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^{14}N NQR in the tetrazole family

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ABSTRACT

^{14}N NQR frequencies and spin–lattice relaxation times were measured in technologically important 5-aminotetrazole and 5-aminotetrazole monohydrate at different temperatures between 77 K and 300 K. Five NQR triplets ν_+, ν_- and ν_0 were found for the five inequivalent nitrogen atoms in each compound between 0.7 MHz and 4 MHz. Carr-Purcell based multipulse sequences were used to accumulate quadrupole echo signals before the FFT analysis. Assignment of the frequencies to atomic positions was made and the results are analysed in relation to the molecular chemical bonds and possible H-bonds in the crystal structures. The new NQR frequencies are reasonably related to the previously published NQR spectrum of the third family member, 1H-tetrazole.

1. Introduction

The tetrazole ring CH_2N_4 (abbrev. TZ, see Fig. 1) appears in a number of new pharmaceutical products as a functional group [1–4]. This pentagonal structure can also act as a starting point for new explosives [5–7], for anti-corrosive coatings [8], is met in photography, in information recording systems [9], and in many synthetic pathways as a precursor of various nitrogen containing heterocycles.

This investigation of tetrazole compounds was connected with studies on the application of nitrogen nuclear quadrupole resonance (^{14}N NQR) for the detection of explosives and the study of polymorphism in some pharmaceuticals [10,17,18].

The majority of drugs in the form of final products are most practically prepared and stored as solid pellets, tablets, capsules, powders, flakes, etc. Drug molecules, before performing the target action, must dissolve in the fluids of the organism. In order to act in the most economic and controlled way, the molecular conformation in the solid must be exactly tailored and programmed. Determination of the molecular conformation in a solid lattice is usually and most reliably done by X-ray diffraction (or some equivalent diffraction method). Casual conformational variations can be the consequence of the polymorphism of pharmaceuticals [11]. Unwanted polymorphic transitions can also occur in finished, ready to use products due to improper storage conditions. The appearance of polymorphism in pharmaceutical products has to be studied as carefully as possible.

In addition to X-ray diffraction (accepted in pharmaceutical research as the gold standard), several spectroscopic techniques like NMR, FT-IR and EPR are used. Recently, NQR, with its ability to identify specific molecules, was also proposed [12,13].

If the NQR spectrum of a particular molecular structure can be detected in the available amount of the investigated sample, it is known that there is practically 100% correspondence between the detected spectrum and the presence of that same structure in the sample [12,13]. In favorable circumstances even concentration variations of the investigated molecular conformation can be monitored by NQR. For further refinement, additional identification of

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Abbreviations: TZ, 1H-tetrazole; ATZ, 5-aminotetrazole; ATZH, 5-aminotetrazole monohydrate; NQR, nuclear quadrupole resonance; NMR, nuclear magnetic resonance; EPR, electron paramagnetic resonance; FT-IR, Fourier transform infra-red spectroscopy; EFG, electric field gradient tensor; *eQ*, electric quadrupole moment; *Q.c.c.* = e^2Qq/h, quadrupole coupling constant; μ_N, nuclear magneton; MO, molecular orbital; FFT, fast Fourier transformation; H-bond, hydrogen bond; RF, radiofrequency; r.t., room temperature; s/n, signal to noise ratio; T_1, spin–lattice relaxation time; RD, repetition delay; CP, Carr-Purcell; PSL, Pulsed-Spin-Locking.

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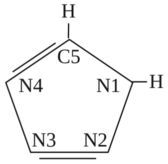

Fig. 1. 1H-tetrazole molecule.

and information on the NQR spectral lines are available: e.g. their dependence on temperature, external fields (electric, magnetic, mechanical stress) or their relaxational properties.

Little attention is paid to the environmental impact of commonly used explosives, whether for peaceful or military purposes. In contrast, the tetrazole ring (Fig. 1), as a basis of new explosives, is relatively flexible to modifications and substitutions, which can thus control the tailored compound's properties. Tetrazole derivatives can explode more cleanly and produce fewer toxic by-products, some modifications can replace poisonous lead-based initial explosives, and they can serve as controllable and safer propellants in rockets [5–7]. In addition to other replacements, they are also used in safety airbag propellants as an alternative to the usual sodium azide. NQR could become a large scale nondestructive contactless technique for checking the structural quality of the final explosive product, as well as for a safe procedure for controlling components used in synthesis and intermediate products, if they are in the form of a solid and NQR active.

