^{15}N and ^{17}O NMR Spectral Parameters of *N*-Nitropyrazoles

Bogdan I. Ugrak,* Valentin S. Bogdanov, Svyatoslav A. Shevelev and Igor L. Dalinger

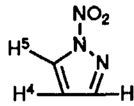
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.
Fax: +7 095 135 9094

^{15}N, ^{14}N and ^{17}O NMR chemical shifts and ^{15}N, ^{1}H spin-coupling constants of *N*-nitropyrazoles (containing NO_2, CH_3, and CN groups in the pyrazole ring) have been measured and a correlation between ^{15}N, ^{14}N and ^{17}O NMR spectral parameters and structure has been determined.

The difference in chemical behaviour between *N*-nitropyrazoles and *C*-nitropyrazoles (*cine*-substitution of nitro-group, N→C rearrangements, nitration of aromatic hydrocarbons, *etc.*) has found applications in synthesis, especially in obtaining pyrazole-containing antibiotics and analogues.[1] One would expect the special chemical properties of *N*-nitropyrazoles to be reflected in their structural characteristics. However, systematic investigations connecting the structure and physico-chemical properties (in particular the spectral prospects) of the *N*-nitropyrazoles are practically non-existent.

This work studies the connection between *N*-nitropyrazoles structure and their ^{15}N, ^{14}N and ^{17}O NMR spectral characteristics.† There are no *N*-nitropyrazole ^{15}N, ^{14}N and ^{17}O NMR studies in the literature, except for ^{15}N NMR data[2] on 1-nitropyrazole abundance at the N-1 and N-2 atoms.

^{15}N, ^{14}N and ^{17}O NMR chemical shifts and ^{15}N, ^{1}H coupling constants for pyrazoles **1–10** have been studied.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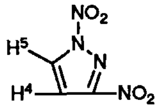
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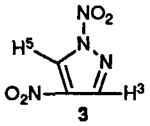
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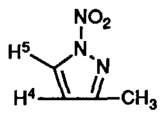
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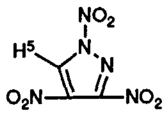
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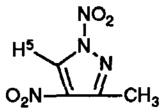
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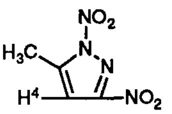
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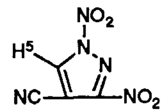
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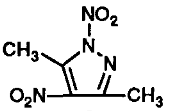
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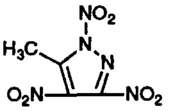
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Compounds **1–4**, **6** and **9** are known[3] and **5**, **7** and **8** were obtained for the first time by us (information on their synthesis will be published separately).

The series of *N*-nitropyrazoles **1–10** chosen contains NO_2, CN and CH_3 substituents on the carbon atoms, which provides the possibility of observing the effects of electron-acceptors (NO_2, CN) or electron-donors (CH_3).

^{15}N NMR chemical shift (CS) data are summarized in Table 1. Signals with CS -108.2 to -118.8 ppm were referred to 'pyrrole-type' atoms N-1 and signals with CS -83.8 to -98.6 ppm to 'pyridine-type' atoms N-2. The signals due to N-1 and N-2 were referred according to ^{15}N CS, ^{15}N, ^{1}H coupling constants and also using the ^{15}N spectral parameters for 1-nitropyrazole.[2] ^{15}N CS for N-1 and N-2 in **1** are -108.20 and -83.80 ppm and are very close to the corresponding CS (-108.50 and -84.60 ppm) in the literature.[2] The difference between the N-1 and N-2 CS in the *N*-nitropyrazole series is 20–25 ppm, while in the *N*-methylpyrazole series it is 100–150 ppm;[4] this can be attributed to the electron-acceptor properties of the nitro-group. The effect of exchange of NO_2 for CH_3 is 60–70 ppm for N-1 and -12 to -18 ppm for N-2.[4] Such substituents as NO_2 (**2**, **3**, **5** and **10**), CN (**8**) and CH_3 (**4**, **6**, **7**, **9** and **10**) in the pyrazole ring lead to a shift to high field for the N-1 and N-2 signals.

