^{35}Cl NQR of 1,5,2-Diazaphosphorine Derivatives *

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NQR frequencies and asymmetry parameters (η) of ^{35}Cl chlorine-containing 1,5,2-diazaphosphorine derivatives are reported and discussed. NMDO calculations with total optimization of geometry have been carried out. The ν_{cal} and η_{cal} values, calculated by means of the Townes and Dailey theory, correlate well with the experimenal data.

Introduction

NQR spectroscopy has occupied its proper place in the chemistry of organophosphorus compounds. This technique has provided a rather efficient tool in both the structural determination of intermediates and reaction products (phosphorylation, for example) [1, 2], and investigations of the electron density distribution in chlorine-containing organophosphorus compounds [3, 4]. This seemed to be the main reason for the ^{35}Cl NQR frequencies of phosphorus compounds containing P–Cl bonds to be compiled [5]. In spite of the great number of chlorine-containing phosphorus compounds examined by ^{35}Cl NQR spectroscopy, the inaccessible 1,5,2-diazaphosphorine chloro derivatives remained poorly understood [1]. The interest in these compounds comes from their aromatic nature on the one hand, and their capability for dimerization leading to diazadiphosphetidines of trigonal bipyramidal structure on the other hand. Complexation of 1,5,2-diazaphosphorines with Lewis acids has not been studied either. All this inspired us to examine the NQR spectra of 1,5,2-diazaphosphorine chloro derivatives.

Results and Discussion

The ^{35}Cl NQR signals of 1,5,2-diazaphosphorine chlorine-containing derivatives can be assigned to chlorine atoms attached to the phosphorus atom (27–30 MHz) and to carbon atoms (35–40 MHz) (Tables 1, 2). The signals of the chlorine atoms in the $\geqslant PCl_2$ group of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorine (**I**) are split considerably ($\Delta\nu =$ 1.5 MHz). Normally, the $\geqslant PCl_2$ group in a six-membered ring shows a lower $\Delta\nu$ value than in the spectrum of **I** [5]. As follows from quantum-chemical calculations (MNDO with total geometry optimization), the two chlorine atoms are practically equivalent (Table 1, Scheme). They have nearly the same charges, bond lengths, and deviate from the ring plane at the same angle. Relying on these data, a singlet or poorly split signal should be expected to correspond to the chlorine atoms in the $\geqslant PCl_2$ group. The asymmetry parameters (η) of the electric field gradient (EFG) for these atoms are presented in Table 1. These η values are higher than those of the P–Cl bond in 5-cyano-4-trichloromethyl-2,2,6-trichloro-2,2-dihydro-1,3,2-diazaphosphorine (Table 1), and of the same order as in diazadiphosphetidines (10%) [6], but lower than the η parameters for the equatorial chlorines in phenyltetrachlorophosphorane (33.5%) [4]. The above features of NQR spectra are possibly caused by dimerization of **I** on crystallization.

2,2,3,4,6-Pentachloro-2,2-dihydro-1,5,2-diazaphosphorine (**II**) contains only one signal related to the P–Cl bond. In this case the EFG asymmetry parameter is lower than in **I**. If the two compounds existed

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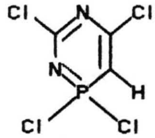
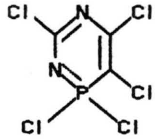
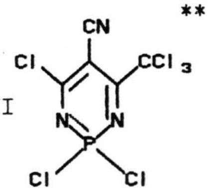
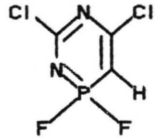
Table 1. The experimental and theoretical* ^{35}Cl NQR frequencies (ν, MHz) and asymmetry parameters of EFG (η, %) of chlorine-containing organophosphorus compounds.

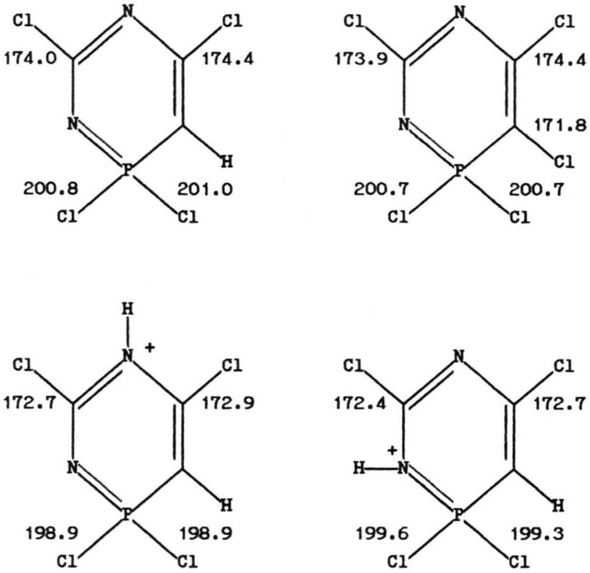
Compounds	ν^{77}_{exp}	η_{exp}	ν_{cal}	η_{cal}
I 	35.620	16.6±0.7	55.638	4.5
	35.964	19.2±1.5	52.830	5.2
	29.308	11.2±0.7	46.559	1.4
	27.788	11.5±1.4	46.558	1.4
II 	38.747	3.5±0.6	56.443	0.6
	36.110	18.7±1.0	56.085	4.7
	35.315	22.3±2.3	53.705	5.7
	29.087	8.6±1.3	47.754	1.1
III  **	41.059	1.3	53.514	0.2
	40.308	0.8	52.220	0.8
	39.643	4.5	52.153	0.8
	35.563	25.5	54.703	5.1
	29.098	1.7	47.902	1.0
	28.838	4.3	48.838	0.9
IV 	36.000			
	35.726			
	35.324			
	35.123			