Many recent investigations and proposed techniques were devoted to the possibility of remote scanning for hidden explosives (and other illicit materials, like narcotics) in baggage, mail packages, vehicles, buried mines, etc. [14,15,17,18]. Provided that enough features of the expected NQR signals are known, the detection circuits, pulse sequences and experimental parameters can be tuned and specialized to greatly improve specific NQR sensitivity [16–18]. Therefore, it is advisable to compile a supplementary library of relevant NQR signals and their corresponding spectral parameters. Our new spectral data can be considered as a small contribution to such developing library.

Earlier research on azoles (also 1H-tetrazole, see Table 1) was reported in the literature [19–21]. Some relevant crystal structures and molecular orbital (MO) calculations for tetrazoles were published [22–25].

In the present study we complemented previous results for 1H-tetrazole by new pure NQR measurements of ^{14}N spectra in 5-aminotetrazole and 5-aminotetrazole monohydrate. The comparison of these data is interesting from several points of view. It deepens our knowledge of the chemical bonding in these molecules. This can be useful in explaining the spectra of different substances where the tetrazole ring is a constitutional part. Since the signals are relatively strong it can also help to improve the detection techniques to enable greater sensitivity in less favorable conditions or samples.

In the next section we shortly repeat basic facts about pure NQR spectroscopy, focusing on ^{14}N NQR with nuclear spin 1. The known tetrazole molecular structures and the features of intramolecular bonding in the relevant molecules are described. Semiempirical, however, instructive Townes–Dailey model is sketched, which correlates small but easily measurable spectral shifts between similar molecules with the influence of the variations of bonding molecular orbital (MO) populations. The quantum-chemical MO calculations in tetrazole derivatives describe these topics more rigorously, but it is not the subject of this paper. We rather wish to turn the reader's attention to the applicability of NQR spectroscopy in tetrazole containing compounds after the NQR collection of structurally related molecules is enriched. For potential future use, in the final section the approximate orbital populations of intermolecular bonds were calculated using Townes–Dailey model, accommodated to the particular molecular geometry.

The experimental section describes technical details of the measurements and samples. It presents our new ^{14}N NQR experimental spectral data, relaxational data and their rough temperature dependences from 77 K to room temperature.

In the last section the comparative assignment of the spectral triplets to equipositional atoms in the related molecules and the agreement between the corresponding atoms from different family members, are discussed. Besides our own perceivings we rely on the results in the publication [21], where the assignments were supported also by specific MO calculations (azole trimers). More than reasonable matching of all the triplets strongly supports correctness of the assignment in both publications.

Estimation of the notable influences of the hydrogen bonds on NQR shifts or temperature dependence is attempted too, using the comparison of their temperature dependences. In four cases, ν_+ and ν_- lines in ATZ and ATZH, measurement of spectral temperature dependence in large temperature interval revealed crossover of the lines at lower temperature (see Fig. 4), meaning larger influence of thermal vibrations at N(1) NQR in ATZH. Generally, such measurements enable the separation of the frequency shift due to lattice vibrations from the frequency shift due to chemical bonds.

In the final section, the NQR spin–lattice relaxation is also discussed. Its practical importance is in restriction of the length of the NQR measurement to obtain sufficient signal. Temperature dependence of T_1 gives interesting information about lattice dynamics around the resonant nucleus provided that sufficiently broad temperature interval has been measured to establish the relaxational model. The lines of N(1) and N(5) in ATZ and ATZH can be characterized by the slowest relaxation.

2. Theory

The electric quadrupole moment eQ of a nucleus describes the deviation of its charge distribution from spherical symmetry. In the nuclear ground state this is a characteristic property like the magnetic dipole moment. Only a nucleus with $I \geqslant 1$ can have a non-zero electric quadrupole moment. In the crystal lattice, interaction occurs between eQ and the surrounding inhomogeneous electric field (more precisely, interaction between the two tensors: the electric quadrupole moment and the electric field gradient, EFG). The dominant contributions to the crystal or molecular electric fields come from inter- and intramolecular chemical bonds caused by the bonding electrons. A phenomenological description

Table 1
^{14}N NQR lines and their assignment in 1-H-tetrazole [19–21].

TZ, N(i)	$\nu_+(300)$ (kHz)	$\nu_+(77)$ (kHz)	$\nu_-(300)$ (kHz)	$\nu_-(77)$ (kHz)	$\nu_0(300)$ (kHz)	Q_{300} (kHz)	η_{300}
1	1889		1420		462	2206	0.425
2	3665		2920	2978	745	4390	0.339
3	3742		2658		1084	4267	0.508
4	3250	3302	2340		910	3727	0.488