^{35}Cl NQR spectra, structure, and mutual influence of substituents in the series of chlorine-containing organic compounds of pentavalent phosphorus

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Regularities of transmission of the effect of equatorial and axial substituents were established for a number of chlorine-containing organic compounds of pentavalent phosphorus using ^{35}Cl NQR spectra. The field constants of ^{35}Cl NQR frequencies of the chlorine atoms participating in the P—Cl bond were estimated for a series of tetrahedral phosphorus ions. The ^{35}Cl NQR frequencies of chlorine atoms in tetracoordinated ions of pentavalent phosphorus and in analogous isoelectronic silicon compounds are related by a linear dependence.

Key words: ^{35}Cl NQR spectra, field constant of NQR frequency, chlorine-containing organic compounds of pentavalent phosphorus.

Peculiarities of the geometry of pentavalent phosphorus compounds have been studied for long.[1] It was reliably established that the molecules of these compounds have, as a rule, a trigonal-bipyramidal configuration with the P atom at the center and, if one of the substituents is eliminated as an anion or becomes a constituent of a complex anion, the remaining cation is transformed into a tetrahedron with the central P atom. However, peculiarities of redistribution of the electron density and local electric fields in the molecules of pentavalent phosphorus compounds and corresponding ions have not been studied in detail as yet.

Nuclear quadrupole resonance (NQR) spectroscopy of halogen atoms provides a unique possibility to trace systematic changes in the mutual influence of substituents in a series of similar molecular and ionic forms of halogen-containing organic compounds of pentavalent phosphorus. This work is dedicated to the study of the transmission of substituent effects through the molecular skeleton of organophosphorus compounds whose molecules contain a P—Cl bond; the conclusions drawn are based on the data on changes in the ^{35}Cl NQR frequencies.

The goals of this work were: (i) to reveal correlations between the spectral and structural characteristics of compounds under study; (ii) to find quantitative relationships of the transmission of substituent effects to axial and equatorial positions with respect to the nature, number, and positions of substituents in molecular forms of pentavalent phosphorus compounds; (iii) to compare the transmission of substituent effects in tetrahedral ions of pentavalent phosphorus and in tetrahedral molecules with a central Si atom; (iv) to compare the ^{35}Cl NQR frequency shifts of molecular and ionic forms of similar phosphorus compounds; and (v) to study transmission of the effect of substituents at the pentavalent phosphorus atom to the chlorine atom of the C—Cl bond in the side chain using ^{35}Cl NQR spectra.

Experimental

Measurements were carried out on an ISSh-2-13 NQR spectrometer-relaxometer (SKB IRE AN SSSR)[2] at 77 K. Most of the spectral data was taken from catalogs,[3—5] original papers, and books.[5—10] A number of spectra were refined and several of them are reported for the first time. Table 1 summarizes the ^{35}Cl NQR spectra of molecular forms of all chlorine-containing derivatives of pentavalent phosphorus compounds with organic and organoelement substituents known to date. The ^{35}Cl NQR spectra (at 77 K) of ionic forms of organic chlorine-containing compounds of pentavalent phosphorus and the types of anions are listed in Table 2. For comparison the spectra of silicon-containing analogs[3—5] are also listed in Table 2. The ^{35}Cl NQR spectra of Cl atoms in the C—Cl bond in the molecules of compounds $[(ClCH_2)_{4-n}PMe_n]^+Cl^-$ as well as in the molecular and ionic forms of p-$ClC_6H_4PCl_4$ are listed in Table 3. For convenience the ^{35}Cl NQR frequencies averaged over crystalline splittings ($\bar{\nu}$) are listed in separate columns (see Tables 1, 2, and 3).

Results and Discussion

Structure—spectrum correlations

The ^{35}Cl NQR spectrum of the molecular form of PCl_5 [3] (**1**) at 77 K consists of three lines (see Table 1),

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† Deceased.