The ^{15}N signals due to be *C*-nitro groups appear in the region -23.0 to -31.0 ppm and are very close to the corresponding CS for 1-methyl-[4] and 1-acetonylnitropyrazoles.[5] The introduction of one CH_3 group into the pyrazole ring leads to a 1–2 ppm low-field shift of the NO_2 group signal for **6**, **7** and **10**, and if two CH_3 groups are introduced the shift is 4 ppm (**9**). NO_2 (**5**) and CN–group (**8**) substitution in the pyrazole ring results in a 5–7 ppm high-field shift of the nitro-group signals. The 3- and 4-nitro group signals in nitropyrazoles **5** and **10** were referred to in ref. 5.

The ^{15}N CS of the *N*-nitro group in the series of *N*-nitropyrazoles studied are -55.0 to -69.0 ppm. The CS of the nitro group in 1-nitropyrazole **1** is -56.62 ppm and is comparable with the same shift in 1-nitropyrazole,[2] where it appears at -56.90 ppm. The introduction of a methyl group into the pyrazole ring (**4**, **6** and **7**) leads to a 1–3 ppm low-field shift in the 1-nitro group signal and the introduction of two methyl groups (**10**) results in a similar shift of 4 ppm. At the same time, the presence of CN (**8**) and NO_2 groups (**2**, **3**, **5** and **6**) leads to 6–12 ppm high-field shift.

The *C*-and *N*-nitro group signals were referred to the ^{15}N CS published in refs. 2, 4 and 5, and ^{14}N NMR spectra were employed for those signals observed within the linewidth range 50–200 Hz (but not the ring nitrogen atoms).

If we compare the ^{15}N CS of the nitrogen group on the carbon atom (CS of the nitro group in *C*-nitropyrazoles is -18.0 to -31.0 ppm) and at the nitrogen atom in *N*-nitroamines in the aliphatic series [CS of nitro group in $CH_3N(H)NO_2$ is -20.90 ppm[6]] and also in *N*-nitropyrazoles (-55.0 to -69.0 ppm) with the ^{15}N CS of $^{+}NO_2BF_4^-$ nitronium salts (-130.20 ppm)[6] we can conclude that the ionic character of the N–NO_2 bond (with appearance of positive charge on the nitrogen group) increases on moving from *N*-nitroamines to *N*-nitropyrazoles. This is similar to the electron-acceptor substituents (NO_2, CN) attached to the cyclic carbon atom (Table 1). This is supported by an

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† *General experimental procedure.* ^{15}N, ^{14}N and ^{17}O NMR spectra were recorded on a Bruker AM-300 at 30.42, 21.68 and 40.69 MHz, respectively, relative to external CH_3NO_2 (^{15}N, ^{14}N) and internal H_2O (^{17}O). ^{15}N and ^{14}N NMR spectra were measured in [$^2H_6$]acetone at 30 °C at concentration 3.0–5.0 mol dm^{-3}, and ^{17}O NMR spectra in [$^2H_3$]acetonitrile at 60 °C and concentration 0.5–1 mol dm^{-3}. The high-field ^{15}N, ^{14}N and ^{17}O CS are presented with a minus sign (δ-scale). ^{14}N and ^{17}O NMR spectra were recorded without broad-band decoupling and ^{15}N spectra were recorded with broad-band decoupling, in the INEPT region,[11] with the aid of ^{1}H→^{15}N polarization selective transferring from one proton and simultaneous selective decoupling with another proton.[12] The accuracy of ^{15}N CS measuring is $\pm$ 0.05 ppm, for ^{14}N and ^{17}O CS it is ± 0.5 ppm and for ^{15}N, ^{1}H coupling constants it is ± 0.05–0.3 Hz, depending upon the experimental technique.

