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^{15}N and ^{13}C solid-state nuclear magnetic resonance study of 5-thiomethyltetrazole

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Abstract

^{15}N and ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra of 5-thiomethyltetrazole have been measured. Two kinds of tetrazole molecules are found in the hydrogen bond chain system depending on the configuration of the S–CH_3 group in relation to the ring hydrogen atom. The two-dimensional ^{15}N CP-MAS experiment excludes the possibility of proton tautomeric dynamics in this system.

Keywords: ^{15}N cross-polarization magic-angle spinning nuclear magnetic resonance ; ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance; Two-dimensional ^{15}N cross-polarization magic-angle spinning nuclear magnetic resonance ; 5-Thiomethyltetrazoles; Hydrogen bond chain system in the solid; S–CH_3 group configuration in the solid

1. Introduction

Tetrazoles have been widely studied by NMR [1–3]. ^{15}N NMR spectroscopy has proved to be a particularly valuable tool for differentiating the properties of nitrogen atoms in polynitrogen systems.

The present work is a continuation of our investigations of prototropic tautomeric equilibria in 5-substituted tetrazoles by ^{14}N and ^{15}N NMR methods in solution [4–6]. Since tautomeric equilibria are strongly influenced by the solvent, it seemed interesting to extend our studies to the solid state. The purpose of the present work was to check whether dynamic effects due to proton transfer and conformation changes are present. 5-Thiomethyltetrazole has been investigated by X-ray crystallography methods, and this complete study will be published separately [7].

2. Experimental

The ^{15}N-labeled compound had ca. 50% of ^{15}N in each of the N-1 and N-4 positions, and ca. 100% of ^{15}N in each of the N-2 and N-3 positions. A compound with natural ^{15}N and ^{13}C isotopic abundances was used for ^{13}C NMR.

^{15}N CP-MAS spectra were recorded at 30.41 MHz, using a Bruker MSL 300 spectrometer with

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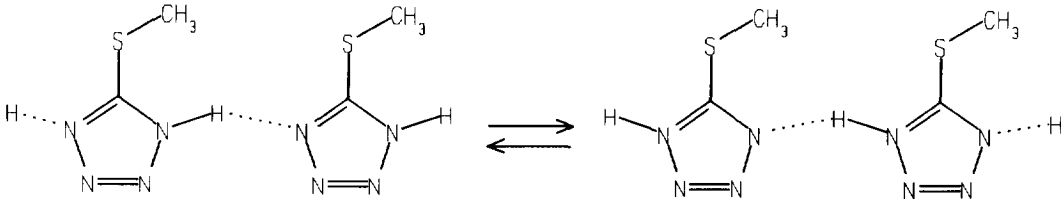


Fig. 1. Two kinds of chain related by a possible proton-exchange mechanism or rotation of thiomethyl groups.

the following acquisition parameters: sweep width of 15 000 Hz, 90° pulses of 5 μs, CP contact time of 10 ms, rotation frequency of 8.5 kHz, and 200 scans. In the two-dimensional ^{15}N CP-MAS experiment, the spectrum was obtained by 32 series of 512-point free-induction decays. A CP contact time of 10 ms, 32 scans, a mixing time of 1.5 s and a rotation frequency of 8.5 kHz were used. The ^{13}C CP-MAS spectrum obtained at room temperature was measured at 75.5 MHz. The compound was synthesized according to a published procedure [8].

3. Results and discussion

A solution of 5-thiomethyltetrazole in dimethylsulfoxide exists as a mixture of tautomers, one with the proton attached to N-1 or N-4 and another with the proton at the N-2 or N-3 nitrogen atom; the relative amounts are ca. 85 and 15%, respectively [4]. ^{15}N NMR studies of the protonated 5-thiomethyltetrazolium cation in CF_3COOH solution show that the cation is protonated at N-1 and N-4.