* MNDO, ** Experimental data [3].

Table 2. The ^{35}Cl NQR frequencies at 77 K (ν^{77}) and signal/noise ratio (s/n) in the spectra of **I** H^+X^- complexes (**I** = 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorine).

X^-	C–Cl bond		P–Cl bond	
	ν^{77}, MHz	s/n	ν^{77}, MHz	s/n
Cl^-	38.012	24	29.500	16
	37.826	26		
$AlCl_4^-$	38.421	11	29.481	10
	37.903	13	29.125	9
$SnCl_6^-$	38.722	6	29.707	3
	37.832	7	29.616	4
$SbCl_6^-$	39.002	4	29.988	6
	37.984	7	29.442	4
PCl_6^-	38.450*	5	30.104	6
	37.809	7	29.834	3
	37.532	6	29.668	5
			29.469	7
			29.191	4

* Broad signal.



Scheme: MNDO calculated lengths of the C–Cl and P–Cl bonds (pm).

in the monomeric form, the spectrum of **II** would be expected to show a higher η value than in **I**, since the accumulation of electron-acceptor substituents leads to an increase in the EFG asymmetry parameters [7].

In **I** the chlorine atoms attached to carbon atoms give rise to two ^{35}Cl NQR signals. The high-frequency signal can be assigned to the chlorine atom in position 6. The same atom possesses a lower EFG asymmetry parameter as well. For molecule **II** two low-frequency signals of those corresponding to the C–Cl bond can analogously be assigned to the chlorine atoms in position 6 and 4. The high-frequency signal arises from the chlorine atom in position 3. The low ν value for this atom is quite surprising. The atom is likely to be displaced from the ring plane. Frequencies and asymmetry parameters of the C_{sp^2}–Cl and P–Cl bonds correlate with the calculated values (Table 1).

$$\nu_{exp} = -16.2 + 0.952\,\nu_{calc}, \quad r = 0.96, \quad s = 1.07 \quad n = 11,$$

$$\eta_{exp} = 2.82 + 3.55\,\eta_{calc}, \quad r = 0.93, \quad s = 2.9 \quad n = 11.$$

The substitution of the chlorine atoms attached to the phosphorus atom by fluorines does not affect very much the ^{35}Cl NQR frequencies of the C–Cl bond.

Molecule **I** does not form complexes either with $SnCl_4$ or with PCl_5. The spectra of homogenized 1:1 mixtures consist of signals characteristic of individual components. The interaction of **I** with HCl was established by ^{35}Cl NQR spectroscopy (Table 2). In the spectrum of the **I** · HCl adduct the NQR frequencies are noticeably higher for the atoms of P–Cl bonds and especially for those of C–Cl bonds.

In an inert solvent saturated with HCl the diazaphorsphorine **I** forms stable salts with Lewis acids ($AlCl_3$, $SnCl_4$, $SbCl_5$ and PCl_5). In this case the changes in frequencies are similar to those observed in the formation 2-chloropyridine salts with mineral acids [8]. The determination of the possible proton localization site is quite difficult. MNDO calculations show the 5-H cation to be by 8.9 kcal/mole more stable than the 1-H isomer. The formation of cations gives rise to the shortening of the C–Cl and P–Cl lengths (Scheme).

Experimental

The NQR frequencies and η values at ^{35}Cl nuclei were measured at 77 K with a pulsed NQR spectrometer of IS-3 type. The η values of polycrystalline substances were determined by use of the spectra of quadrupole spin echo envelopes modulated with a constant outer magnetic field, the intensity of which is about $5 \cdot 10^3$ A · m^{-1}. The modulation spectrum was obtained from an experimental interferogram by a routine program of fast Fourier transformation. The method used for determining the asymmetry parameters is described in more detail in [9].

2,2,4,6-Tetrachloro-2,2-dihydro-1,5,2-diazaphosphorine (**I**) was synthesized by the reaction of PCl_5 with N-acetylurea [1].

2,2,3,4,6-Pentachloro-2,2-dihydro-1,5,2-diazaphosphorine (**II**) was prepared by heating 1-(trichlorophosphoazo)-1,3,4-trichloro-2-aza-1,3-butadiene [2].

Calculation of ν_{cal} and η_{cal} was performed by the Townes and Dailey theory.

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