Nitropyrazoles

9.* Parameters of the ^1H, ^{13}C, and ^{15}N (^{14}N) spectra and the structures of *N*-aminonitropyrazoles

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The structures of substituted *N*-aminonitropyrazoles and 1- and 2-amino-4-nitro-1,2,3-triazoles as well as the site of protonation of 1-aminopyrazole were determined based on the ^1H, ^{13}C, and ^{15}N (^{14}N) NMR spectra. The ^{13}C NMR spectra were recorded under conditions of ^{13}C—{^1H,^{14}N} triple resonance. Effects of substituents in the pyrazole ring on the ^{13}C and ^{14}N chemical shifts were studied. The ^{13}C,^1H and ^{15}N,^1H spin-spin coupling constants, obtained using techniques of [^1H]→^{13}C and [^1H]→^{15}N polarization transfer (SPT, INEPT), were measured, fully assigned, and discussed.

Key words: 1-aminopyrazole, substituted *N*-aminopyrazoles, ^1H, ^{13}C, ^{14}N, and ^{15}N NMR, ^1H, ^{13}C, ^{14}N, and ^{15}N chemical shifts, ^{13}C,^1H and ^{15}N,^1H spin-spin coupling constants.

Recently[2,3] a general method for *N*-amination of pyrazoles by hydroxylamine-*O*-sulfonic acid in an aqueous solution at a constant pH has been developed. This made it possible to synthesize *N*-aminopyrazoles with electron-withdrawing substituents in the ring, including nitro groups; previously these compounds had been difficult to prepare or inaccessible. In the present paper we studied parameters of the NMR spectra of a number of *N*-aminonitropyrazoles and model aminopyrazoles (**1**—**21**).

The ^1H NMR spectra (Table 1) exhibit signals corresponding to protons of the ring, methyl groups, and *C*- and *N*-amino groups. For compound **5**, we observed even the H(5),N(NH_2) spin-spin coupling constant across four bonds, which is equal to 0.6 Hz. In the case of compound **17**, in the differential ^1H NMR spectrum of the nuclear Overhauser effect (NOE), preirradiation of the amino group causes a "response" of one of the two protons of the amide group with a chemical shift of 8.12 ppm, while preirradiation of the amide group proton with a chemical shift of 8.12 ppm causes a "response" of the amino group, which attests to a *cis*-arrangement of these groups of protons.

^{13}C NMR spectra have been reported only for unsubstituted *N*-aminoazoles (pyrazole, imidazole, 1,2,4-triazole, and tetrazole)[4,5] and for methyl- and phenyl-substituted *N*-aminopyrazoles.[6] In the present work, we studied mostly nitro-*N*-aminopyrazoles, therefore ^{13}C NMR spectra were recorded under conditions of ^{13}C-{^1H,^{14}N} triple heteronuclear selective resonance; the ^{13}C nuclei were observed with broadband proton decoupling and selective decoupling of the ^{14}N nuclei of the nitro groups. This made it possible: (1) to obtain a narrow ^{13}C signal of the carbon atom bearing the nitro group after a relatively small number of scans; (2) to measure geminal and vicinal ^{13}C,^1H spin-spin coupling constants for the carbon atom bearing the nitro group; and (3) to assign the ^{13}C NMR signals corresponding to the carbon atoms of the pyrazole ring, bearing the nitro groups, as well as ^{15}N (^{14}N) NMR signals of the nitro groups.

Parameters of the ^{13}C NMR spectra are listed in Table 2. The C-NO_2 chemical shifts of the carbon atoms in 1-amino-3-pyrazoles **3**, **9**, **13**, and **18** are 150.0—155.19, those in 1-amino-4-nitropyrazoles **5**, **7**, **8**, **11**, **12**, **15**, **16**, and **17** are 116.16—133.33, and these chemical shifts in the nitro derivatives of 1-amino-5-nitropyrazoles **4**, **10**, and **18** are 142.05—149.98 ppm, and they do not overlap. The C(3) chemical shifts in 1-amino-3-methylpyrazoles **7** and **10** amount to 142.11—142.89, and the C(5) chemical shifts in nitro derivatives of 1-amino-5-methylpyrazoles **8** and **9** are 138.75—140.75 ppm. The C(3) chemical shift in 1,3-diamino-4-nitropyrazole **12** is 149.10, and the C(5) chemical shifts in nitro- or cyano derivatives of 1,5-diaminopyrazoles **11** and **14** are 144.67—150.02 ppm.