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Table 1. ^{35}Cl NQR spectra of molecular forms of chlorine-containing compounds of pentavalent phosphorus with general formula R_nPCl_{5-n} (T = 77 K)

Compound	ν_{eq}/MHz		ν_{ax}/MHz		Δ^a/MHz
	ν_{eq}^{exp}	$\bar{\nu}_{eq}$	ν_{ax}^{exp}	$\bar{\nu}_{ax}$	
PCl_5 (**1**)[b]	33.751 33.751 33.751	33.75	29.274 29.242	29.26	4.49
$PhPCl_4$ (**2**)	33.744 33.588	33.67	25.510 24.608	25.06	8.61
Ph_2PCl_3 (**3**)	33.450	33.45	22.336 22.336	22.34	11.11
p-$ClC_6H_4PCl_4$ (**4**)	33.840 33.420	33.63	25.535 25.060	25.30	8.33
p-$MeC_6H_4PCl_4$ (**5**)	33.828 33.730 33.572 33.572	33.68	25.048 25.048 24.638 24.590	24.83	8.85
$PhCH=CHPCl_4$ (**6**)	33.297 33.233	33.26	25.998 24.543	25.27	7.99
$C_6F_5PCl_4$ (**7**)	34.480 34.380 34.290	34.38	25.300	25.30	9.08
Cl_3CPCl_4 (**8**)	32.040 32.040 32.040	32.04	28.260	28.26	3.78
$(Cl_3C)_2PCl_3$ (**9**)	29.495	29.50	—	—	—
F_3CPCl_4 (**10**)	31.10 31.10 31.10	31.10	28.80	28.80	2.30

[a] $\Delta = \nu_{eq} - \nu_{ax}$.

[b] Molecular form.

a high-frequency line and two low-frequency lines, the former being triply as intense as each of the latter. This makes it possible to unambiguously assign the spectral lines. The high-frequency line corresponds to the Cl atoms lying in the equatorial plane of the trigonal PCl_5 bipyramid. Since the molecule in the crystal is on axis *3* passing through the axial Cl atoms and the P atom, the low-frequency doublet corresponds to the axial Cl atoms (Fig. 1, spectrum *1*, see Table 1).

The ^{35}Cl NQR spectrum of compound $PhPCl_4$ (**2**), obtained by replacement of one Cl atom by the Ph group, consists of two equally intense doublets with strongly differing frequencies[7] and corresponds to the general position of the molecule in the crystal. One doublet, whose frequencies are close to that of the line assigned to equatorial atoms in the spectrum of PCl_5, corresponds to the remaining equatorial Cl atoms. The frequencies of the other doublet, corresponding to axial Cl atoms, are appreciably shifted towards low frequencies. The ^{35}Cl NQR spectra of compounds **4** and **6** are patterned analogously (see Table 1).

Further substitution of Cl atoms in the equatorial position by Ph groups results in the compound Ph_2PCl_3 (**3**) whose ^{35}Cl NQR spectrum[7] consists of two lines, a

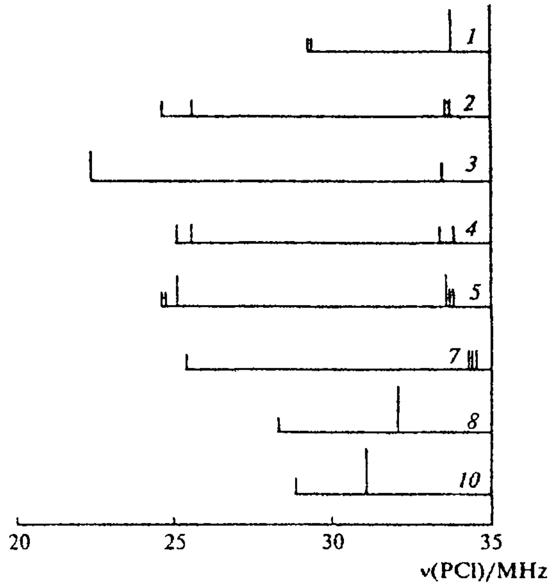

Fig. 1. Schematic view of the ^{35}Cl NQR spectra of molecular forms of pentavalent phosphorus compounds containing a P—Cl bond. The numbering of the spectra corresponds to that of the compounds in Table 1.