Table 1 ^{15}N Chemical shifts (ppm) and indirect coupling constants (Hz) of *N*-nitropyrazoles

Compared	N–1	N–2	1–NO$_2$	3–NO$_2$	4–NO$_2$
1	−108.20 m	−83.80m	−56.62 s	—	—
2	−113.10 d.d ($^2J_{N,H-5}$ 2.5, $^3J_{N,H-4}$ 8.2)	−93.56 s	−63.20 d ($^4J_{N,H-4}$ 1.1)	−25.10 s	—
3	−109.91 d.d ($^2J_{N,H-5}$ 2.0, $^3J_{N,H-3}$ 8.8)	−84.22 d ($^2J_{N,\ H-3}$ 12.6)	−63.03 s	—	−23.20 s
4	−112.51 d.d $^2J_{N,H-5}$ 3.0, $^3J_{N,H-4}$ 8.0)	−88.14 q (3.2)	−55.71 s	— —	— —
5	−117.01 d (3.0)	−95.57 s	−68.65 s	−31.02 s	−30.76 s
6	−116.55 d (1.3)	−88.62 q (3.5)	−62.32 s	—	−21.15 q (0.4)
7	−113.96 d.q. (8.1, 2.1)	−92.36 s	−59.78 d ($^4J_{N,H-4}$ 1.5)	−24.20 s	—
8	−113.38 d (1.9)	−91.65 s	−68.06 s	−30.25 s	−109.44 s (CN)
9	−114.80 q (2.3)	−91.74 q (3.4)	−58.88 s	—	−18.91 q (0.8)[a]
10	−118.83 q (2.2)	−98.58 s	−65.71 s	−29.82 s	−28.83 s

[a] $^4J_{4-NO_2,5-CH_3}$ 0.8 Hz.

Table 2 ^{17}O Chemical shifts (9ppm) and line-width ($\Delta\nu_{1/2}$/Hz) of *N*-nitropyrazoles

Compound	1–NO$_2$	3–NO$_2$	4–NO$_2$
1	481.8 (270)	—	—
2	482.2 (340)	594.7 (320)	—
4	478.1 (280)	—	—
6	482.5 (340)	—	592.6 (400)
7	494.6 (280)	593.2 (370)	—
9	497.8 (320)	—	595.5 (380)

increase in the N–NO$_2$ bond length in *N*-nitropyrazoles in comparison with aliphatic *N*-nitroamines (X-ray investigation data)[7] and also by the ability of 1-nitropyrazole to be an electrophilic nitrating agent for aromatic hydrocarbons in the presence of acids.[8]

The same dependence is observed in ^{17}O NMR spectra, so the CS of cyclic nitro groups in positions 3 and 4 are 592–596 and in *N*–NO$_2$, 478–497 ppm (Table 2), whereas the CS of $^+NO_2BF_4^-$ is 420 ppm at high field.[9]

All possible coupling constants in the series of substituted nitropyrazoles are presented in this article (Table 1).

The geminal (^2J) coupling constant N^2, H^3 was measured only in the case of **3** and its value was 12.6 Hz, comparable with analogous coupling constants in 1-methyl-4-nitropyrazole (12.1 Hz).[4] The N^1, H^5 geminal coupling constants for **2**–**6** and **8** are only 1.30–3.0, while in substituted *N*-methylpyrazoles they are 3.0–4.5 Hz.[4]

The vicinal (^3J) N^1, H^3 coupling constant for **3** is 8.8, but the N^1, H^3 coupling constants in *N*-methylpyrazoles [4] are 9.1 and for N^1, H^4 are 6.0–6.6 Hz. We have also measured the ^{15}N, ^{1}H vicinal coupling constants of N^1 with 5-CH$_3$ and of N^2 with 3-CH$_3$ groups, giving values of 1.9–2.3 for **7**, **9** and **10** and 3.2–3.5 Hz for **4**, **6** and **9**, respectively. Other coupling constants (^4J) of N^1 with 5-CH$_3$ and of N^2 with 5-CH$_3$ groups are < 1 Hz and are not observable.

A discussion of geminal and vicinal ^{15}N, ^{1}H coupling constants in the series of substituted pyrazoles is presented in refs. 4 and 10.

We have also managed to measure long-range ^{15}N, ^{1}H coupling constants: in 1,4-dinitropyrazole **6** $^4J_{4-NO_2,3-CH_3}$ is 0.4 and in 1,4-dinitro-3,5-dimethylpyrazole **9** $^4J_{4-NO_2,5-CH_3}$ is 0.8 Hz. We have also measured the ^4J coupling constant of the nitrogen group in position-1 with H^4: for **2** its value is 1.1 and for **7** it is 1.5 Hz.

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