The X-ray diffraction data of 5-thiomethyltetrazole [7] indicate that this compound forms chains of hydrogen-bonded molecules, connected by N-1–H $\cdots$ N-4′ bonds (2.88 Å). There are two kinds of chain in the crystal with S–CH_3 groups in the *cis* or *trans* configuration with respect to the ring hydrogen atom; in both cases the S–CH_3 group lies exactly in the plane of the tetrazole ring (Fig. 1).

^{15}N NMR spectra of solid tetrazole are shown in Fig. 2. The resonances were assigned to the four nitrogen atoms by comparison with the solution data (Table 1). We note that the signals of the N-1–H and N-4 nitrogen atoms are split into doublets with chemical shift differences of 2.0 and 3.9 ppm, respectively. This effect is due to the presence of two fixed orientations of the thiomethyl groups. This splitting disappears at higher temperature due to the increased amplitude of thermal motions of this group.

Only one averaged resonance of the N-1 and N-4 atoms exists in solution, because of two rapid processes on the NMR time scale: rotation around the C–S bond and proton tautomeric exchange.

The two orientations of the S–CH_3 group result in a different screening of the N-1 and N-4 atoms, but should also have some effect on the chemical shift of the methyl carbon. The ^{13}C CP-MAS NMR spectrum shows no splitting of the CH_3 resonance (Fig. 3) which is too small to be discernible in the spectra. The presence of a methoxy or hydroxy group in the benzene ring is responsible for the significant splitting (2–6 ppm)

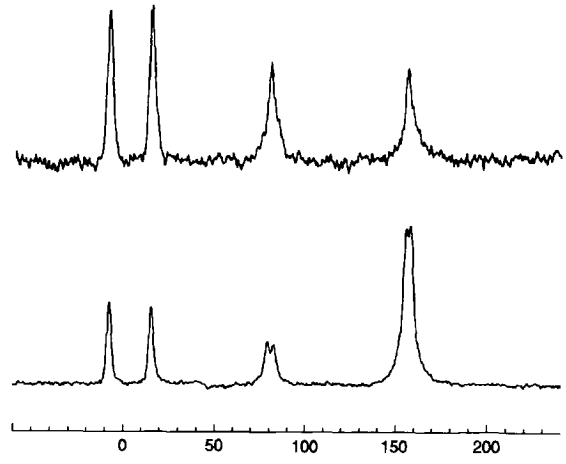


Fig. 2. ^{15}N CP-MAS NMR spectra of 5-thiomethyltetrazole recorded at different temperatures: bottom 300 K, top 380 K.

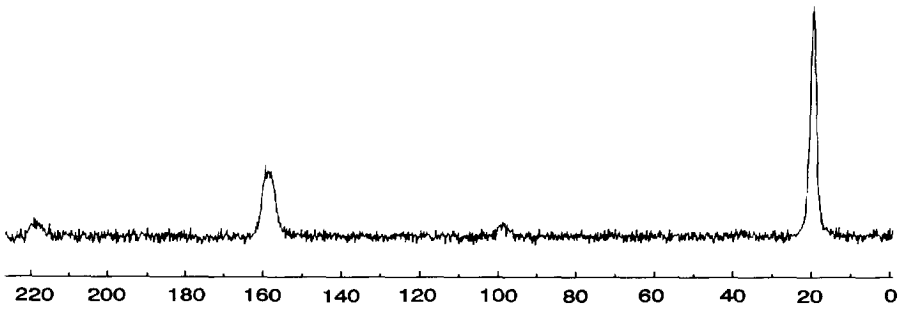


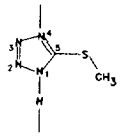
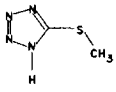
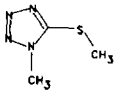
Fig. 3. ^{13}C CP-MAS NMR spectrum of 5-thiomethyltetrazole at room temperature.

of the *ortho* carbon peaks; a smaller one is observed for the *meta* carbons in the ^{13}C CP-MAS NMR spectra. No splitting was observed for the CH_3 resonance [9].