Table 2. ^{35}Cl NQR spectra of ionic forms $[R^1R^2R^3PCl]^+ \cdot M^-$ (**11a—29a**) and isoelectronic compounds-analogs $R^1R^2R^3SiCl$ (**11b—29b**) (T = 77 K)

Compared compounds	R^1	R^2	R^3	ν(SiCl)/MHz		ν(PCl)/MHz		M^-
				ν_{exp}	$\bar{\nu}$	ν_{exp}	$\bar{\nu}$	
11a,b	Cl	Cl	Cl	20.464 20.415 20.408 20.273	20.39	32.275	32.28	Cl^-
12a,b	F	Cl	Cl	19.753	19.75	31.89 31.89 31.26	31.68	F^-
13a,b	Me	Cl	Cl	19.155 19.020 18.955	19.04	31.25 31.25 30.95	31.15	Cl^-
14a,b	Me	Me	Cl	17.756	17.76	29.88	29.88	Cl^-
15a,b	Me	Me	Me	16.506	16.51	29.09	29.09	Cl^-
16a,b	Et	Cl	Cl	18.864 18.840 18.756	18.82	31.45 31.36 30.05	30.95	Cl^-
17a,b	Et	Et	Cl	17.651 17.543 17.407 17.324	17.48	29.978 29.636	29.81	Cl^-
18a,b	Pr^i	Pr^i	Cl	17.391 17.208	17.30	29.965 29.273	29.62	Cl^-
19a,b	Pr^i	Pr^i	Pr^i	16.15	16.15	28.666	28.67	Cl^-
20a,b	Bu^t	Cl	Cl	18.94 18.94 18.79	18.89	30.97	30.97	Cl^-
21a,b	Bu^t	Bu^t	Cl	17.04 16.94	16.99	29.364	29.36	Cl^-
22a,b	Ph	Cl	Cl	19.160 19.130 19.050	19.11	31.03	31.03	$[SbCl_6]^-$
23a,b	Ph	Ph	Cl	18.342 17.871	18.11	30.53 29.95	30.24	$[PCl_6]^-$
24a,b	Ph	Ph	Ph	17.67 17.49	17.58	30.01	30.01	$[SnCl_5]^-$[a]
25a,b	*p*-MeOC$_6$H$_4$	Cl	Cl	19.151 19.084 18.900	19.04	31.536 31.536 30.606	31.23	Cl^-
26a,b	*p*-MeC$_6$H$_4$	Cl	Cl	19.353 19.099 19.099	19.18	31.152 31.152 31.104	31.14	$[PCl_6]^-$
27a,b	*p*-ClC$_6$H$_4$	Cl	Cl	19.475 19.386 19.386	19.42	31.390 31.150 31.108	31.22	$[PCl_6]^-$
28a,b	Et	Ph	Ph	17.304	17.30	29.629	29.63	Cl^-
29a,b	Et$_2$N	Cl	Cl	—	—	31.082 30.889 (32.191)[b]	30.99	Cl^-

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[a] The ^{35}Cl NQR spectrum of the $[SnCl_5]^-$ anion at 77 K: ν_{eq} = 21.050, 20.805, and 20.677 MHz; and ν_{ax} = 18.380 and 18.055 MHz.

[b] This frequency was not used in the averaging over crystalline splittings (see Ref. 19).

low-frequency line corresponding to axial atoms and a high-frequency one corresponding to equatorial atoms, the former being twice as intense as the latter. It should be noted that the high-frequency line is only slightly shifted towards low frequencies, whereas the shift of the low-frequency line is appreciable. As in the preceding

Table 3. ^{35}Cl NQR spectra of compounds of pentavalent phosphorus containing C—Cl bond (T = 77 K)

Compound	ν(CCl)	$\bar{\nu}$(CCl)
	MHz	
p-$ClC_6H_4SiCl_3$ (**27b**)	34.993 34.830	34.91
p-$ClC_6H_4PCl_4$ (**4**)	35.238	35.24
$[p\text{-}ClC_6H_4PCl_3]^+ \cdot [PCl_6]^-$ (**27a**)	35.885	35.88
$[(ClCH_2)_4P]^+ \cdot Cl^-$ (**30**)	39.480 39.445 39.263 38.927	39.28
$[(ClCH_2)_3MeP]^+ \cdot Cl^-$ (**31**)	38.780 38.486 38.245	38.50
$[(ClCH_2)_2Me_2P]^+ \cdot Cl^-$ (**32**)	37.814 37.590 37.590 37.436	37.61
$(ClCH_2)_3PO$ (**33**)	37.271 37.230 37.067	37.19
Cl_3CPCl_4 (**8**)	39.689	39.69
$(Cl_3C)_2PCl_3$ (**9**)	39.749 39.609	39.70

case, the high-frequency and the low-frequency line correspond to the equatorial Cl atom and to two axial Cl atoms, respectively.

