Chemistry of Heterocyclic Compounds, Vol. 38, No. 5, 2002

^{14}N AND ^{15}N NMR SPECTROSCOPY OF 2-METHYL-4,5-DINITRO-1,2,3-TRIAZOLE AND OF SUBSTITUTED 2-METHYL-4(5)-NITRO-1,2,3-TRIAZOLE 1-OXIDES

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Analysis of the ^{14}N and ^{15}N NMR spectroscopic data of 2-methyl-4,5-dinitro-1,2,3-triazole and of substituted 2-methyl-4(5)-nitro-1,2,3-triazole 1-oxides has shown the possibility of applying them for confirmation of the structures of the studied compounds.

Keywords: 2-methyl-4(5)-nitro-1,2,3-triazole 1-oxides, nitro group, N-oxide fragment, triazole ring, NMR spectroscopy, chemical shifts of ^{14}N/^{15}N signals.

In the natural mixture of nitrogen isotopes the content of ^{14}N is more than 99%. Its sensitivity in NMR spectroscopy is barely lower than that of the ^{15}N isotope, but the high natural content fully compensates for this drawback. Another important feature of ^{14}N nuclei is the fact that they have a spin equal to unity (J = 1) and consequently, unlike nuclei with spin J = 1/2 (^{15}N, ^{1}H, ^{13}C, ^{19}F, etc.), possess a quadrupole moment. The interaction of the nuclear quadrupole moment of ^{14}N with the electronic environment is the most effective mechanism of nuclear relaxation. Due to the rapid relaxation the signals in ^{14}N NMR spectra are, as a rule, strongly broadened ($\Delta\nu_{1/2}$, the signal width at half-height, reaches 1000 Hz and more) [1]. The effectiveness of the quadrupole relaxation primarily depends on the symmetry of the electronic environment (electronic field gradient): the greater the symmetry, the lower the gradient, and the lower the width of the ^{14}N atom signal [2,3].

In ^{14}N NMR spectroscopy besides the chemical shift there is one further parameter, the signal width (relaxation time), which enables signals in the spectrum to be assigned correctly and sheds light on the charge distribution in the molecules being studied. The present work is devoted to clarification of the basic regularities in the variation of chemical shifts and relaxation times of ^{14}N nuclei in the heterocycle and nitro groups of 2-methyl-4,5-dinitro-1,2,3-triazole (**1**) and of substituted 2-methyl-4(5)-nitro-1,2,3-triazole 1-oxides **2a-k**. The obtained ^{14}N NMR spectroscopic data of compounds **1** and **2a-k** are given in Table 1. When analyzing them, it must be noted primarily, that in the ^{14}N NMR spectrum of triazole **1** only one narrow signal is observed for the nitro groups, which indicates unequivocally the symmetry of the molecule and the location of the methyl group on the second nitrogen atom of the heterocycle. The symmetry of the molecule is also confirmed by the coincidence of the signals of the nitrogen atoms in positions 1 and 3 in the ^{15}N NMR spectrum and of the signals of the carbon atoms in positions 4 and 5 in the ^{13}C NMR spectrum.

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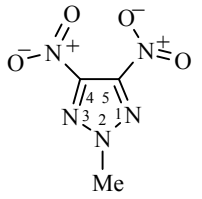
TABLE 1. Chemical Shifts (CS) of ^{14}N Atoms (δ, ppm) and Signal Widths ($\Delta\nu_{1/2}$, Hz) in ^{14}N NMR Spectra of Compounds **1** and **2a-k**



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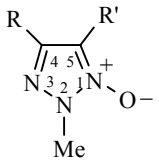