The values of ^{13}C,^1H spin-spin coupling constants across various numbers of bonds are significant parameters in identification of *N*-aminoazoles. As can be seen from Table 2, the direct (^1J) C(5),H(5) coupling constants in compounds **1**—**3**, **5**—**7**, **12**, and **13** linked to nitro groups are larger (189.0—204.6 Hz) than the C(3),H(3) coupling constants in compounds **1**, **2**, **4**—**6**, **8**, **11**, and

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* For Part 8, see Ref. 1.

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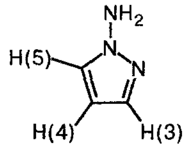

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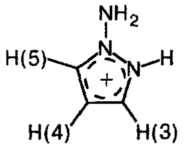

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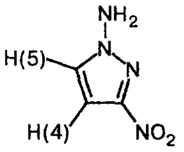

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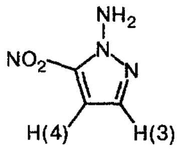

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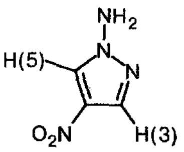

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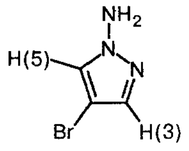

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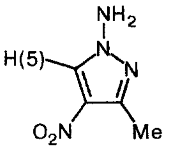

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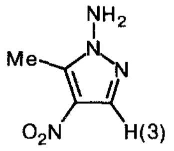

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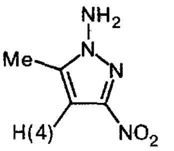

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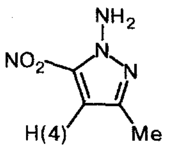

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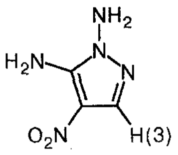

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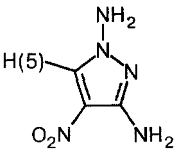

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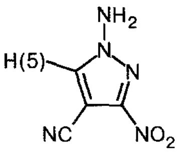

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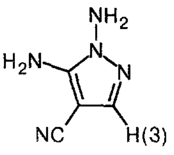

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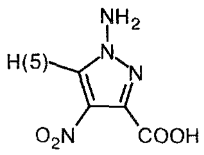

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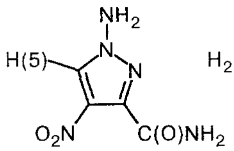

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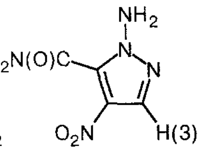

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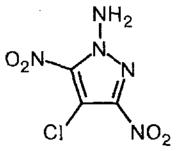

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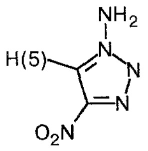

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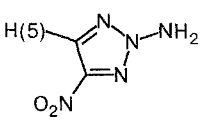

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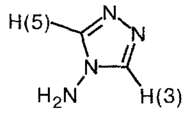

