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Review

Nuclear Quadrupole Resonance Spectroscopy: Tautomerism and Structure of Functional Azoles

Lyudmila I. Larina

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1, Favorsky Str., 664033 Irkutsk, Russia; larina@irioch.irk.ru; Fax: +7-3952-419346

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Abstract: The Nuclear Quadrupole Resonance spectroscopy data of functionalized azoles (imidazoles, triazoles and corresponding benzazoles) are reviewed and critically discussed. The possibility of studying the tautomerism of azoles by the NQR method is considered.

Keywords: ^{35}Cl NQR spectra; structure; tautomerism; imidazoles; triazoles; benzimidazoles; benzothiazole

1. Introduction

The studies of the structural peculiarities and tautomeric transformations of functionalized azoles and related heterocycles by multinuclear Nuclear Magnetic Resonance (NMR) Spectroscopy, Nuclear Quadrupole Resonance (NQR) spectroscopy and Electron Spin Resonance (ESR spectroscopy, quantum chemistry, and other physico-chemical techniques were performed by us over decades [1–36]. The outcomes of these studies are discussed in monography, reviews, and a dissertation [37–46]. The azole core occupies an important place in the chemistry of heterocyclic compounds. Their unique properties and unusual biological activity attract great attention from a wide circle of researchers. Azole derivatives are employed as pharmaceuticals, high power materials, radiosensitizers, ionic liquids, multi-faceted bases in peptide nucleic acids, coloring pigments, regulators of plant growth, pesticides and herbicides, plastifying agents, precursors of nanocomposites, and building blocks for organic chemistry [37,46–49]. Extensive employment of azoles necessitates a deeper understanding of the features of their electron structure, spectral characteristics, and tautomeric transformations. Tautomerism of azoles is one of the most appealing issues in theoretical investigations of their reactivity and electronic properties. The reasonable interpretation of the chemical behavior and biological activity of these heterocycles is improbable without determination of tautomeric forms and the factors influencing the relative stability. The prototropic exchange in the azoles in the solution occurs rather quickly on the NMR time scale, therefore the change in the temperature of the solution does not cause changes in the spectra. As a rule, time-averaged signals appear in the NMR spectra. Therefore, the study of azoles in the solid state is necessary for understanding the tautomeric processes.

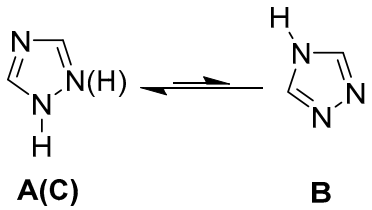
2. The Structure and Tautomerism of Substituted Azoles

2.1. Chlorinated Five-Membered Azoles

Possible chlorotropic rearrangements in 1,2,3-triazoles and benzotriazoles were analyzed [50], since it was disclosed that chlorine exchange occurred in 1-chloro-4,5-diphenyl-1,2,3-triazole [51]. The intensive subsequent NMR [46,50], and NQR [46], studies evidenced that the compound turned out to be symmetrical 2-chloro-4,5-diphenyl-1,2,3-triazole5,6-dichloro-4,7-dimethylbenzotriazole. Some examples of chlorotropic transformations in other azoles are also known [52,53]. The chlorotropic exchange in 1-chlorobenzimidazole revealed by NMR spectroscopy is due to the rapid intermolecular

transfer of a chlorine atom between 1-chlorobenzimidazole and benzimidazole in a $CCl_4/CH_3OH/K_2CO_3$ medium [52,53]. A similar chlorotropic rearrangement was observed in the equilibrium exchange process between 1-chloroindole and 3-chloro-3*H*-indole, i.e., the fast intermolecular transformations of 1-chloroindole to 3-chloroindole in the related media were detected [53]. The base-promoted intermolecular mechanism rationalizes chlorotropic processes in *N*-chlorosubstituted azoles. NQR spectroscopy data are missing.