The spectrum of p-$MeC_6H_4PCl_4$ (**5**, see Table 1) consists of two multiplets with strongly differing frequencies and corresponds to two independent molecules with different crystallographic symmetry in the unit cell. Unfortunately, the ^{35}Cl NQR spectrum of the molecular form of Ph_3PCl_2 is unknown; this compound exists only as the ionic form $[Ph_3PCl]^+ \cdot Cl^-$.[6,7]

The other group of compounds (**7**, **8**, and **10**, see Table 1) contains electron-acceptor substituents with a key carbon atom.[3,4] Particularly illustrative is the ^{35}Cl NQR spectrum of $C_6F_5PCl_4$ (**7**). It consist of four equally intense lines, of which three lines form a triplet with frequencies close to those of the equatorial Cl atoms in PCl_5, whereas the fourth line is appreciably shifted toward low frequencies. Based on this spectral pattern, one can argue that the $C_6F_5PCl_4$ molecule is in the general position in the crystal and the C_6F_5 substituent is in the axial position. Spectra of compounds containing CCl_3 and CF_3 groups are similar to the preceding spectrum; the only exception is that, because of crystallographic symmetry, the high-frequency triplet is merged into a singlet line that is triply as intense as the low-frequency line. Therefore, the pattern of the ^{35}Cl NQR spectra indicates that electron-acceptor substituents are in the axial position.

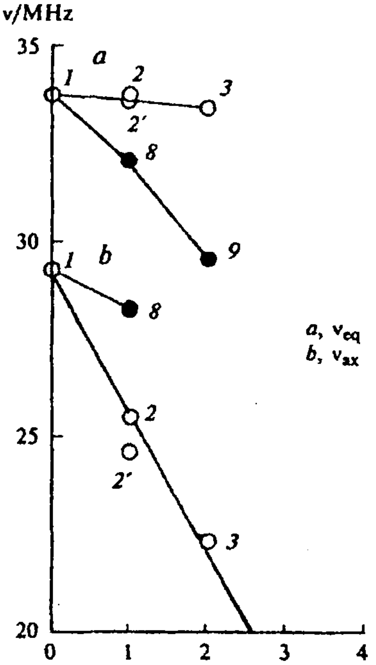

Fig. 2. Dependence of the ^{35}Cl NQR frequencies on the number of similar substituents in the Ph_nPCl_{5-n} (open circles) and $(Cl_3C)_nPCl_{5-n}$ (filled circles) series. The numbering of points corresponds to that of the compounds in Table 1; the points *2* and *2′* indicate crystalline splitting in the spectrum.

Determination of quantitative relationships of the transmission of substituent effects to axial and equatorial positions using ^{35}Cl NQR spectra of molecular forms of chlorine-containing organic compounds of pentavalent phosphorus

The dependence of changes in the ^{35}Cl NQR frequencies (ν) of chlorine atoms bonded to the pentavalent phosphorus atom on the number (n) of similar substituents is shown in Fig. 2. The ν(n) dependence for compounds Ph_nPCl_{5-n} is given for n from 0 to 2. At n = 3, only the ionic form of compounds, $[Ph_3PCl]^+ \cdot Cl^-$, exists; therefore, the corresponding frequency (30.12 MHz)[8] drops out of the series.

From Fig. 2 it can be seen that the substitution of Cl atoms in equatorial position causes almost linear changes in the NQR frequencies with change in n. The difference in the behavior of the ^{35}Cl NQR frequencies of axial and equatorial chlorine atoms is that the rate of decrease in the frequencies of axial Cl atoms (ν_{ax}) is by a factor of 25 higher than that of decrease in the frequencies of equatorial Cl atoms (ν_{eq}), though the substitution occurs in the equatorial plane. This is clearly seen in Fig. 3, in which the dependence of the ν_{eq} NQR frequencies on ν_{ax} upon successive introduction of aryl and more electron-acceptor substituents is shown. For aryl substituents (see compounds **1**—**5** in Table 1), this dependence is as follows:

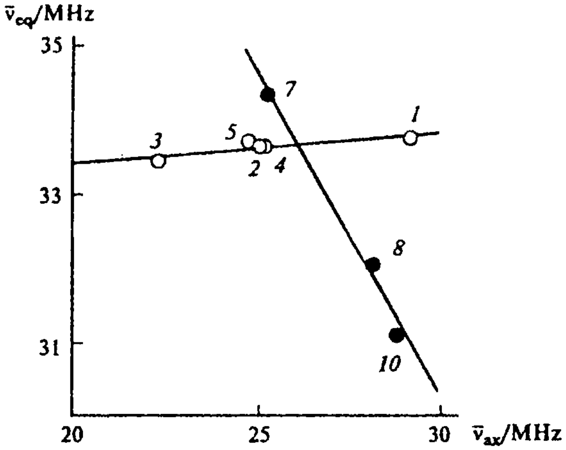

Fig. 3. Dependence of the ^{35}Cl NQR frequencies of equatorial Cl atoms on the frequencies of axial Cl atoms for aryl (open circles; see Eq. (1)) and electron-acceptor substituents (filled circles; see Eq. (2)). The numbering of points corresponds to that of the compounds in Table 1.

$$\bar{\nu}_{eq} = (32.628 + 0.0397\bar{\nu}_{ax})\pm0.04 \text{ MHz},\quad n = 5,\ r = 0.88; \qquad (1)$$

while for acceptor substituents (see compounds **7**, **8**, **10** in Table 1) it has the form:

$$\bar{\nu}_{eq} = (56.881 - 0.8878\ \bar{\nu}_{ax})\pm0.17 \text{ MHz},\quad n = 3,\ r = 0.99. \qquad (2)$$

From relationship (2) it follows that the $\bar{\nu}_{eq}$ NQR frequencies increase as the splitting ($\bar{\nu}_{eq} - \bar{\nu}_{ax} = \Delta$) (see Table 1) increases, whereas the rates of the decrease in the $\bar{\nu}_{ax}$ frequencies are close. Therefore, successive introduction of substituents of different nature results in qualitatively different consequences: electron-donor substituents occupy equatorial positions, whereas electron-acceptor substituents occupy axial positions, which strongly affects the change in the type of transmission of the substituent effects to equatorial and axial positions of molecular forms of pentavalent phosphorus compounds (see dependences (1) and (2)).

Comparison of transmission of substituent effects in tetrahedral ions of pentavalent phosphorus and in tetrahedral molecules with central silicon atom

Replacement of a Cl atom in the PCl_5 molecule by stronger electron-donor substituents than the aryl radical and its derivatives leads, as a rule, to elimination of one of the chlorine atoms as a negative ion.[9] In this case the Cl^- ion can either exist for itself or become a constituent of a complex anion of the type $[PCl_6]^-$, $[SnCl_5]^-$, *etc.* The cation geometry becomes tetrahedral and the ionized atom of pentavalent phosphorus becomes isoelectronic to the silicon atom. Comparison of the ^{35}Cl NQR frequencies of complex phosphorus cations and analogous silicon compounds makes it possible to make sense of the apparent "chaos" in the shifts of the frequencies of Cl atoms participating in the P—Cl bond[7–10] and establish the difference in the polarizabilities of chlorine atoms in the P—Cl and Si—Cl bonds. The dependence of the ^{35}Cl NQR frequencies in the $[R^1R^2R^3PCl]^+ \cdot M^-$ ionic forms (**11a—29a**) and in the $R^1R^2R^3SiCl$ compounds (**11b—29b**) (see Table 2) shown in Fig. 4 is described by the following equation:

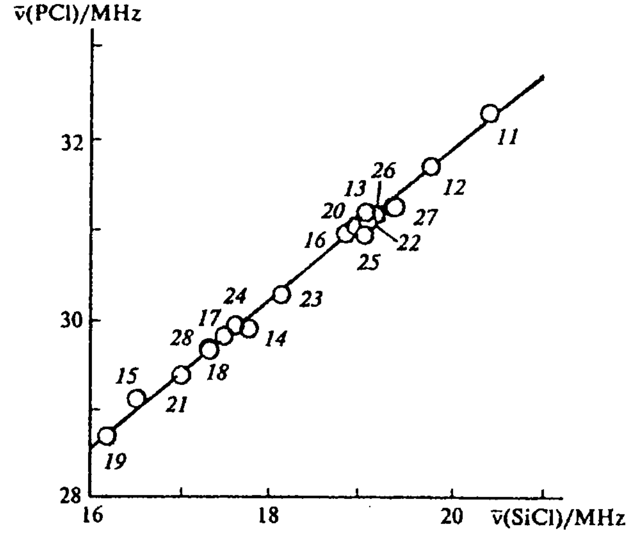

Fig. 4. Dependence of the ^{35}Cl NQR frequencies of ionic forms $[R^1R^2R^3PCl]^+ \cdot M^-$ on the frequencies of corresponding organosilicon analogs $R^1R^2R^3SiCl$ (see Eq. (3)). The numbering of points corresponds to that of the compounds in Table 2.