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14 (184.8—196.8 Hz) or the C(4),H(4) constants in compounds **1—4**, **9**, **10** (176.2—187.1 Hz). The same tendency can also be followed in the case of *N*-amino-4-nitro-1,2,3-triazoles **19** and **20**: $^1J_{C(5),H(5)}$ in 1-amino-4-nitro-1,2,3-triazole **19** is 210.0, whereas in 2-amino-4-nitro-1,2,3-triazole **20**, it is only 205.6 Hz. Geminal (^2J) C(4),H(5) coupling constants in compounds **1—3**, **5—7**, **12**, **13**, **15**, and **16** (5.2—8.8 Hz) are similar to the C(4),H(3) constants in compounds **1**, **2**, **4—6**, **8**, **11**, **14**, and **17** (5.0—9.5 Hz). In compounds **1—4**, **9**, and **10**, the C(5),H(4) coupling constants are larger (5.2—8.8 Hz) than the C(3),H(4) coupling constants (1.3—5.3 Hz). The geminal C(4),H(5) constant in compound **19** (6.5 Hz) is smaller than that in compound **20** (8.0 Hz). The same regularities of variation of direct and geminal spin-spin coupling constants have also been observed by us in the series of *N*-acetonylnitropyrazoles and 1,2,3-triazoles.[7] The vicinal $^3J_{C(3),H(5)}$ constants in compounds **1—3**, **5—7**, **12**, **13**, **15**, and **16** are 6.0—9.8, whereas $^3J_{C(5),H(3)}$ in compounds **1**, **2**, **4—6**, **8**, **11**, **14**, and **17** are only 1.8—5.0 Hz.

Vicinal $^3J_{C(5),N(NH_2)}$ coupling constants, are the most significant for identification of *N*-aminoazoles. They amount to 1.2—3.2 Hz, which indicates that the *N*-amine group and the C(5) atom of the ring are located in close proximity. Previously, an analogous spin-spin coupling constant has been measured only for 1-amino-1,2,4-triazole and amounted to 3.2 Hz (see Ref. 3). In addition, we were able to determine vicinal C,C(NH$_2$) coupling constants: $^3J_{C(4),5\text{-}NH_2}$ in compound **14** and $^3J_{C(3),C(O)NH_2}$ in compound **16** are 3.4 Hz each, and $^3J_{C(5),C(O)NH_2}$ in compound **17** is 2.0 Hz, whereas geminal spin-spin coupling constants are not manifested. More distant $^4J_{C(4),N(NH_2)}$ and $^4J_{C(3),N(NH_2)}$ coupling constants are smaller than 1 Hz, and as a rule, they are not observed.

Data on parameters of the ^{15}N NMR spectra have been reported only for unsubstituted *N*-aminoazoles.[5,8]

It should be noted that the signal of the 3-NH$_2$ group in compound **12** is recorded in a lower field (−320.11 ppm) than signals of the 5-NH$_2$ groups in compound **11** (−326.91 ppm) or **14** (−328.21 ppm). Signals of the N—NH$_2$ group are recorded in the region of −276 to −315 ppm and depend on both the substituents in the azole ring and type of the ring itself.

The chemical shift of the NH$_2$ group in *N*-aminopyrazole **1** is −296.20 ppm. Introduction of a 3-NO$_2$ (compound **2**), 4-NO$_2$ (compound **5**), or 4-Br

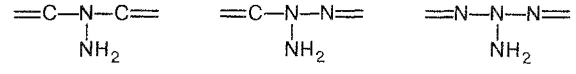
Table 1. ^{1}H NMR chemical shifts (ppm) and ^{1}H,^{1}H spin-spin coupling constants (Hz) in *N*-aminonitroazoles