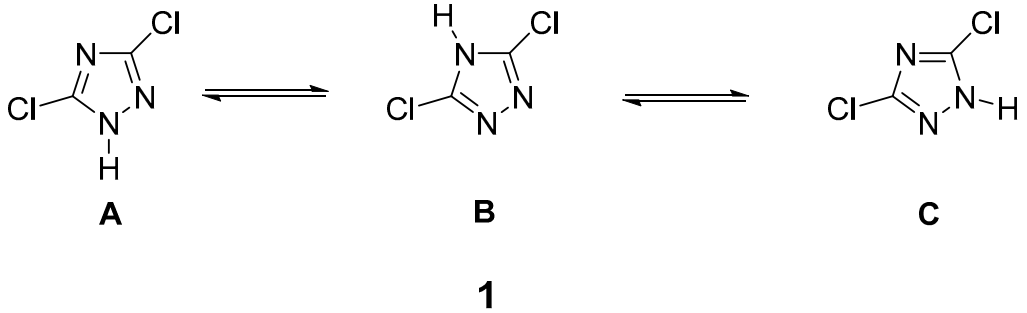
X-ray single-crystal analysis of 1,2,4-triazole (Scheme 1) have revealed a crystalline state of the asymmetric 1*H*(2*H*)-tautomer (**A**, **C**) [54,55]. Quantum-chemical (ab initio) calculations of 1,2,4-triazole tautomers suggest the prevailing of 1*H*(2*H*)-1,2,4-triazole in gas phase as compared to 4*H*-1,2,4-tautomer by ~7 kcal/mol [56–59], that agrees with experimental data [60,61].



Scheme 1. The possible tautomeric forms of 1,2,4-triazole.

In addition, 1*H*-form [62–65] is favorable in a solution, and the alkylation of 1,2,4-triazole affords two isomers: 1-alkyl- and 4-alkyl-1,2,4-triazole in a ratio of ~10:1 [66]. A low content of 2*H*-1,2,4-triazole (~5%) can be contained in a strong polar solvent [60]. It is not a surprise that 3-nitro-1-nitromethyl-1*H*-1,2,4-triazole is presented as 1*H*-form in the solid state [67].

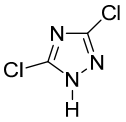
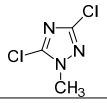
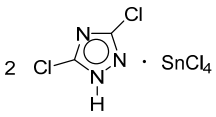
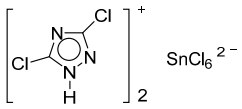
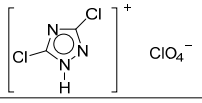
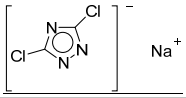
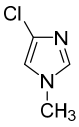
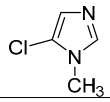
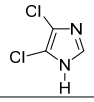
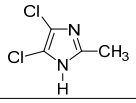
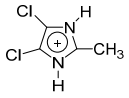
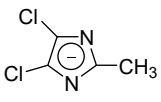
We studied the 3,5-dichloro-1,2,4-triazole (**1**) by ^{35}Cl NQR spectroscopy and showed that it also exists as the 1*H*-tautomer (Scheme 2) (Table 1) [46,68,69].



Scheme 2. The possible tautomers of 3,5-dicloro-1,2,4-triazole.

The ^{35}Cl NQR spectral data of a polycrystalline sample of 3,5-dichloro-l,2,4-triazole (**1**) differs insignificantly in the signal intensity ratios from those reported previously (Table 1) [70]. The ^{35}Cl NQR spectrum of **1** also differs from that expected from the single crystal X-Ray analysis (ambient temperature) [71]. These data assume that compound **1** could be a 1-*H* tautomer (**A**). Establishing the structure of the compounds using nuclear quadrupole spectroscopy ^{35}Cl and the assignment of signals in the experimental spectra without attracting quantum chemical calculations in many cases quite is difficult.

Table 1. The ^{35}Cl NQR frequencies at 77 K (ν, MHz) and signal-to noise ratio (s/n) in the spectra of chloro-containing 1,2,4-triazoles (**1**–**6**) and imidazoles (**7**–**12**).