There have been no previous estimations of the magnitude of the effect of various orientations of the S–CH_3 group on the shielding of a nitrogen nucleus in compounds containing two *ortho* nitrogens with respect to the substituent. In order to assign the resonances to the *trans* or *cis* orientation a theoretical calculation of nitrogen shielding is necessary.

As mentioned above, the N-2 and N-3 nitrogen chemical shifts are close to their solution values obtained for the 1-methyl-5-thiomethyltetrazole derivative, but the signal of N-4 is shifted to a ca. 30 ppm lower frequency in the ^{15}N CP-MAS spectrum. This significant shielding increase is related to the N-1–H · · · N-4 hydrogen bond for-

Table 1
Comparison of nitrogen chemical shifts [a] obtained for 5-thiomethyltetrazoles in the solid state and solution

Compound	N-1	N-2	N-3	N-4
	-157.1 [b] -159.1 [b]	-16.7	5.9	-80.5 [b] -84.4 [b]
CP-MAS				
	-102 [c]	-6 [c]		
DMSO [3]				
	-157.7	-7.0	11.2	-55.3
DMSO [3]				

[a] Referred to external CH_3NO_2, referenced originally to solid-state NH_4Cl, recalculated according to Ref. [10] −341.2 ppm.
[b] For N-1 and N-4 two chemical shift values were obtained depending on S–CH_3 group versus N-1–H configuration.
[c] Data obtained from ^{14}N NMR spectrum, N-1 and N-4, N-2 and N-3 signals averaged due to fast proton exchange.

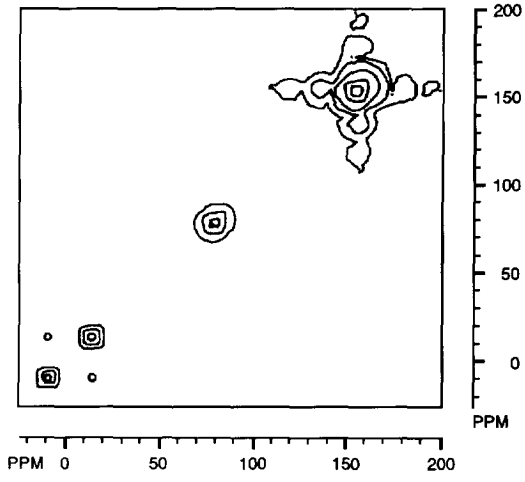


Fig. 4. Contour plot of the two-dimensional EXSY ^{15}N CP-MAS NMR experiment performed on 5-thiomethyltetrazole at 300 K.

mation. In dilute dimethylsulfoxide solutions these bonds are replaced by N-1–H $\cdots$ O = S < bonds because dimethylsulfoxide has a hydrogen bond acceptor character that is stronger than that of the N-4 nitrogen atom of this tetrazole system.

An interesting question concerns the possibility of observing dynamic proton transfer in this hydrogen-bonded structure. Increasing the temperature up to 380 K caused no coalescence of the N-1 and N-4 signals, indicating that if any proton transfer is present, it is slow on the NMR time-scale (Fig. 2). The two-dimensional experiment with a mixing time of 1.5 s was thus carried out to follow the possibility of slow exchange. The contour plot (Fig. 4) shows no cross-peaks between N-1 and N-4 signals, confirming that there is no proton exchange between them. Small cross-peaks between the N-2 and N-3 signals indicate that on the time scale of 1.5 s some spin-diffusion takes place between these neighbours.

The fact that proton dynamics are not observed in 5-thiomethyltetrazole is in agreement with the expectation that the transfer of a proton from N-1 to N-4 should be correlated coherently in the whole chain and thus require much higher energy than the single transfer which could occur in a dimer.

Acknowledgements

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