Compound	δ ($J_{^1H,^1H}$)							
	H(3)	H(4)	H(5)	1-NH$_2$	3-NH$_2$	5-NH$_2$	3-Me	5-Me
1	7.32 dd (2.1, 0.9)	6.17 dd (2.1, 2.1)	7.51 dd (2.1, 0.9)	6.43 s	—	—	—	—
2	7.51 dd (3.3, 0.9)	6.27 dd (3.3, 3.3)	7.63 dd (3.3, 0.9)	5.72 s	—	—	—	—
3	—	6.87 d (2.5)	7.70 d (2.5)	6.63 s	—	—	—	—
4	7.40 d (2.3)	7.05 d (2.3)	—	7.08 s	—	—	—	—
5	7.97 d (0.9)	—	8.39 d.t (0.9, 0.6)	6.55 s	—	—	—	—
6	7.34 d (1.0)	—	7.67 d (1.0)	6.36 s	—	—	—	—
7	—	—	8.31 s	6.60 s	—	—	2.29 s	—
8	7.90 s	—	—	6.39 s	—	—	—	2.49 s
9	— (0.7)	6.73 q	—	6.66 s	—	—	—	2.29 d (0.7)
10	—	6.85 q (0.6)	—	6.66 s	—	—	2.17 d (0.6)	—
11	7.73 s	—	—	5.99 s	—	6.85 s	—	—
12	—	—	8.11 s	6.06 s	6.47 s	—	—	—
13	—	—	8.70 s	7.40 s	—	—	—	—
14	7.44 s	—	—	5.96 s	—	6.28 s	—	—
15	—	—	8.56 s	7.20 s	—	—	—	—
16	—	—	8.57 s	6.92 s	7.68 s, 7.96 s			
17	8.05 s	—	—	6.74 s	7.96 s, 8.20 s			
18	—	—	—	7.55 s	—	—	—	—
19	—	—	9.07 s	7.50 s	—	—	—	—
20	—	—	8.47 s	8.19 s	—	—	—	—
21	—	—	8.48 s	6.45 s	—	—	—	—

group (compound **6**) into compound **1** results in the signal associated with the amino group shifting downfield by 3—6 ppm, whereas introduction of a 5-CH$_3$ group (**19**, **20**) into *N*-amino-4- (**5**) or *N*-amino 3-nitropyrazole (**3**) results in a 6—7 ppm upfield displacement of this signal. The 3-NH$_2$ group in compound **12** has almost no effect on the chemical shift of the signal of the *N*-amino group, whereas the 5-NH$_2$ group in compound **11** results in this signal shifting upfield by 15 ppm.

Compounds **19** and **20** differ in position of the NH$_2$ group in the 4-nitro-1,2,3-triazole ring; the signal corresponding to the amino group in the spectrum of compound **19** is shifted 17 ppm upfield (−293.60 ppm) with respect to that in compound **20** (−276.76 ppm), which is due to the different chemical environments of the NH$_2$ groups in compounds **19** and **20**.

A comparison of ^{15}N chemical shifts of the *N*-amino groups in *N*-aminoimidazole, 4-amino-1,2,4-triazole, *N*-aminopyrazole, *N*-amino-4-substituted pyrazoles, 1-amino-1,2,4-triazole, 1-amino-1,2,3-triazole, and 2-amino-1,2,3-triazole implies that shielding of nitrogen nuclei in the NH$_2$ group decreases in the following order:



$$=\!C{-}\underset{NH_2}{\underset{|}{N}}{-}C\!= \qquad =\!C{-}\underset{NH_2}{\underset{|}{N}}{-}N\!= \qquad =\!N{-}\underset{NH_2}{\underset{|}{N}}{-}N\!=$$

−311÷−315 ppm −290÷−303 ppm −277 ppm

This may be used for identification of the type of azole system or isomers in the series of 1,2,3-triazoles and tetrazoles. Similar regularities have been observed in the ^{15}N spectra of *N*-methyl-[9] and *N*-acetonylazoles.[7]

The direct (^1J) ^{15}N,^{1}H spin-spin coupling constants for the C—NH$_2$ groups in aminoazoles **11**, **12**, and **14** are 87.6—90.2 Hz, while those for N—NH$_2$ groups in

Table 2. ^{13}C NMR chemical shifts (ppm) and ^{13}C,^{1}H spin-spin coupling constants (Hz) in *N*-aminonitroazoles