Compound	Structure	ν, MHz	s/n
1		37.322 38.085 38.203 38.899	8 22 15 17
2		36.791 37.120 38.014	8 5 9
3		38.916 39.744 19.452 19.657	15 15 4 4
4		40.734 41.608 16.040 16.312 17.776	10 11 3 2 6
5		40.526 41.408	20 20
6		35.491 35.629 36.111	11 5 4
7		35.034	8
8		36.720 36.924	9 8
9		36.172 37.409	11 12
10		36.070 37.394	10
11		39.025	7
12		34.716	8

The C(3)-C1(3) and C(5)-C1(5) bond lengths are slightly different [72]. So, it can be anticipated that the spectrum would contain a doublet or two sets of signals. Nevertheless, the real spectrum shows four NQR resonance signals. Two extremal signals display splitting, $\Delta\nu \sim 1.6$ MHz, while the two other ones are detected in the center of this quadruplet. The distinction of the experimental and the expected spectra can be caused by a phase transition and, hence, different crystalline phases for monocrystalline and polycrystalline samples, as well as the existence of a mixture of tautomers in polycrystalline samples.

Commonly, analogous splitting of signals is detected in the spectrum of 1-methyl-3,5-dichloro-1, 2,4-triazole (**2**). This cannot be rationalized by the formation of a mixture of two tautomers. The signals of triazole **2** are downfield shifted as compared to those of **1**. This relates qualitatively to a ratio of the inductive constants of the CH_3 and H substituents. According to ab initio calculations the 1-*H* tautomer **1** is a little bit stable (by 3.1 kcal/mol) compared to the 4-*H* tautomer [46].

Thus, on the basis of multiple signals in the ^{35}Cl NQR spectrum, slightly different from the expected from X-ray data, it has been found that 3,5-dichloro-1,2,4-triazole (**1**) is present as 1*H*-tautomer with an uncommon phase composition. Later Elguero with co-authors [72] has shown that in crystal, this triazole is present as trimer with intermolecular hydrogen bonds N(1)-H ... N(2).

The "pyridinic" nitrogen in the ClCN moiety causes the decrease of the NQR frequency of the chlorine atom as compared with the "pyrrolic" nitrogen [68,73]. This is supported by experimental and calculated frequencies. This regularity should also be observed in 3,5-dichloro-l,2,4-triazole derivatives.

The complexation of **1** with $SnCl_4$ and protonation augment the ^{35}Cl NQR frequency (Table 1). Here, the electron-withdrawing properties of the triazole cycle enhance, and the negative charge on chlorine atoms reduces simultaneously. The spectral characteristics assume a complex formation and protonation with participation of the N(4) atom. When the N(2) atom is involved in the coordination, a singlet or slightly split signal are anticipated. The calculated frequency splitting of a 4-H cation agrees well the experimental data. The calculations show that this cation is more stable than the 2-*H* isomer [68]. The augmentation of the ^{35}Cl NQR frequency on going from a neutral molecule to a cation is ~2.6 MHz for **1** and 2.2 MHz for **11**. The transition from a neutral state to an anion includes the frequency lowering to 2.6 and 2.0 MHz for **1** and **11**, respectively. The value of the frequency change in going from the anion to the cation is greater for the triazole cycle than for the imidazole cycle. Asymmetry in the alteration of the chlorine electronic density is manifested for two heterocycles, if these compounds are transformed into an ionic form. The generation of a cation induces a higher rearrangement of the chlorine electron density than that which is observed upon transition to the anion. The calculations [68] predict another situation because in the anion the negative charge is localized only in the cycle and on two chlorine atoms. In the cation, a part of the positive charge is transferred by hydrogen atoms and, therefore, the chlorine atoms are not "sensitive" enough to the alterations in the charge state. The discrepancy between the experimental and calculated data is probably owing to the electron deficiency of the rings.