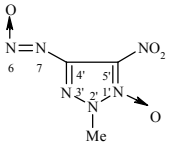
2a–k

Compound	Substituents R and R'	Nitrogen atoms of heterocycle		Nitro group (position in cycle)	
		CS ^{14}N*	$\Delta\nu_{1/2}$	CS ^{14}N	$\Delta\nu_{1/2}$
1*[2]	4-NO_2 5-NO_2	$N_{(2)}$ -149.1	350	(4) -32.93 (5) -32.93	11 11
2a*[3]	4-NO_2 5-NO_2	$N_{(1)}$ -78.3	135	(4) -34.33 (5) -40.18	14 7
2b	4-NH_2 5-NO_2	$N_{(1)}$ -83.9	120	(5) -30.42	37
2c	4-NO_2 5-NH_2	$N_{(1)}$ -97	>300	(4) -25.33	30
2d	4-$NHCH_3$ 5-NO_2	$N_{(1)}$ -85	>300	(5) -30.73	25
2e	4-NO_2 5-$NHCH_3$	$N_{(1)}$ -95 $N_{(2)}$ -150	400 500	(4) -25.6	45
2f	4-NHC_2H_5 5-NO_2	$N_{(1)}$ -83.7	120	(5) -30.55	20
2g	4-NO_2 5-NHC_2H_5	$N_{(1)}$ -100 $N_{(2)}$ -155	350 600	(4) -25.44	37
2h	4-OCH_3 5-NO_2	$N_{(1)}$ -80.3	110	(5) -34.07	14
2i	4-NO_2 5-OCH_3	$N_{(1)}$ -83	150	(4) -29.02	23
2j*[3]	4-NO 5-NO_2	$N_{(1)}$ -78.5	100	(5) -37.49	7
2k*[4]	4-R 5-NO_2	$N_{(1)}$ and $N_{(1')}$ -80	>300	(5) -39.33 (5') -34.69	9 20

* No signal was observed for the N atoms indicated.

*[2] ^{13}C NMR spectrum: 143.57 ($C_{(4)}$, $C_{(5)}$), 44.53 ppm (CH_3). ^{15}N NMR spectrum: -48.84 ($N_{(1)}$, $N_{(3)}$), -139.04 ppm ($N_{(2)}$).

*[3] In a mixture with compound **2a**. ^{15}N NMR spectrum: -75.10 ($N_{(1)}$), -142.85 ($N_{(2)}$), -97.07 ppm ($N_{(3)}$); $^3J_{N(1),CH_3} = 1.92$, $^2J_{N(2),CH_3} = 2.36$, $^3J_{N(3),CH_3} = 2.30$ Hz.

*[4] R =  For $^{14}N_{(6)}$ CS is -67.65 ppm, $\Delta\nu$ = 40 Hz.

It was shown previously for pyridines, s-triazines, alkyl- and phenylpyrazines, their hydroxy derivatives [4,5] and also for furazans [6] that the introduction of N-oxide fragment into the molecule of these nitrogen-containing heterocycles leads to redistribution of the electron density in the ring, which appears as a high-field shift of the signals for the ^{13}C atoms neighboring the N-oxide group. An increase in π-electron density on the

latter was confirmed by quantum-mechanical calculations. The size of the high field shift was approximately 100 ppm for one electron [5]. It may be assumed that analogous regularities will also be displayed in the ^{13}C and ^{15}N NMR spectra of 1,2,3-triazole 1-oxides **2a-k**.

In reality the presence of N-oxide fragment leads to a high-field shift of 3.8 ppm of the signal of the neighboring $N_{(2)}$ atom in the ^{15}N NMR spectrum (see data of ^{15}N NMR of compounds **1** and **2a** in Table 1), i.e. the π-electron density is increased not only for neighboring carbon atoms but also for neighboring nitrogen atoms. The phenomenon noted therefore has a more general character.

A far greater high-field change of chemical shift occurs for the signal of the $N_{(3)}$ atom (from -48 to -97 ppm, see Table 1, compounds **1** and **2a**). There is a principal difference in the transmission of the effect of the N-oxide oxygen atom through two bonds along the O←N–C–C chain in N-oxides of pyridines and pyrazines from the transmission along the O←N–N–N chain in N-oxides of 1,2,3-triazoles. In the case of the carbon chain the effect is not only reduced 3-4-fold but is also changed in sign. A low-field shift is observed for the signal of the ^{13}C atom two bonds remote from the N-oxide fragment in pyridine N-oxide [5].

The effect of the N-oxide oxygen atom in 4,5-dinitro-substituted N-oxide **2a** is transmitted to the nitro groups in positions 4 and 5, though an approximately two times larger effect is observed at the 5-NO_2 group closest to the N→O fragment. The signals of the ^{14}N atoms of both nitro groups are shifted towards high field and simultaneously become narrower, the signals of the 5-NO_2 group to a greater extent. Assignment of the signals of the nitro groups in compound **2a** was made by analogy with nitrofuroxans [7] and was confirmed by analysis of the data of Table 1.