Compound	δ ($J_{^{13}C,^{1}H}$)			
	C(3)	C(4)	C(5)	Me	CN, C=O
1	135.64 ddd (184.8, $^2J_{C,H(4)}$ = 4.7, $^3J_{C,H(5)}$ = 8.7)	103.72 ddd (176.2, $^2J_{C,H(3)}$ = 9.2, $^2J_{C,H(5)}$ = 8.3)	128.73 dddt (189.0, $^2J_{C,H(4)}$ = 8.8, $^3J_{C,H(5)}$ = 4.0, 2.3)	—	—
2	135.56 ddd (192.7, $^2J_{C,H(4)}$ = 5.3, $^3J_{C,H(5)}$ = 7.8)	107.46 ddd (183.5, $^2J_{C,H(3)}$ = 5.0, $^2J_{C,H(5)}$ = 5.2)	134.18 ddd (195.6, $^2J_{C,H(4)}$ = 5.2, $^3J_{C,H(3)}$ = 4.5)	—	—
3	152.96 dd ($^2J_{C,H(4)}$ = 1.6, $^3J_{C,H(5)}$ = 9.8)	102.17 dd (187.1, 8.8)	132.80 ddt (194.6, 5.2, 2.8)	—	—
4	133.60 dd (187.6, 7.2)	104.72 dd (187.4, 5.0)	142.26 ddt ($^2J_{C,H(4)}$ = 5.4, $^3J_{C,H(3)}$ = 4.8, 2.9)	—	—
5	132.96 dd (197.2, 6.1)	133.33 dd (5.5, 5.5)	128.32 ddt (199.8, 1.8, 3.0)	—	—
6	135.97 dd (192.3, 7.4)	89.81 dd ($^2J_{C,H(3)}$ = 6.7, $^2J_{C,H(5)}$ = 6.2)	128.96 dd (196.5, 3.1)	—	—
7	142.89 qd (7.1, 7.3)	130.84 qd (2.7, 2.9)	129.34 dt (200.1, 2.8)	12.94 q (129.6)	—
8	132.86 d (196.8)	130.81 qd (2.7, 6.3)	138.75 ddt (2.1, 7.0, 2.8)	10.61 q (131.6)	—
9	150.24 d (1.3)	100.36 dq (185.6, 3.7)	140.75 qd (6.8, 7.2)	10.41 q (130.0)	—
10	142.11 qd (7.0, 3.3)	103.03 dq (184.8, 3.7)	142.05 d (6.0)	13.04 q (128.5)	—
11	131.13 d (196.2)	116.16 d (6.6)	144.67 dt (5.0, 2.4)	—	—
12	149.10 d (6.8)	118.65 d (6.8)	126.18 dt (200.1, 3.2)	—	—
13	150.62 d (9.0)	87.30 d (7.5)	137.91 dt (204.6, 2.8)	—	110.68 d (1.9)
14	136.82 d (192.1)	70.70 dt (9.5, $^3J_{C,5\text{-}NH_2}$ = 3.4)	150.02 dt (3.3, $^3J_{C,1\text{-}NH_2}$ = 2.5)	—	115.37 d (1.7)
15	136.97 d (6.3)	131.29 d (5.2)	129.79 d (202.7)	—	161.94 s
16	140.11 dd (6.0, $^3J_{C,NH_2}$ = 3.4)	130.09 d (5.3)	129.14 dt (202.5, 2.7)	—	161.96 s
17	132.46 d (198.7)	130.12 d (6.2)	134.74 dtd (8.5, 2.0, $^3J_{C,NH_2}$ = 1.8)	—	159.16 s
18	155.19 s	115.03 s	149.98 t (1.8)	—	—
19	—	151.20 d (6.5)	123.02 dt (210.0, 1.7)	—	—
20	—	149.58 d (8.0)	129.30 d (205.6)	—	—
21	144.65 ddt (212.2, 3.9, 1.2)	—	—	—	—

N-aminoazoles **1**, **3**, **5—14**, **16**, and **21** are only 70.4—73.9 Hz and almost do not depend on the substituents in the ring.

Geminal $^2J_{N(2),H(3)}$ constants in compounds **1**, **5**, **6**, **8**, **11**, and **14** amount to 12.1—13.1 Hz, while $^2J_{N(1),H(5)}$ in compounds **1**, **2**, **3**, **5**, **6**, **7**, and **13** are only 1.6—4.2 Hz.

Vicinal $^3J_{N(1),H(3)}$ spin-spin coupling constants in compounds **1**, **2**, **4—6**, **8**, **11**, and **14** are 6.5—9.7 Hz, and $^3J_{N(1),H(4)}$ in compounds **1—4** are 4.7—7.5 Hz.

