^{6A}$	110	$H^{6A}C^{5A}C^{10A}$	109(3)	$C^{4C}C^{3C}C^{9C}$	112.2(8)	$C^{4C}C^{5C}C^{10C}$	126.8(8)
$C^{6A}C^{5A}C^{10A}$	109(2)	$C^{1A}C^{6A}C^{5A}$	110(2)	$C^{4C}C^{5C}C^{6C}$	102.9(7)	$C^{1B}C6CC^{5C}$	108.8(7)
$C^{1A}C^{6A}H^{7A}$	108	$C^{1A}C^{6A}H^{8A}$	111(2)	$C^{6C}C^{5C}C^{10C}$	107.4(8)	$C^{8C}C7C^{10C}$	101.3(7)
$C^{5A}C^{6A}H^{7A}$	109	$C^{5A}C^{6A}H^{8A}$	111(2)	$C^{8C}C^{7C}C^{9C}$	105.3(7)	$C^{1B}C8CC^{7C}$	109.0(8)
$H^{7A}C^{6A}H^{8A}$	108	$H^{9A}C^{7A}C^{8A}$	112(3)	$C^{9C}C^{7C}C^{10C}$	123.9(8)	$C^{5C}C^{10C}C^{7C}$	101.3(8)
$H^{9A}C^{7A}C^{9A}$	109	$H^{9A}C^{7A}C^{10A}$	112(3)	$C^{3C}C^{9C}C^{7C}$	112.8(8)		

mp 239–240°C. Found, %: C 26.01; H 1.26; N 53.55. $C_4H_3N_7O_2$. Calculated, %: C 26.53; H 1.67; N 54.14.

3-Nitro-4-(tetrazol-5-yl)pyrazole (IV). Sodium azide, 3.9 g, and 3.21 g of ammonium chloride were added to a solution of 6.9 g of 4-cyano-3-nitropyrazole (**VI**) in 150 ml of DMF. The mixture was heated at 110°C for 24 h, after which the precipitate was filtered off, the solution was concentrated to 30–40 ml and poured into 150 ml of water. The solution was acidified with HCl to pH 2–3. The reaction product was extracted with ethyl acetate, the extract was dried with magnesium sulfate, the solvent was removed by distillation, and the residue was recrystallized from ethanol. Yield 4.52 g (50%), mp 225–226°C. Found, %: C 27.11; H 0.86; N 53.15. $C_4H_3N_7O_2$. Calculated, %: C 26.53; H 1.67; N 54.14.

1-(Adamanthan-1-yl)-4-nitro-3-(pyrazol-4-yl)-pyrazole (VII). Adamanthanol **I**, 0.76 g, was added to a solution of 0.89 g of 4-nitro-3-(pyrazol-4-yl)-pyrazole (**II**) in 30 ml of a 4:1 H_3PO_4–AcOH mixture. The reaction mixture was heated at 60°C for 6 h and then poured into 200 ml of water, and the precipitate was filtered off and washed with water (2 × 25 ml). Yield 0.86 g (55%), mp 127–128.C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.78 (6H, Ad), 2.2 (9H, Ad), 8.31 (2H, H^3, H^5), 8.29 (1H, $H^{5'}$). Found, %: C 61.53; H 7.19; N 21.95. $C_{16}H_{19}N_5O_2$. Calculated, %: C 61.3; H 6.11; N 22.35.

1-(Adamanthan-1-yl)-3-[(1-(adamanthan-1-yl)-pyrazol-4-yl]-4-nitropyrazole (VIII). Adamanthanol **I**, 1.52 g, was added to a solution of 0.89 g of 4-nitro-3-(pyrazol-4-yl)pyrazole (**II**) in 30 ml of a 4:1

H_3PO_4–AcOH mixture. The reaction mixture was heated at 60°C for 42 h and poured into 200 ml of water, and the precipitate was filtered off and washed with water (2.25 ml). Yield 0.89 g (40%), mp 231–233°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.83 (12H, Ad), 2.23 (18H, Ad), 8.29 (1H, H^3), 8.28 (1H, H^5), 8.14 (1H, $H^{5'}$). Found, %: C 70.32; H 8.16; N 16.12. $C_{26}H_{33}N_5O_2$. Calculated, %: C 69.77; H 7.43; N 15.63.

3-[2-(Adamanthan-1-yl)tetrazol-5-yl]-4-nitropyrazol (IX). Adamanthanol **I**, 1.52 g, was added to a solution of 1.81 g of 4-nitro-3-(tetrazol-5-yl)pyrazole (**III**) in 30 ml of 96% H_2SO_4. The reaction mixture was allowed to stand at 20°C for 1 h and then poured into 200 ml of water. The precipitate was filtered off and washed with water (2 × 25 ml). Yield 1.26 g (40%), mp 191–193°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (6H, Ad), 2.35 (9H, Ad), 8.83 (1H, H^5). Found, %: C 52.79; H 5.95; N 30.87. $C_{14}H_{17}N_7O_2$. Calculated, %: C 53.33; H 5.43; N 31.09.