$$\bar{\nu}(\text{PCl}) = (15.529 + 0.8154\bar{\nu}(\text{SiCl}))\pm0.07 \text{ MHz},\quad n = 18,\ r = 0.996. \qquad (3)$$

Rather good statistical characteristics of dependence (3) indicate that the plot shown in Fig. 4 can be used to estimate the polarizabilities of the chlorine atom in the P—Cl and Si—Cl bonds.

As is known, the field constant of the NQR frequency $d\nu/dE_z$,[11] where E_z is the electric field strength at the resonance atom and z is the specified direction coinciding in our case with that of the axis of the element—Cl bond, can serve as a measure of the polarizability of an atom in the molecule.[11–13] Since the coefficient at ν(SiCl) in linear equation (3) is $d\nu(\text{PCl})/d\nu(\text{SiCl})$, it can be represented in the form $[d\nu(\text{PCl})/dE_z][d\nu(\text{SiCl})/dE_z]^{-1} = 0.8154$ (see Eq. (3)).

Taking into account the known[12] value $d\nu(\text{SiCl})/dE_z = 24.5\pm1.5$ Hz cm kV^{-1}, from here it follows that $d\nu(\text{PCl})/dE_z = 20\pm1.5$ Hz cm kV^{-1}, *i.e.*, the polarizability of the Cl atom in a $[R^1R^2R^3PCl]^+$ complex ion is about 20% lower than that of the Cl atom participating in the Si—Cl bond.

Previously,[12–15] it has been shown that, if the field constants of ^{35}Cl NQR frequencies are small, they are

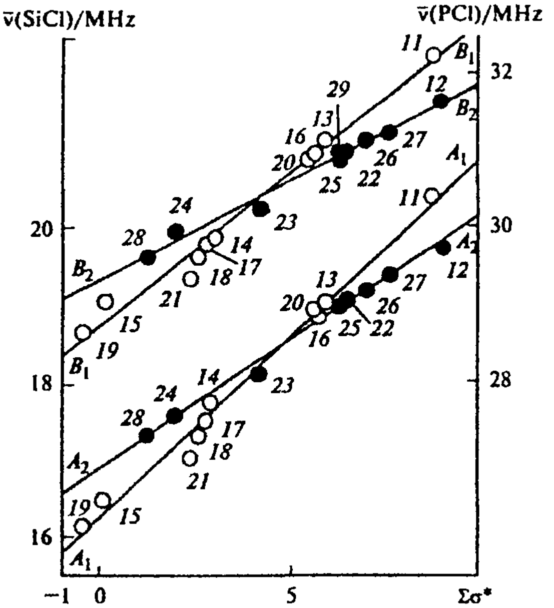

Fig. 5. Dependence of the ^{35}Cl NQR frequencies in tetrahedral ions of pentavalent phosphorus and in silicon-containing analogs on the Σσ* values of corresponding substituents: A_1, alkyl derivatives of silicon (Eq. (4)); A_2, aryl derivatives of silicon and its compounds containing substituents with the lone electron pair (Eq. (5)); B_1, alkyl derivatives of phosphorus (Eq. (6)); and B_2, aryl derivatives of phosphorus and its compounds containing substituents with the lone electron pair (Eq. (7)). The numbering of points corresponds to that of the compounds in Table 2; open circles correspond to A_1 and B_1 and filled circles correspond to A_2 and B_2.

highly characteristic of the state of the partner atom, *i.e.*, one can consider a $\mathrm{d}\nu(\mathrm{PCl})/\mathrm{d}E_z$ value of 20±1.5 Hz cm kV^{-1} to be characteristic of all Cl atoms which are constituents of complex cations of pentavalent phosphorus. Therefore, it is hoped that the search for correlation dependences between the ^{35}Cl NQR frequencies and the Σσ* sums, where σ* is the Taft parameter characterizing the inductive effect of the individual substituent, will be successful. Similar dependences for silicon compounds are well known.[12,14–18]