We used vicinal spin-spin coupling constants of the methyl group with the adjacent atom of the ring, N(1) or N(2), for determining the position of the methyl group in the pyrazole ring. The N(1),5-CH_3 coupling constants in compounds **8** and **9** are 1.8—2.4 Hz, and the N(2),3-CH_3 constants in compounds **7** and **10** are 3.0—3.2 Hz. More distant constants $^4J_{N,CH_3}$ are smaller than 1 Hz and are normally not observed. We found the vicinal spin-spin coupling constants of N(1) with the adjacent 5-NH_2 group in compounds **11** and **14** to be 1.6 and 2.7 Hz, respectively.

Let us consider in more detail the proof of the structures of isomeric pyrazoles **3** and **4**, **7** and **8**, **9** and **10**, **11** and **12**, and **16** and **17**, as well as 4-nitro-1,2,4-triazoles **19** and **20**, which differ only in substituents in positions 3 and 5 and have identical substituents in position 4. The structures of these compounds were determined using ^{13}C, ^{15}N, and ^{14}N NMR (^{13}C, ^{15}N, and ^{14}N chemical shifts and ^{13}C,^{1}H and ^{15}N,^{1}H spin-spin coupling constants across various numbers of bonds). For example, the difference between chemical shifts of the substituted C(3) atom and unsubstituted C(5) atom

Table 3. ^{15}N NMR chemical shifts (ppm) and ^{15}N,^{1}H spin-spin coupling constants (Hz) in *N*-aminonitroazoles

Compound	δ ($J_{^{15}N,^1H}$) N(1)	 N(2)	 N-NH$_2$	 C-NH$_2$	 3-NO$_2$	 4-NO$_2$
1	−161.89 ddd ($^2J_{N,H(5)}$ = 3.0, $^3J_{N,H(3)}$ = 8.7, $^3J_{N,H(4)}$ = 6.7)	−72.12 d ($^2J_{N,H(3)}$ = 12.4)	−296.20 t (70.8)	—	—	—
2	−172.79 ddd ($^2J_{N,H(5)}$ = 2.4, $^3J_{N,H(3)}$ = 6.5, $^3J_{N,H(4)}$ = 4.7)	−132.60 br.s	−300.31 s	—	—	—
3	−158.32 dd ($^2J_{N,H(5)}$ = 2.3, $^3J_{N,H(4)}$ = 8.0)	−78.37 s (71.6)	−290.34 t	—	−20.45	—
5	−156.78 dd ($^2J_{N,H(5)}$ = 1.6)	−69.91 d ($^2J_{N,H(3)}$ = 12.1)	−291.36 t (71.8)	—	—	−18.72 s
6	−160.47 dd ($^2J_{N,H(5)}$ = 3.0, $^3J_{N,H(3)}$ = 8.8)	−68.65 d ($^2J_{N,H(3)}$ = 13.1)	−293.89 t (70.8)	—	—	—
7	−163.53 td (2.1, 2.8)	−73.67 q (3.0)	−292.25 t (71.5)	—	—	—
8	−158.55 dqt (9.7, 2.4, 2.3)	−75.70 d (12.2)	−298.36 t (72.5)	—	—	
9	−159.53 dq (7.5, 1.8)	−65.39 s	−296.60 t (72.0)	—	—	
10	*	−79.89 s	−311.65 t (72.2)	—	—	
11	−190.36 td ($^3J_{N,CNH_2}$ = 1.6, 8.7)	−88.11 d (12.3)	−306.81 t (73.9)	−326.91t (88.5)	—	
12	*	*	−291.16 t (71.2)	−320.11t (90.2)	—	—
13**	−156.65 dt (4.2, 2.4)	−74.55 s (72.0)	−287.12 t	—	−26.21 s	—
14	−187.29 td ($^3J_{N,CNH_2}$ = 2.7, 8.7)	−87.85 d (12.4)	−307.51 t (73.9)	−328.21 t (87.6)	—	—
16	−160.87 t (2.1)	*	−291.01 t (71.9)	−268.86 t (87.7)	—	
17	−159.90 dt (10.2, 2.3)	−73.65 d (12.2)	−293.50 t (72.2)	−264.61 t (89.0)		
18	*	*	−286.20 s	—	−28.60 s	—
19	*	*	−293.60 s	—	—	−25.50
20	−52.45 d (10.4)	−114.00 d (13.8)	−276.76 s	—	—	−25.50
21	−67.41 d (13.1)	−197.34 t (7.1)	−314.88 t (71.2)	—	—	—