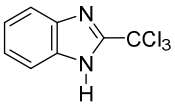
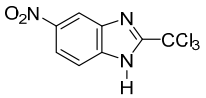
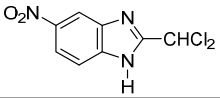
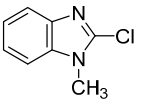
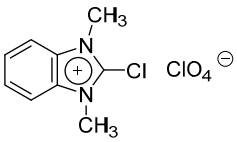
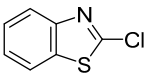
In going to the cation this ability enhances notably, which increases the Cl frequency. Here, one should bear in mind that in going from the neutral state to the cation the degree of p-π- conjugation also augments and this, in turn, lowers the NQR frequency.

For example, the 1*H*-tautomer of 3-nitro-1,2,4-triazole and its 5-substituted is the most stable both in gas phase and solution [74–80]. Here the "labile" hydrogen relates to the heteroatom, the most distant from the nitro moiety. The labile proton in 5-amino-1,2,4-triazole is close to the nitrogen atom adjacent to the amino group (X-ray data) [81,82], i.e., the 5-amino-1-hydrogen-1,2,4-triazole structure is formed.

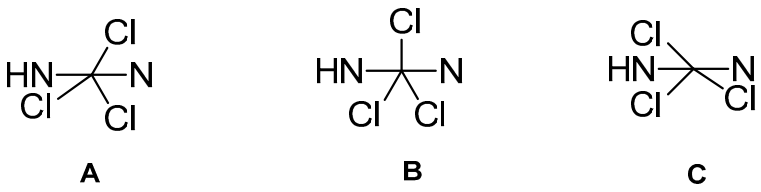
2.2. *Chloro-Containing Benzazoles*

We studied ^{35}Cl NQR spectra at 77 K of the chloro-containing benzimidazole derivatives (**13**–**18**) (Table 2) [46,83].

Table 2. The ^{35}Cl NQR frequencies at 77 K (ν, MHz) and signal-to noise ratio (s/n) in the NQR spectra of chloro-containing benzimidazoles and benzothiazole (**13**–**18**).

Compound	Structure	ν, MHz	s/n
13		40.174 39.848 39.728 39.642 39.516 39.136	7 8 6 7 7 8
14		40.574 39.724	11 19
15		37.445 37.253	33 35
16		36.296	10
17		39.618	7
18		37.740	8

Calculations of the 2-trichloromethylbenzimidazole molecule have been carried out for three possible orientations of the trichloromethyl group relative to the benzimidazole ring plane (Scheme 3, conformation **A**, **B**, **C**) [38,46,83].



Scheme 3. Conformations of the trichloromethyl group in benzimidazole cycle plane.

If the situation is realized when the dihedral angle φ = 0° (conformation **A**), then in the ^{35}Cl NQR spectrum should expect one low frequency signal and two high-frequency signals (possibly only one, but double intensity). For conformations with φ = 180° (conformation **C**) calculations, as in the classic Towns–Daley approximation, and with using the modified Equation (1) show that there should be one signal in the spectrum high frequency and two low frequency signals (or one double intensity signal). In the case of perpendicular orientation of one chlorine atoms to the cycle plane (conformer **B**) three signals should be recorded.

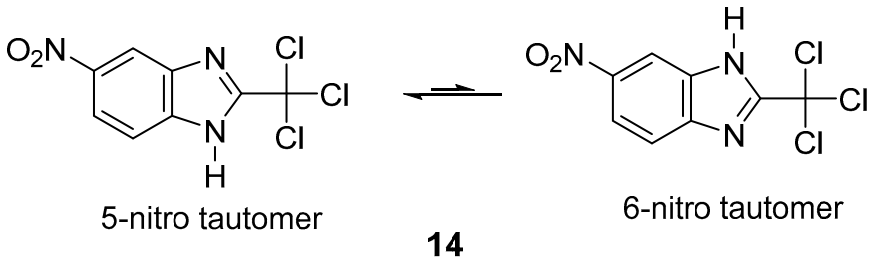
The modification of the Townes–Dailey equation does not account for the effect of the different diffusivity of the p_i-orbital on gradient of the electric field (Equation (1)) [68,84].

