^{35}Cl NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF 3(5)-ARYL-5(3)-CHLORO-1,2,4-TRIAZOLE

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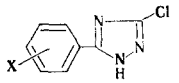
The ^{35}Cl nuclear quadrupole resonance (NQR) spectra of a number of 3(5)-aryl-5(3)-chloro-1,2,4-triazoles were studied. The energically most favorable tautomeric forms of the molecules were established, and a correlation between the ^{35}Cl NQR frequencies and the σ_m and σ_0 reaction constants of the substituents in the aromatic ring was found.

The ^{35}Cl nuclear quadrupole resonance (NQR) spectra of chloro-1,2,4-triazoles have made it possible to establish their energically most favorable tautomeric forms [1]. 3(5)-Aryl-5(3)-chloro-1,2,4-triazoles with the general formula I evidently also have the same form, since their ^{35}Cl NQR spectra (Table 1) are found in the same frequency region as the previously studied 3(5)-substituted 5(3)-chloro-1,2,4-triazoles [1] and differ relatively little in frequency from the spectra of 3(5)-phenyl-5(3)-chloro-1,2,4-triazole ($\approx 36.80 \pm 0.4$ MHz). Only the ^{35}Cl NQR frequency of 3(5)-(p-nitrophenyl)-5(3)-chloro-1,2,4-triazole substantially exceeds this value (Table 1).



I X=H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *o*-Br, *o*-NO_2, *m*-NO_2, *p*-NO_2

The ^{35}Cl NQR frequencies of 3(5)-substituted 5(3)-chloro-1,2,4-triazoles correlate with the σ^* inductive constants of substituents X. The coefficient of transmission of the inductive effect of the substituents to the chlorine atom in this series of compounds is quite high ($\rho = 0.54$) [1]. One might therefore expect that varying the substituents in the aryl group would affect the electron distribution of the chlorine atom of 3(5)-aryl-5(3)-chloro-1,2,4-triazole. This is confirmed by correlation of their ^{35}Cl NQR frequencies with the σ_m and σ_0 reaction constants of substituents X [2] ($\nu^{77} = 36.773 + 0.500\sigma$, r = 0.94) (Fig. 1).

The points corresponding to 3(5)-aryl-5(3)-chloro-1,2,4-triazoles with substituents in the para position of the phenyl ring deviate from the correlation line. Compounds of this type possibly form their own linear correlation with a considerably larger transmission coefficient ρ. The high transmission of the electronic effect of para substituents in the phenyl ring to the chlorine atom of these compounds can be explained by the large value of the ^{35}Cl NQR frequency of 3(5)-(p-nitrophenyl)-5(3)-chloro-1,2,4-triazole. However, this assumption is based on the NQR spectra of only three compounds (I, IV, and VIII in Table 1) and requires further study.

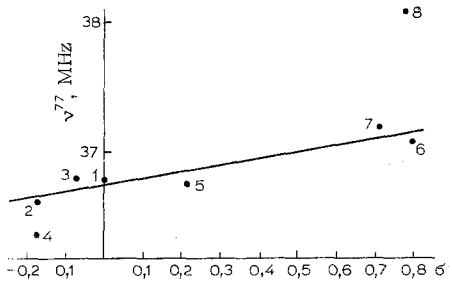


Fig. 1. Correlation between the ^{35}Cl NQR frequencies (ν^{77}) of 3(5)-aryl-5(3)-chloro-1,2,4-triazole and the σ constants of the substituents. The numbers of the points correspond to the numbering of the compounds in Table 1.

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TABLE 1. ^{35}Cl NQR Frequencies at 77°K (ν^{77}) of 3(5)-Aryl-5(3)-chloro-1,2,4-triazoles

Compound	X	ν^{77}, MHz	Signal/noise
1	H	36,800	2
2	o-CH_3	36,642	2
3	m-CH_3	36,805	5
4	p-CH_3	36,389	2
5	o-Br	36,786	5
6	o-NO_2	37,117	10
7	m-NO_2	37,207	10
8	p-NO_2	38,084	10

EXPERIMENTAL

The ^{35}Cl NQR spectra at 77°K were obtained with an NQR pulse spectrometer of the ISSh-1-12 type. The synthesis of the chloro-1,2,4-triazoles was previously described in [3].

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SYNTHESIS AND REACTIONS OF AZIDES OF HETEROCYCLIC COMPOUNDS

5.* SYNTHESIS AND INVESTIGATION OF 1,2,3-TRIAZOL-2-INES THAT CONTAIN BENZOTHIAZOLE RESIDUES

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The reaction of 2-methyl-5- and 2-methyl-6-azidobenzothiazoles with alkyl acrylates was used to synthesize 1,2,3-triazol-2-ines, which are cleaved in the presence of bases to give the corresponding diazopropanoic acid esters. Oxidation of the triazolines leads to the corresponding triazoles.

It is known that aromatic azides and benzyl azide add to α,β-unsaturated esters of carboxylic acids to give the corresponding 1,2,3-triazol-2-ines [2]. It seemed of interest to study the same reactions of benzothiazole azides.

For the investigation we selected 5-azido-2-methyl- (I) and 6-azido-2-methylbenzothiazoles (II), which were previously described in [3] and react with methyl and ethyl acrylates to give colorless crystalline 1-benzothiazolyl-1,2,3-triazol-2-ines (III-VI).

Vibrations at 2080-2200 cm^{-1} (N_3) are absent in the IR spectra of III-VI, while bands are present at 1230-1250 cm^{-1} ($-N-N=N-$) and 1740-1750 cm^{-1} (COOR). The PMR spectra of triazolines III-VI contain a quartet at ~5.25 ppm (4-H), a multiplet centered at ~4.0 ppm (5-H), and a singlet at 2.8 ppm (2'-CH_3).

*See [1] for Communication 4.

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