A ^{35}Cl NQR and MNDO study of 3,5-dichloro-1,2,4-triazole and its ionic forms*

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The ^{35}Cl NQR spectra of 3,5-dichloro-1,2,4-triazole derivatives have been examined. MNDO calculations of chloroazoles (imidazole, triazole) including their ionic forms have been carried out. In 3,5-dichloro-1,2,4-triazole complexation and protonation occur of position 4 at the triazole ring.

Introduction

Some nitrogen-containing heterocycles can form both anionic (with abstraction of the N–H proton) and cationic derivatives (with addition of the proton to the pyridinic nitrogen atom). These include, in particular, 3,5-dichloro-1,2,4-triazole and 4,5-dichloro-2-methylimidazole. These compounds were studied by ^{35}Cl NQR spectroscopy [1, 2]. Quantum-chemical analyses of the electronic structure of chlorine-containing azoles and their ionic forms have not been carried out. The molecular structure of some chloroazoles was established by X-ray diffraction [3–5]. Data from the X-ray study and NQR have not been compared.

Results and Discussion

The ^{35}Cl NQR spectrum of a polycrystalline sample of 3,5-dichloro-1,2,4-triazole (**I**) presented in Table 1 differs slightly in the signal intensity ratios from that published earlier [1].

The ^{35}Cl NQR spectrum of **I** is also different from the spectrum that could be expected from the single-crystal X-Ray data (room temperature) [3]. According to these data compound **I** is (should be) a 1-H tautomer. The lengths of C(3)–Cl(3) and C(5)–Cl(5) bonds are somewhat different [3]. Thus, one might expect a spectrum consisting of a doublet or of two groups of signals. In the real spectrum, however, there are four NQR signals. The extreme signals show splitting, $\Delta\nu \approx 1.6$ MHz, the two other signals being in the centre of this quadruplet. Possible reasons for the difference between the experimental and the expected spectrum may be a phase transition and therefore different crystalline phases for monocrystalline and polycrystalline samples as well as the presence of a mixture of tautomers in the polycrystalline sample.

In general, a similar splitting pattern of signals is observed in the spectrum of 1-methyl-3,5-dichloro-1,2,4-triazole (**II**). This cannot be explained by a mixture of two tautomers. The signals of **II** are shifted down in frequency field with respect to those of **I**. This corresponds qualitatively to the ratio of the inductive constants of the CH_3 and H substituents.

In **I** the bond lengths calculated by MNDO with total optimization of geometry are by 1–7 pm longer than the experimental values. The N(1)–N(2) bond is, on the contrary, by 3 pm shorter than the experimental one. The H(1) N(1) C(5) angle, 115°, is noticeably smaller than the calculated angle 128.7°, whereas the H(1) N(1) N(2) angle of 139° is greater than the experimental angle of 121°. The distortion of geometry seems to be due to hydrogen bonds [3].

According to MNDO calculations, the 4-H tautomer of **I** is slightly more stable (3.3 kcal/mole) than the 1-H tautomer, although in the crystalline state it exists as the 1-H tautomer.

The NQR frequencies of the chlorine atoms in the C(3)–Cl C(5)–Cl bonds of **I**, calculated by MNDO with total optimization of geometry (Table 2), are almost similar, their splitting ($\Delta\nu_{cal} \approx 0.35$ MHz) being different from the experimental value. The use of the real geometry in the calculations gives nearly the experimental splitting ($\Delta\nu \approx 1.48$ MHz). The calculation

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Table 1. The ^{35}Cl NQR frequencies at 77 K (ν^{77}) and signal/noise ratio (s/n) in the spectra of 3,5-dichloro-1,2,4-triazole and its derivatives