1-(Adamanthan-1-yl)-3-[2-(adamanthan-1-yl)-tetrazol-5-yl]-4-nitropyrazole (X). Adamanthanol **I**, 3.04 g, was added to a solution of 1.81 g of compound **III** in 30 ml of a 4:1 H_3PO_4–AcOH mixture. The reaction mixture was heated at 60°C for 6 h and then poured into 200 ml of water. The precipitate was filtered off and washed with water (2 × 25 ml). Yield 2.2 g (49%), mp 255–257°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.82 (12H, Ad), 2.23, 2.42 (18H, Ad), 8.38 (1H, H^5). Found, %: C 63.62; H 6.09; N 21.28. $C_{24}H_{31}N_7O_2$. Calculates, %: C 64.12; H 6.95; N 21.81.

1-(Adamanthan-1-yl)-4-[2-(adamanthan-1-yl)-tetrazol-5-yl]-3-nitropyrazole (XI). Adamanthanol **I**, 3.04 g, was added to a solution of 1.81 g of 3-nitro-4-(tetrazol-5-yl)pyrazole (**IV**) in 30 ml of 85% H_2SO_4. The reaction mixture was allowed to stand at 20°C for 48 h and then poured into 200 ml of water. The precipitate was filtered off and washed with water (2 × 25 ml). Yield 1.75 g (39%), mp 258–260°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (12H, Ad), 2.35, 2.25 (18H, Ad), 8.0 (1H, H^5). Found, %: C 64.88; H 6.08; N 21.54. $C_{24}H_{31}N_7O_2$. Calculated, %: C 64.12; H 6.95; N 21.81.

4-[2-(Adamanthan-1-yl)tetrazol-5-yl]-3-nitropyrazole (XII). Adamanthanol **I**, 1.52 g, was added to a solution of 1.81 g of 3-nitro-4-(tetrazol-5-yl)-pyrazole (**IV**) in 30 ml of 96% H_2SO_4. The reaction mixture was allowed to stand at 20°C for 1 h and then poured into 200 ml of water. The precipitate was filtered off and washed with water (2 × 25 ml). Yield 1.58 g (50%), mp 270–271°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (6H, Ad), 2.3 (9H, Ad), 8.3 (1H, H^5). Found, %: C 53.05; H 6.16; N 31.77. $C_{14}H_{17}N_7O_2$. Calculated, %: C 53.33; H 5.43; N 31.09.

Synthesis of 3-(azol-1-yl)-4-nitro-5-R-pyrazoles by *cine* substitution *(general procedure).* A solution of 0.1 mol of azole (pyrazoles, 1,2,4-triazole) in 35–50 ml of ethanol was added dropwise to a solution of 0.05 mol of 1,4-dinitro-3-R-pyrazole in 25 ml of ethanol, maintaining the reaction temperature. The mixture was heated for 0.5–3 h at 45–78°C. A solution of 0.05 mol of sulfamic acid in 30 ml of water, and the mixture was heated at the reaction temperature for an additional 0.5 h. The solvent was removed by distillation, and the solid residue was recrystallized from aqueous ethanol (1 : 1) with charcoal added.

3-(4-Chloropyrazol-1-yl)-5-methyl-4-nitropyrazole (XIIIc). Reaction time 3 h under reflux. Yield 7.05 g (62%), mp 153–155°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.80 (3H, Me^5), 7.9 (1H, $H^{3'}$), 7.65 (1H, $H^{5'}$). Found, %: C 36.51; H 3.21; N 31.26. $C_7H_6ClN_5O_2$. Calculated, %: C 36.94; H 2.66; N 30.77.

3-(4-Bromo-3,5-dimethylpyrazol-1-yl)-5-methyl-4-nitropyrazole (XIIId). Reaction time 2 h under reflux. Yield 8.25 g (55%), mp 217–218°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.25, 2.1 (6H, $Me^{3'}$, $Me^{5'}$), 2.85 (3H, Me^5). Found, %: C 36.98; H 2.95; N 24.06. $C_9H_{10}BrN_5O_2$. Calculated, %: C 36.02; H 3.36; N 23.34.

3-(4-Chloropyrazol-1-yl)-4-nitropyrazole (XIVb). Reaction time 2 h at 45°C. Yield 6.2 g (58%), mp 173–175°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 7.65 (1H, $H^{3'}$), 8.1 (1H, $H^{5'}$), 8.65 (1H, H^3). Found, %: C 33.85; H 1.55; N 33.31. $C_6H_4ClN_5O_2$. Calculated, %: C 33.74; H 1.89; N 32.79.