Attention is drawn to the parallelism of the changes of chemical shift of the signals of the nitro group ^{14}N nuclei and their widths (see Fig. 1), irrespective of what position (4 or 5) there is a nitro group. This is followed for all the oxides **2** studied in the present work. It follows from this fact that the shift of the nitro group signals towards high field and the reduction of their widths is caused by one reason, by the increase in electron density at the carbon atom carrying the nitro group. In this way a smoothing occurs in the asymmetry of the electronic environment of the ^{14}N nuclei of the nitro group and there is a reduction in the widths of their signals.

Comparison of the data for the ^{14}N nuclei of compounds **1** and **2a** shows that the N-oxide oxygen atom causes a high-field shift of the signals of the ^{14}N atoms of nitro group in position 4 of 1.4 and in position 5 of 7.3 ppm. It may be assumed that the contributions of the N-oxide oxygen to the chemical shift of the nitro group signals in the indicated positions do not depend on the presence and the nature of the other substituents R, i.e. the contributions of substituents R and of the N-oxide oxygen atom may be added together. Such a property of the additivity of the contributions of substituents was demonstrated previously in the NMR spectroscopy of ^{1}H [8] and ^{13}C [9] nuclei for alkanes and substituted benzenes.

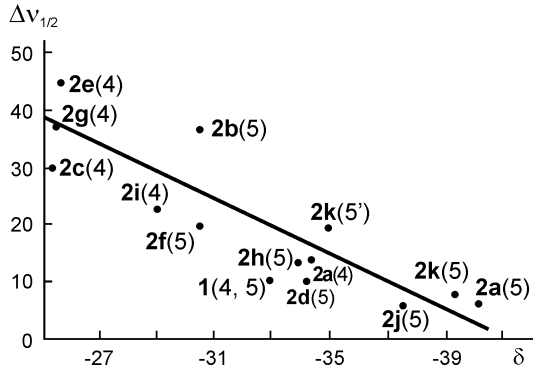


Fig. 1. Correlation of the chemical shifts (δ, ppm) and widths ($\Delta\nu_{1/2}$) of the ^{14}N atom signals of the nitro groups for compounds **1** and **2a-k** (the position of the nitro group is shown in parentheses).

To check this assumption it would be necessary to compare the chemical shifts of the nitro group signals of substituted 2-methyl-4(5)-nitrotriazoles and of the corresponding N-oxides as was done in the case of compounds **1** and **2a**. Such a comparison will be carried out later after obtaining ^{14}N NMR data for substituted 2-methyl-4(5)-nitrotriazoles. However even on comparing pairs of isomers with the same substituents R (**2b,c**; **2d,e**; **2f,g**; **2h,i**) attention is drawn to the fact that the difference in sizes of the chemical shifts of the nitro group ^{14}N atoms in positions 4 and 5 is approximately 5 ppm, as for the nitro groups in positions 4 and 5 in compound **2a**. This indicates that irrespective of the nature of substituent R the effect of the N-oxide oxygen atom on the chemical shifts of the nitro group remains constant, i.e. the contributions of substituent R and of the N-oxide oxygen atom are additive.

If the chemical shifts of the nitro group ^{14}N are plotted on a graph, shifts of ^{14}N of 4-nitro isomers on the ordinate and those of ^{14}N of 5-nitro isomers on the abscissa, then the points lie on the straight line $\delta(4\text{-}NO_2) = \delta(5\text{-}NO_2) + B$ (Fig. 2). The intercept of this straight line on the ordinate axis (B) gives a value of 5.4 ppm, i.e. the mean difference of the contributions of the N-oxide oxygen atom to the chemical shifts of the signals of the ^{14}N of the nitro groups in positions 4 and 5. The size of the contributions of substituents R will possibly be obtained later from the data for unsubstituted 2-methyl-4(5)-nitro-1,2,3-triazole 1-oxides.

The tight disposition on the graph of points belonging to the amino derivatives indicates the absence of effect from the substituents on the amino group on the electron density distribution in the molecule.