* No signals are recorded. ** −114.36 ppm (CN).

in ^{13}C NMR spectra of 1,3-isomers is 13.5—23.0 ppm, whereas in the spectra of 1.5-isomers, the difference between chemical shifts of the substituted C(5) atom and unsubstituted C(3) atom amounts to 2.0—13.5 ppm, which is due to different electronegativities of sp^2-hybridized (N(2)) and sp^3-hybridized (N(1)) nitrogen atoms in the pyrazole ring. It can be seen that for the whole series of isomers, these ranges merge together, but for each particular pair of isomers, the difference between the chemical shifts of the substituted C(3) and C(5) atoms is very large and is equal to 7.5—13.0 ppm. The ^{13}C,^{1}H coupling constants also provide evidence for the structures of isomeric pyrazoles. Direct C(5),H(5) spin-spin coupling constants are always greater than C(3),H(3) constants by 3—7 Hz. Vicinal coupling constants of C(5) with the protons of the *N*-amino group (2.4—3.2) unequivocally point to the positions of substituents in the ring: $^3J_{C(5),NH_2}$ in 1,3-isomers is manifested, along with the direct spin-spin coupling constant, whereas in 1,5-isomers, no direct coupling constant is observed. The structures of trisubstituted isomers **9** and **10** were determined in a similar way. The C(3)-NO$_2$ signal in compound **9** and the C(5)-NO$_2$ signal in compound **10** were assigned based on their broadening and also based on the differences between the chemical shifts of $\underline{C}$-NO$_2$ and $\underline{C}$-CH$_3$: in 1-amino-3-nitro-5-methylpyrazole (**9**) they differ by 10 ppm, and in 1-amino-3-methyl-5-pyrazole, the difference is 0 ppm. This arrangement of the CH$_3$ groups is also indicated by their chemical shifts: the signal of the 3-CH$_3$ group (13.04 ppm) is recorded in a lower field than the signal of the 5-CH$_3$ group (10.41 ppm).

The presence of coupling constants of N(1) ($^3J_{N(1),H(3)}$ = 9.7—10.2 Hz) and N(2) ($^2J_{N(2),H(3)}$ = 12.2—12.3 Hz) in the ^{15}N NMR spectra of 1,5-substituted pyrazoles **4**, **8**, **11**, and **17** unambiguously indicates that there are no substituents in position 3, whereas in 1,3-substituted pyrazoles **3**, **7**, and **16**, only the $^2J_{N(1),H(5)} \le 2.8$ Hz constants are observed, and the $^3J_{N(2),H(5)}$ constants are smaller than 1 Hz or are not manifested at all. Additional evidence for the arrangement of the methyl groups in isomers **7** and **8**, **9** and **10** is provided by their vicinal spin-spin coupling constants with N(1) and N(2). If the CH_3 group is attached to the C(3) atom, only the coupling constant with N(2), equal to 3.0—3.2 Hz, is manifested (**7**, **10**); if this group is located at the C(5) atom, only the coupling constant with N(1), equal to 1.8—2.4 Hz, is observed (**8**, **9**).