In fact, the dependences for each of the bonds (P—Cl, Si—Cl) fall into two subdependences (Fig. 5), *viz.*, one (A_1 and B_1) for alkyl-substituted compounds and the other (A_2 and B_2) for aryl derivatives and the substituents with the lone electron pair (F, Et_2N). The corresponding equations have the form:

$$A_1\colon \bar{\nu}(\mathrm{SiCl}) = (16.303 + 0.4586\ \Sigma\sigma^*)\pm 0.13\ \mathrm{MHz},\quad n = 10,\ r = 0.992; \tag{4}$$

$$A_2\colon \bar{\nu}(\mathrm{SiCl}) = (16.945 + 0.3238\ \Sigma\sigma^*)\pm 0.06\ \mathrm{MHz},\quad n = 8,\ r = 0.996; \tag{5}$$

$$B_1\colon \bar{\nu}(\mathrm{PCl}) = (28.803 + 0.3868\ \Sigma\sigma^*)\pm 0.1\ \mathrm{MHz},\quad n = 10,\ r = 0.989; \tag{6}$$

$$B_2\colon \bar{\nu}(\mathrm{PCl}) = (29.398 + 0.2495\ \Sigma\sigma^*)\pm 0.07\ \mathrm{MHz},\quad n = 9,\ r = 0.989. \tag{7}$$

Assuming that both ν and σ* depend on E_z, the coefficients at Σσ* in Eqs. (4)—(7) can be expressed as follows[15,18]:

$$\mathrm{d}\nu/\mathrm{d}\sigma^* = (\mathrm{d}\nu/\mathrm{d}E_z)\cdot(\mathrm{d}\sigma^*/\mathrm{d}E_z)^{-1}, \tag{8}$$

i.e., the ratio of the coefficients must be equal to the ratio of the field constants at $\mathrm{d}\sigma^*/\mathrm{d}E_z$ = const. Therefore, taking into account that $B_i/A_i \approx 0.807\pm0.04$, the field constant of the ^{35}Cl NQR frequency for the Cl atom in the P—Cl bond is 20.2±0.8 Hz cm kV^{-1}. This virtually coincides with the value 20±1.5 Hz cm kV^{-1} found above.

Relation between ^{35}Cl NQR frequencies of molecular and ionic forms of compounds

The search for the relation between ^{35}Cl NQR frequencies of molecular and ionic forms of corresponding compounds, *e.g.*, for aryl-substituted derivatives of pentavalent phosphorus (see Table 1 and 2), is of particular interest. The ν_{ax} and ν_{eq} frequencies of molecular forms of the compounds appeared to be related to the ^{35}Cl NQR frequencies of their ionic forms by a linear dependence. Comparison was performed for the series of compounds with general formula R_nPCl_{5-n} and $[R_nPCl_{4-n}]^+\cdot M^-$ at the same n and R:

$$\bar{\nu}_{eq} = (29.280 + 0.140\ \bar{\nu}_{ion})\pm 0.04\ \mathrm{MHz},\quad n = 5,\ r = 0.90; \tag{9}$$

$$\bar{\nu}_{ax} = (-80.754 + 3.403\ \bar{\nu}_{ion})\pm 0.23\ \mathrm{MHz},\quad n = 5,\ r = 0.99. \tag{10}$$

The plots of these dependences are shown in Fig. 6. The intersection point at which $\nu_{eq} = \nu_{ax}$ corresponds to a hypothetical substituent at which the equatorial and axial chlorine atoms become equivalent. Generally, Eqs. (9) and (10) make possible predicting the ^{35}Cl NQR spectra of molecular and ionic forms of Ar_nPCl_{5-n} compounds if the spectrum of one of them is known.

Spectra of ionic forms with the Cl$^-$ anion are unknown since the NQR frequencies of the Cl$^-$ ion lie in the region 2 to 3 MHz and the signals are difficult to detect because of instrumental problems. The ^{35}Cl NQR spectra of complex ions of the type $[E^VCl_6]^-$ have been reported; however, the prospects of their detailed interpretation remain unclear. At the same time the structure of the $[SnCl_5]^-$ anion can be unambiguously established from its ^{35}Cl NQR spectrum (see note "*a*" to Table 2), consisting of five lines grouped into a low-frequency doublet and a high-frequency triplet with strongly different frequencies. This spectral pattern indicates that the $[SnCl_5]^-$ anion occupies a general position in the crystal and has a trigonal-bipyramidal structure similar to that of the molecular form of PCl_5.