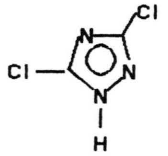
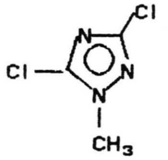
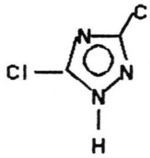
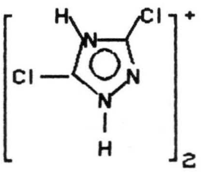
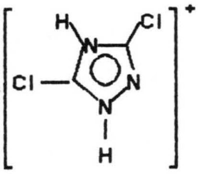
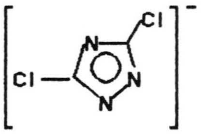
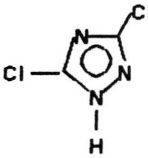
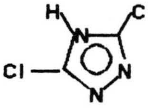
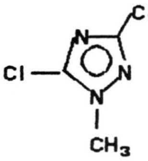
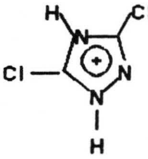
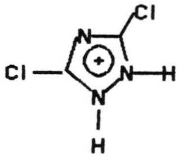
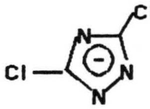
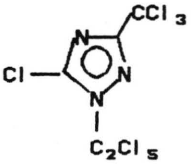
N	Compounds	ν^{77}, MHz	s/n
I		37.322 38.085 38.203 38.899	8 22 15 17
II		36.791 37.120 38.014	8 5 9
III	2  · $SnCl_4$	38.916 39.744 19.452 19.657	15 15 4 4
IV	 $SnCl_6^{2-}$	40.734 41.608 16.040 16.312 17.776	10 11 3 2 6
V	 ClO_4^-	40.526 41.408	20 20
VI	 Na^+	35.491 35.629 36.111	11 5 4

Table 2. The MNDO calculated ^{35}Cl NQR frequency (ν, MHz), optimized lengths of C–Cl bonds (r) and heats of formation (H) of 3,5-dichloro-1,2,4-triazole derivatives.

N	Compounds	ν_{cal}	r_{pm}	$H_{kcal/mole}$
I		57.509 57.865	171.38 171.20	34.25
VII		58.027	170.92	30.94
VIII		57.344 57.577	171.42 171.32	31.68
IX		64.594 65.229	169.95 169.85	210.95
X		64.065	169.84	226.36
XI		49.520	173.29	−26.85
XII		59.851	171.08	18.3

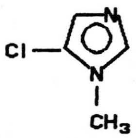
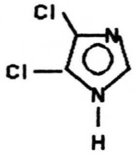
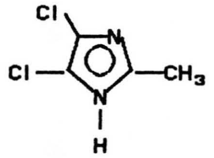
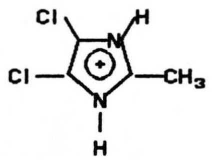
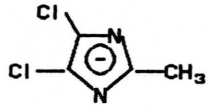
of frequencies was performed with the Townes and Dailey theory.

The absolute calculated frequencies are considerably lower than the experimental values. This has been reported previously for chlorine-containing compounds (see, for example [6, 7]).

The "pyridinic" nitrogen atom in the ClCN group is responsible for the lowering of the NQR frequency of the chlorine atom compared to the "pyrrolic" nitrogen atom [2, 8]. This is confirmed by experimental and calculated frequencies. The above regularity should also be met for 3,5-dichloro-1,2,4-triazole derivatives.

The calculated C–Cl bond lengths (Tables 2, 3) correspond qualitatively to this regularity, being in correlation with the experimental frequencies (Table 1): in chloroimidazoles the C(4)–Cl bond is longer than the

Table 3. The MNDO calculated ^{35}Cl NQR frequency (ν, MHz), optimized lengths of C–Cl bonds and experimental ν^{77}_{exp} of chloroimidazole derivatives [2, 4].

N	Compounds	ν_{cal}	r_{pm}	ν^{77}_{exp}
XII		53.624	172.41	35.034
XIV		53.850	172.16	36.720 36.924
XV		55.005 55.542	171.98 171.55	36.172 37.409
XVI		54.953 55.498	172.01 171.60	36.070 37.394
XVII		61.774	170.44	39.025
XVIII		47.684	173.99	34.716

C(5)–Cl bond, whereas in 3,5-dichloro-1,2,4-triazole 1-derivatives the C(3)–Cl bond is longer than the C(5)–Cl bond.

The lengths of these bonds correlate with experimental frequencies:

$$\nu_{\mathrm{exp}} = 314 - 1.609\, r, \qquad r = 0.93,\ s = 0.75,\ n = 13\,,$$

$$\nu_{\mathrm{exp}} = -55.4 + 469.4\,(100/r)^3, \quad r = 0.93,\ s = 0.74,\ n = 13\,.$$

An attempt to make use of the correlation derived by Weiss for compunds having C_{sp^2}–Cl bonds [9], was unsuccessful.