Amination of 4-nitro-1,2,3-triazole results in a mixture of two isomers **19** and **20**. The difference between the chemical shifts of the C(4) and C(5) atoms in compound **20** is 20 ppm, and that in compound **19** is 28 ppm, which is due to different electronegativities of the N(1) atoms in compounds **20** and **19**. The direct, geminal, and vicinal $^{13}C,^{1}H$ constants confirm the structures of isomers **19** and **20**. In fact, the direct C(5),H(5) constant in compound **19** (210.0 Hz) is greater than that in compound **20** (205.6 Hz), and the geminal C(4),H(5) coupling constant in compound **19** (6.5 Hz) is smaller than that in compound **20** (8.0 Hz). We were able to measure the vicinal coupling constant of C(5) with the protons of the *N*-amino group (1.7 Hz) in the spectrum of compound **19**, which is an important criterion for determining the position of the *N*-amino group in 1,2,3-triazoles. The ^{15}N NMR spectrum of **20**, recorded using the selective $^{1}H\rightarrow^{15}N$ transfer of polarization from H(5), exhibits two doublets with chemical shifts of −52.45 ppm ($^{2}J_{N(1),H(5)} = 13.8$ Hz) and 114.00 ppm ($^{3}J_{N(2),H(5)} = 10.4$ Hz), which correspond to the N(1) and N(2) atoms, respectively. If the amino group were located at the N(1) atom, rather than at N(2), spin-spin coupling constants of H(5) neither with N(1) nor with N(2) would be manifested. Previously we observed similar regularities in the ^{13}C and ^{15}N NMR spectra of 1- and 2-acetonyl-4-nitro-1,2,3-triazoles.[7]

It was shown by ^{13}C and ^{15}N NMR spectra that *N*-aminopyrazole **1** is protonated at the N(2) atom, rather than at the NH_2 group, since the C(4) and C(5) signals in the ^{13}C NMR spectrum of the protonated *N*-amino pyrazole **2** (recorded in H_2SO_4) are displaced 3.7 and 5.4 ppm downfield with respect to those in compound **1**. In addition, all the direct $^{13}C,^{1}H$ spin-spin coupling constants in compound **2** are greater than those in compound **1** by 6.6—7.9 Hz. Similar regularities in the variation of the ^{13}C chemical shifts and $^{13}C,^{1}H$ spin-spin coupling constants are given for neutral *N*-methylpyrazole and *N*-methylpyrazole protonated at N(2).

The ^{15}N NMR chemical shifts of compound **1** are: −296.0 (NH_2), −161.89 (N(1)), and −72.12 (N(2)), those of protonated **2** are: 300.31 (NH_2), −172.79 (N(1)), and −132.60 (N(2)), *i.e.*, on protonation, the signal of N(2) shifts appreciably upfield (by 60.48 ppm), whereas chemical shifts of the other nitrogen atoms almost do not change. This indicates quaternization of the N(2) atom, *i.e.*, this atom is protonated.

Experimental

NMR spectra were recorded on a Bruker AM-300 instrument operating at 300.13, 70.45, 30.42, and 21.68 MHz for ^{1}H,^{13}C, ^{15}N, and ^{14}N, respectively, using tetramethylsilane as the internal standard (^{1}H and ^{13}C) or $CH_3{}^{15}NO_2$ enriched by 60 % with the ^{15}N isotope as the external standard (^{15}N and ^{14}N). High-field ^{15}N and ^{14}N chemical shifts are given with "minus" signs (the δ-scale). All of the spectra were recorded in DMSO-d_6 at 30 °C for solutions with concentrations of 3—5 mol L^{-1}. ^{13}C NMR spectra were obtained under conditions of ^{13}C-{^{1}H,^{14}N} triple selective heteronuclear resonance (gated decoupling, Gasel), and ^{13}C and ^{15}N NMR spectra were obtained with broad-band proton decoupling under INEPT conditions[11] by virtue of selective $^{1}H\rightarrow^{13}C$ and $^{1}H\rightarrow^{15}N$ transfer of polarization and also by using selective polarization transfer from one proton with the simultaneous selective decoupling of another proton.[12] The errors of determining ^{1}H and ^{13}C chemical shifts were ±0.025, those of determining ^{15}N chemical shifts were ±0.05, and for ^{14}N chemical shifts, the errors were ±0.5 ppm; $^{13}C,^{1}H$ and $^{15}N,^{1}H$ spin-spin coupling constants were determined with an accuracy of 0.05—0.3 Hz depending on the purpose of the particular experiment.

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