3-(4-Bromo-3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (XIVc). Reaction time 1 h at 45°C. Yield 7.15 g (50%), mp 260–261°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.1, 2.12 (6H, $Me^{3'}$, $Me^{5'}$), 8.8 (1H, H^5). Found, %: C 33.98; H 2.56; N 23.89. $C_8H_8Br \cdot N_5O_2$. Calculated, %: C 33.59; H 2.82; N 24.48.

5-Methyl-4-nitro-3-(1,2,4-triazol-1-yl)pyrazole (XVb). Reaction time 3 h at 40°C. Yield 4.27 g (44%), mp 210–212°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.6 (3H, Me^3), 8.1 (1H, $H^{3'}$), 8.75 (1H, $H^{5'}$). Found, %: C 37.59; H 3.98; N 43.76. $C_6H_6N_6O_2$. Calculated, %: C 37.12; H 3.11; N 43.29.

5-R-3-(3,5-dimethyl-4-nitropyrazol-1-yl)-4-nitropyrazoles. 3-(3,5-Dimethylpyrazol-1-yl)-4-nitro-5-methylpyrazole [4] or 3-(3,5-dimethylpyrazol-1-yl)-4-nitropyrazol [4] was dissolved with stirring in 15 ml of concentrated sulfuric acid (*d* 1.84), after which

2 ml of concentrated nitric acid (*d* 1.41) was added, maintaining the temperature at 20°C. The reaction mixture was allowed to stand at 20°C for 24 h and then poured into 100 ml of water. The precipitate was filtered off.

3-(3,5-Dimethyl-4-nitropyrazol-1-yl)-5-methyl-4-nitropyrazole (VIIIe). Yield 2.82 g (53%), mp 188–190°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.20, 2.10 (6H, $Me^{3'}$, $Me^{5'}$), 2.85 (3H, Me^5). Found, %: C 41.21; H 4.58; N 30.74. $C_9H_{10}N_6O_4$. Calculated, %: C 40.61; H 3.79; N 31.57.

3-(3,5-Dimethyl-4-nitropyrazol-1-yl)-4-nitropyrazole (XIVd). Yield 2.77 g (55%), mp 195–197°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.45 (6H, Me^3, Me^5), 8.85 (1H, $H^{5'}$). Found, %: C 38.76; H 3.88; N 33.41. $C_8H_8N_6O_4$. Calculated, %: C 38.10; H 3.21; N 33.32.

4-Nitro-3-(1,2,4-triazol-4-yl)pyrazole (XVa). 3-Amino-4-nitropyrazole, 6.4 g, was mixed with 8.8 g of diformylhydrazine, and the mixture was heated at 180–200°C for 1 h. The melt was then cooled, and the solid material was recrystallized from aqueous ethanol (1:1). Yield 2.88 g (36%), mp 261°C (ethanol–water). ^{1}H NMR spectrum, δ, ppm: 8.85 (2H, $H^{3'}$, $H^{5'}$), 9.0 (1H, H^3). Found, %: C 34.09; H 3.12; N 46.87. $C_5H_5N_6O_2$. Calculated, %: C 33.34; H 2.24; N 46.66.

1-(Adamanthan-1-yl)-3-(4-chloropyrazol-1-yl)-5-methyl-4-nitropyrazole (XVIc). A 4:1 H_3PO_4–AcOH mixture, 25 ml, 3-(4-chloropyrazol-1-yl)-5-methyl-4-nitro-pyrazole (**XIIIc**), 1.14 g, and 0.76 g of adamanthanol **I** was heated for 24 h at 60°C and then poured into 150 ml of water. The precipitate that formed was filtered off and washed with water (2 × 25 ml). Yield 0.58 g (32%), mp 118–120°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.65 (6H, Ad), 2.3 (9H, Ad), 2.85 (3H, Me^5), 7.8 (1H, $H^{3'}$), 7.65 (1H, $H^{5'}$). Found, %: C 55.79; H 6.14; N 20.11. $C_{17}H_{20}ClN_5O_2$. Calculated, %: C 56.43; H 5.57; N 19.36.

1-(Adamanthan-1-yl)-3-(4-bromo-3,5-dimethylpyrazol-1-yl)-5-methyl-4-nitropyrazole (XVId). A 4:1 H_3PO_4–AcOH mixture, 25 ml, 3-(4-bromo-3,5-dimethylpyrazol-1-yl)-5-methyl-4-nitropyrazole (**XIIIg**), 1.5 g, and 0.76 g of adamanthanol **I** was heated for 24 h at 60°C and then poured into 150 ml of water. The precipitate that formed was filtered off and washed with water (2 × 25 ml). Yield 0.43 g (20%), mp 159–160°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.65 (6H, Ad), 2.2 (9H, Ad), 2.3, 2.1 (6H, $Me^{3'}$, $Me^{5'}$), 2.83 (3H, Me^5). Found, %: C 51.98; H 6.12; N 16.77. $C_{19}H_{24}BrN_5O_2$. Calculated, %: C 52.54; H 5.57; N 16.12.