Judging by the measured C–Cl bond lengths and the above correlations one should expect 37.8–38.69 MHz for the triazole **I** and 38.23 or 38.63 MHz for the imidazole XVI. In the spectrum of the imidazole XVI only one signal should occur since the two C–Cl bonds are of almost the same length.

The theoretical NQR frequencies for chloroazoles correlate with the experimental values:

$$\nu_{\mathrm{exp}} = 16.6 + 0.369\, \nu_{\mathrm{cal}} \quad r = 0.94,\ s = 0.69,\ n = 13.$$

From this correlation the NQR frequencies for compounds **I** have been found in the expected region (38.00 and 37.99 MHz). As far as the other triazole (**XII**) is concerned, all the signals in the experimental spectrum [5] are located beyond the calculated frequency (38.69 MHz).

The complexation of **I** with $SnCl_4$ and protonation are accompanied by an increase of the ^{35}Cl NQR frequency (Table 1). In this case a simultaneous strengthening of electron acceptor properties of the triazole ring and a decrease in the negative charge on chlorine atoms take place. The spectral characteristics suggest complexation and protonation to involve the N(4) atom. If the N(2) atom had taken part in coordination, a singlet or slightly split spectrum would have been expected. The calculated splitting of the 4-H cation frequencies is in qualitative agreement with the experimental values. According to calculations, this cation is more stable than the 2-H isomer (Table 2).

The increase in the ^{35}Cl NQR frequency in going from the neutral compound to the cation is 2.83 MHz for **I** and 2.29 MHz for **XVII**. The change in theoretical frequencies is 7.23 and 6.55 MHz, respectively. The transition from the neutral state to the anion involves a frequency lowering to 2.64 and 2.0 MHz for **I** and **XVII**, respectively, the theoretical values for these compounds being 8.17 and 7.54 MHz. The magnitude of the change in frequencies in going from the anion to the cation is higher for the triazole ring than for the imidaze ring. For the two heterocycles an asymmetry in the change of the chlorine atom's electronic density is observed when these compounds are transformed into ionic derivatives. The formation of a cation causes a greater rearrangement of the chlorine electron density than that occurring in the transition to the anion. Based on calculations, one should expect a quite different situation since in the anion the negative charge is localized only on the ring and on two chlorine atoms. In the cation some portion of the positive charge is carried by hydrogen atoms and thus the chlorine atoms are not "sensitive" enough to the change in the charge state. The difference between the experimental and theoretical changes is most likely to be due to electron deficiency of the rings.

In the transition to the cation this ability increases even more, which leads to an increase in the Cl frequency. In this case it should be borne in mind that in going from the neutral state to the cation the degree of p-π conjugation is also increased and this, in turn, will lower the NQR frequency.

For this contribution be taken into consideration it is necessary to measure the EFG asymmetry parameters.

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[1] V. V. Makarskii, M. G. Voronkov, V. P. Feshin, V. A. Lopyrev, N. I. Berestennikov, E. F. Shibanova, and L. V. Volkova, Doklady AN SSSR **220,** 101 (1975).
[2] A. N. Nesmeyanov, D. N. Kravtsov, A. N. Zhukov, I. M. Kochergin, and G. K. Semin, Doklady AN SSSR **179,** 102 (1968)
[3] G. L. Starova, O. V. Frank-Kamenetskaya, and V. V. Markarskii, Kristallografiya **35,** 769 (1990).
[4] Shi-Qi Dou and A. Weiss, Z. Naturforsch. **47 A,** 177 (1992).
[5] Yu. I. Matveev, V. I. Gorbatenko, L. I. Samarai, S. V. Sereda, and Yu. T. Struchkov, Zhurnal Organ. Khimii **24,** 2216 (1988).
[6] V. A. Kirillovich and A. A. Bredikhin, Izv. Akad. Nauk, Ser. Khim. 1078 (1992).
[7] B. A. Suvorov, Zhurnal Fiz. Khimii **66,** 2831 (1992).
[8] M. L. S. Garcia, J. A. S. Smith, P. M. G. Bavin, and C. R. Ganelin, J. Chem. Soc. Perkin Trans. **II,** 1391 (1983).
[9] S. Brummer, and A. Weiss, Ber. Bunsenges. Phys. Chem. **94,** 497 (1990).