$$\nu_{M.T.D.} = k_2\left((\xi_z)^3 P_{zz} - \frac{(\xi_x)^3 P_{xx} + (\xi_y)^3 P_{yy}}{2}\right) \quad (1)$$

where ν is the calculated NQR frequency, k is the empirical constant, P_{xx}, P_{yy} and P_{zz} are the population of the corresponding p-orbital of the indicator atom, and ξ_z is the exponent index of the corresponding p_i-orbital of the Slater type.

Thus, the ^{35}Cl NQR experimental spectrum of 2-trichloromethyl-benzimidazole (**13**), consisting of six signals (Table 2), can be explained by the presence in the crystal unit cell of two molecules, having a conformation close to **B**.

The ^{35}Cl NQR spectral data of 2-trichloromethyl-5(6)-nitrobenzimidazole (**14**) and the AM1 and PM3 calculation results of its tautomers show that the 5-nitro tautomer is more favorable than 6-nitro tautomer (Scheme 4) [38,46,68,85].



14

Scheme 4. Tautomers of 2-trichloromethyl-5(6)-nitrobenzimidazole.

The introduction of the nitro group into 2-trichloromethylbenzimidazole increases the ^{35}Cl NQR average frequency owing to the electron-withdrawing effect of the nitro group despite its distant location from the indicator atom. The presence of two ^{35}Cl signals, assigned to three chlorine atoms, with an intensity ratio of 1:2 (40.574 and 39.724 MHz) in the NQR spectrum of this compound evidences that its existence in the view of the conformer **A** or **C** where two chlorine atoms are located over and under the plane of the benzimidazole ring, and the third chlorine atom is placed in the ring plane. The data of the quantum-chemical calculations demonstrate a preference of conformer **C**, while H-bonding stabilizes the conformer **A** (Scheme 3) [83,85]. The enthalpy of the conformers **A** and **C** of 2-trichloromethyl-5(6)-nitrobenzimidazole **14** calculated by AM1 and PM3 methods and the ^{35}Cl NQR frequencies computed from the Townes–Dailey equation (TD) [86], and the modified Townes–Dailey Equation (1) [68,84], have been studied (Table 3) [83,85].

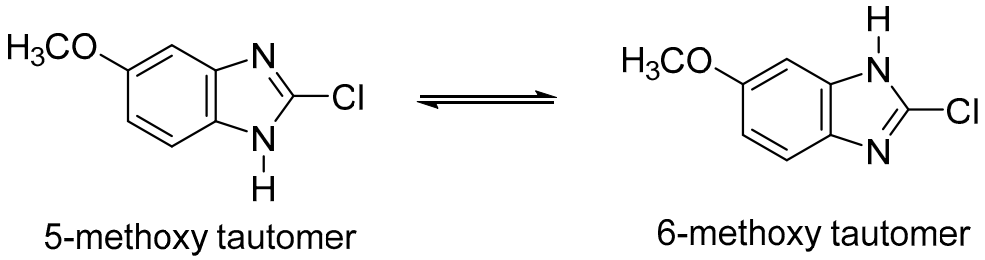
Table 3. The formation heats (H, kcal/mol) of the conformers **A** and **C** of 2-trichloromethyl-5(6)-nitrobenzimidazole and ^{35}Cl NQR frequencies (v, MHz), obtained from Townes–Dailey (TD) and modified Townes–Dailey (MTD) equations [38,46,68].