We also noted a correlation of the chemical shifts of the nitro groups with the known inductive constants of the substituents [10]. It is shown in Fig. 3 that in the studied compounds the effect of a substituent is transmitted by inductive mechanism. In spite of the minimal number of points plotted on the graph it may be

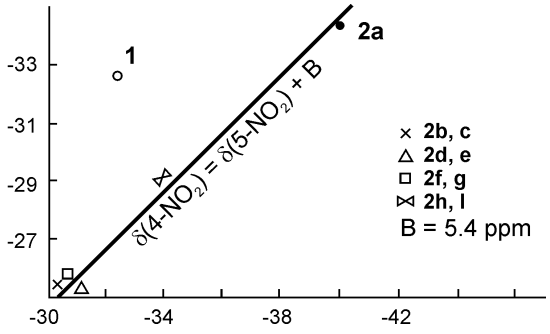


Fig. 2. Correlation of the chemical shifts (δ, ppm) of the ^{14}N atom signals of 4- and 5-nitro groups for the pairs of isomers **2b,c**, **2d,e**, **2f,g**, and **2h,i**.

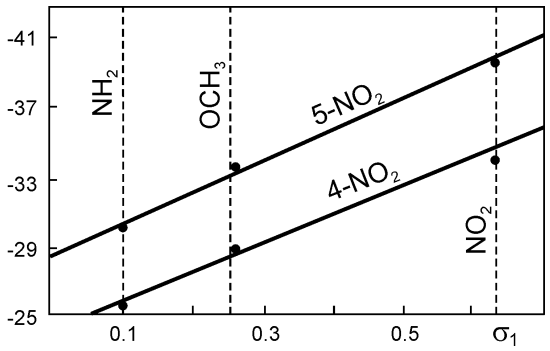
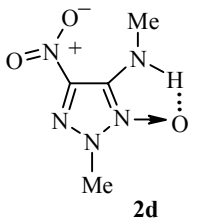


Fig. 3. Correlation of chemical shifts of the signals of the ^{14}N atoms of the nitro groups with the inductive constants of substituents (σ_1) for compounds **2a,b,c,h,i**.

assumed that the chemical shifts of the ^{14}N atoms of the nitro groups in unsubstituted nitro derivatives will be found at about -24 for the 4-nitro isomer and -29 ppm for the 5-nitro isomer. In the case of substituents NH_2, $NHCH_3$, or $NHCH_2CH_3$ in position 5 of the ring (compounds **2c,e,g**) a significant high-field shift of 10-20 ppm is observed for the signal of the oxide group ^{14}N atom, and an increase of its width compared with the analogous signal of the corresponding 4-isomers (compounds **2b,d,f**). It may be assumed that this is related to the formation of an intramolecular hydrogen bond, as shown for compound **2d**.



2d

Full confirmation of this assumption may be obtained later on the basis of the spectra of dialkylamino derivatives for which the formation of a similar hydrogen bond is excluded.

The main regularities revealed in the present work have enabled unequivocal assignment of the signals for the ^{14}N and ^{15}N atoms by analyzing the appropriate NMR spectra of the isomeric 4- and 5-nitro-substituted triazole oxides. However they are not always capable of determining the position of the nitro group (4 or 5) in these compounds. For example, on the basis of ^{14}N NMR data alone it is impossible to say with complete confidence in what position the nitro group in compound **2k** is in relation to the N-oxide fragment (see Table 1). An unequivocal answer may be given by ^{13}C NMR spectroscopy, and finally by X-ray diffraction analysis. As a result of the investigations carried out it has been shown possible to apply ^{14}N and ^{15}N NMR spectroscopy to confirm the structure of 2-methyl-4(5)-nitro-1,2,3-triazole 1-oxides.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker AM 300 spectrometer at frequencies of 21.67 (^{14}N), 30.42 (^{15}N), and 75.47 MHz (^{13}C), solvent was acetone-d_6. Measurements were carried out at room temperature. The chemical shifts for ^{14}N and ^{15}N are given in the δ scale relative to nitromethane as external standard. The ^{13}C NMR spectra were obtained under conditions of broad band quenching of spin-spin interactions with protons. The ^{15}N NMR spectra were obtained with the aid of the standard impulse sequences INVGATE and INEPT. The procedures for the synthesis of the investigated substituted 2-methyl-4(5)-nitro-1,2,3-triazole 1-oxides have been described previously [11-14].

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