1-(Adamanthan-1-yl)-3-(3,5-dimethyl-4-nitropyrazol-1-yl)-5-methyl-4-nitropyrazole (XVIe). 3-(3,5-Dimethyl-4-nitropyrazol-1-yl)-5-methyl-4-nitropyrazole (**XIIIb**), 1.33 g, and 0.76 g of adamanthanol **I** were added to 25 ml of a 4:1 H_3PO_4–AcOH mixture. The resulting mixture was heated for 24 h at 60°C and then poured to 150 ml of water. The precipitate that formed was filtered off and washed with water (2 × 25 ml). Yield 0.8 g (40%), mp 207–208°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.83 (6H, Ad), 2.195, 2.145, 2.08 (9H, Ad), 2.52, 2.48 (9H, $Me^{3'}$, $Me^{5'}$, Me^5). Found, %: C 57.38; H 7.09; N 21.59. $C_{19}H_{24}N_6O_4$. Calculated, %: C 56.99; H 6.04; N 20.99.

1-(Adamanthan-1-yl)-3-(3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (XVIIa). A 4:1 H_3PO_4–AcOH mixture, 25 ml, 3-(3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (**XIVa**), 1.04 g, and 0.76 g of adamanathanol **I** was heated for 8 h at 60°C and then poured into 150 ml of water. The precipitate that formed was filtered off and washed with water (2 × 25 ml). Yield 0.68 g (40%), mp 129–130°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (6H, Ad), 2.23 (9H, Ad), 2.2 (6H, $Me^{3'}$, $Me^{5'}$), 6.0 (1H, $H^{4'}$), 8.9 (1H, H^5). Found, %: C 64.18; H 7.21; N 21.28. $C_{18}H_{23}N_5O_2$. Calculated, %: C 63.32; H 6.79; N 20.51.

1-(Adamanthan-1-yl)-3-(4-chloropyrazol-1-yl)-4-nitropyrazole (XVIIb). A 4:1 H_3PO_4–AcOH mixture, 25 ml, 3-(4-chloropyrazol-1-yl)-4-nitropyrazole (**XIVb**), 1.06 g, and 0.76 g of adamanthanol **I** was heated for 8 h at 60°C and then poured into 150 ml of water. The precipitate that formed was filtered off and washed with water (2.25 ml). Yield 0.95 g (55%), mp 121–123°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (6H, Ad), 2.2, 2.3 (9H, Ad), 7.71 (1H, $H^{5'}$), 8.15 (1H, $H^{3'}$), 8.9 (1H, H^5). Found, %: C 56.12; H 5.98; N 19.89. $C_{16}H_{18}ClN_5O_2$. Calculated, %: C 55.25; H 5.22; N 20.14.

1-(Adamanthan-1-yl)-3-(4-bromo-3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (XVIIc). 3-(4-Bromo-3,5-dimethylpyrazol-1-yl)-4-nitropyrazole (**XIVb**), 1.43 g, and 0.76 g of adamanthanol **I** were added to 25 ml of a 4:1 H_3PO_4–AcOH mixture. The resulting mixture was heated for 8 h at 60°C and then poured into 150 ml of water. The precipitate that formed was filtered off and washed with water (2.25 ml). Yield 1.00 g (47%), mp 160–161°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (6H, Ad), 2.2 (9H, Ad), 2.25, 2.3 (6H, $Me^{3'}$, $Me^{5'}$), 8.95 (1H, H^5). Found, %: C 51.98; H 6.18; N 17.41. $C_{18}H_{22}BrN_5O_2$. Calculated, %: C 51.44; H 5.28; N 16.66.

1-(Adamanthan-1-yl)-3-(3,5-dimethyl-4-nitropyrazol-1-yl)-4-nitropyrazole (XVIId). A 4:1

H_3PO_4–AcOH mixture, 25 ml, 1.26 g of 3-(3,5-dimethyl-4-nitropyrazol-1-yl)-4-nitropyrazole (**XIVd**), and 0.76 g of adamanthanol **I** was heated for 8 h at 60°C and then poured into 150 ml of water. The precipitate that formed was filtered off and washed with water (2.25 ml). Yield 1.18 g (61%), mp 155–156°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 1.8 (6H, Ad), 2.2 (9H, Ad), 2.5 (6H, $Me^{3'}$, $Me^{5'}$), 9.1 (1H, H^5). Found, %: C 56.21; H 6.65; N 21.06. $C_{18}H_{22}N_6O_4$. Calculated, %: C 55.95; H 5.74; N 21.75.

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