Method		5-Nitro Tautomer				6-Nitro Tautomer			
	φ	0		180		0		180	
		TD	MTD	TD	MTD	TD	MTD	TD	MTD
AM1	H	56.487		56.126		57.097		56.780	
	ν	50.452	45.650	51.557	46.481	50.496	45.724	51.535	46.524
		50.443	45.646	49.179	44.666	50.502	45.729	49.107	44.657
		48.425	43.957	48.719	44.304	48.558	44.098	49.098	44.657
PM3	H	20.300		20.437		20.786		21.066	
	ν	54.414	46.961	55.666	47.542	54.512	47.105	55.734	47.624
		54.370	46.977	52.419	45.642	54.460	47.109	52.541	45.865
		51.477	44.691	52.384	45.743	51.629	44.885	52.445	45.775

The analyses of these, others, and our data [84,87–91] shows that usage of the modified Townes–Dailey equation is more preferable then Townes–Dailey equation for the elucidation of structure and assignment of signals in the ^{35}Cl NQR spectra of organochlorine compounds.

The average frequency of the ^{35}Cl NQR signals of compound **14** (Table 2) is higher than compound **13,** that can be rationalized by the electron-withdrawing influence of the nitro group, despite its being removed from the indicator atom. The reducing of the resonance frequency of the ^{35}Cl NQR signals of compounds **15** and **16** as compared to **13** is apparently due to a decrease in the number of chlorine atoms in the substituent in position 2 of the benzimidazole cycle. The protonation of the molecule **13** leads to the formation of cation **17** (benzimidazolium perchlorate), and is accompanied by an augmentation of the ^{35}C1 NQR frequency (Table 2). A slight splitting in the NQR spectrum of compound **15** excludes the orientation of one of the chlorine atoms in the plane of the benzimidazole ring (i.e., the conformations of similar **A** and **C**). Otherwise, there should be a substantial nonequivalence of these chlorine atoms, similar to the trichloromethyl derivative **13** and **14**.

Prototropic exchange in 2-chloro-5(6)-methoxybenzimidazole in THF at 173 K is decelerated and two tautomers are separately detected (Scheme 5) [92,93].



Scheme 5. Tautomers of 2-chloro-5(6)-methoxybenzimidazole.

Forty percent of 5-methoxy and 60% of 6-methoxy tautomer are observed, which corresponds to an equilibrium constant of 0.67. Unfortunately, the NQR spectrum of this compound could not be obtained.

3. Conclusions

Tautomeric transformations, structural peculiarities and distribution of electron in tautomeric and non-tautomeric imidazole derivatives (2-methyl-5-nitroimidazoles, metronidazole) [94,95], 5-substituted tetrazoles [96], 1,3,4-thiadiazole derivatives [97], indazoles [98], benzimidazoles [99], and other nitrogen-containing compounds [100–103], were investigated by NMR–NQR double resonance and quantum chemical methods. The asymmetry parameter in derivatives of 5-nitroimidazoles is reduced with augmentation of the substituent size. The insertion of the substituent in position 1 of the imidazole cycle redistributes p-electron density and its delocalization from the nitrogen atom –N (N-3) to the nitrogen NH (N-1). Even very weak substituent effects could substantially alter the change the electron density distribution in imidazoles [94,95]. Unfortunately, authors [94,95] gave a wrong name of imidazoles (2-nitro-5-methylimidazoles), which are indeed 2-methyl-5-nitroimidazoles. As mentioned above, the numbering of azoles starts from the NH nitrogen atom (or *N*-organyl) to other heteroatoms. The π–electron density and N-1 bond population, calculated by the Townes–Dailey approach, described by Dr. Lucken [86] and Dr. Dolgushin [68,83,84,87–91], enhances with lengthening of the substituent in the position 1 (N-1) [94,95]. The data of NMR–NQR study and quantum-chemical investigations of thermodynamic stability of the tautomeric forms of indazole show that the 1*H* form is more highly stable (21.4 kJ mol^{-1}) than the 2H form [98].

Thus, NQR spectroscopy is crucial for the investigation of the tautomerism of functional heterocyclic compounds. In addition, NQR spectroscopy is an excellent tool for studying the structure of chlorine derivatives of heteroatomic and heterocyclic compounds.

This review is dedicated to the memory of Dr. G.V. Dolgushin, who for many years headed the research of organic and elementoorganic compounds using nuclear quadrupole resonance spectroscopy.

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