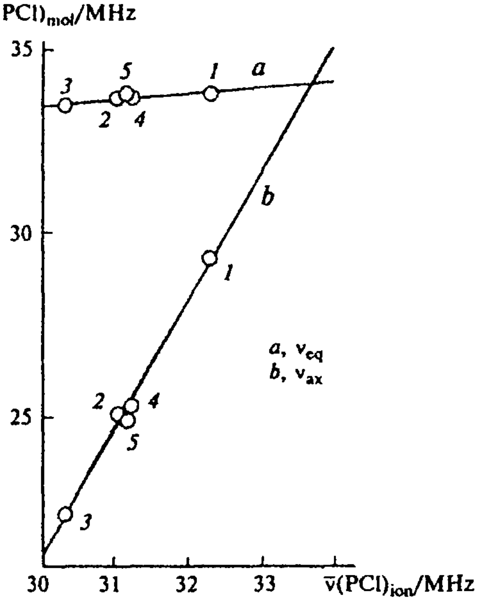

Fig. 6. Dependence of the ^{35}Cl NQR frequencies of molecular forms of compounds with general formula R_nPCl_{5-n} (R is aryl and aryl derivatives) on the frequencies of corresponding ionic forms $[R_nPCl_{4-n}]^+ \cdot M^-$ at the same *n* and R. The numbering of points corresponds to that of the compounds in Tables 1 and to their analogs (**11a**, **22a**, **23a**, **27a**, and **26a**) in Table 2.

Transmission of effects of the substituents at the pentavalent phosphorus atom to the chlorine atom of the C—Cl bond in the side chain

Using ^{35}Cl NQR data on changes in the NQR frequencies of chlorine atoms bonded to the carbon atoms in the side chain (see Table 3), it is also possible to characterize the effect of substitution in the compounds of pentavalent phosphorus. The ^{35}Cl NQR spectra of *para*-substituted derivatives of chlorobenzene p-ClC_6H_4X (**4**, **27a,b**) (X = $SiCl_3$, PCl_4, PCl_3^+) are shown in Table 3. The ^{35}Cl NQR frequency increases by 0.33 MHz on going from the $SiCl_3$ substituent to PCl_4, which indicates that the PCl_4 group has more pronounced electron-acceptor properties. The frequency shift increases by 0.64 MHz for the ionic form of the same compound. In contrast to the case of the equatorial orientation of substituents (see compounds **4**, **27a,b** in Table 3), the frequencies of substituents in the axial positions (see compounds **8** and **9** in Table 3) remain virtually unchanged upon introduction of the second CCl_3 group in the axial position, whereas the frequencies of equatorial atoms change appreciably (see compounds **8**, **9** in Table 1). Transmission of substituent effects in the Cl—C—P chain can be studied using ^{35}Cl NQR spectroscopy, taking compounds of the series $[(ClCH_2)_{4-m}Me_mP]^+ \cdot Cl^-$ as an example. Replacement of a chloromethyl group by methyl group leads to a linear dependence of the NQR frequencies of the rest of the chloromethyl groups on the number of methyl groups at the phosphorus atom (see compounds **30**—**32** in Table 3):

$$\bar{\nu} = (35.958 + 0.835m) \pm 0.02 \text{ MHz}, \quad n = 3,\ r = 0.999, \qquad (11)$$

i.e., the changes are additive.

* * *

Thus, the pattern of the ^{35}Cl NQR spectrum makes it possible to unambiguously assign the lines to the equatorial and axial Cl atoms in trigonal-bipyramidal R_nPCl_{5-n} molecules. The ^{35}Cl NQR frequencies of equatorial Cl atoms always are higher than those of axial atoms and, hence, the electron density on axial Cl atoms is higher than on equatorial ones. This, in turn, provides an explanation why electron-donor substituents occupy the equatorial positions in the molecule, whereas electron-acceptor substituents occupy the axial positions. The effect of aryl substituents introduced into a molecule (they primarily occupy equatorial positions) is transmitted to axial positions to a much greater extent than to the equatorial plane. Introduction of trichloromethyl groups, which first go to the axial positions, considerably changes the NQR frequencies of equatorial atoms, whereas those of the second trichloromethyl group in the axial position remain virtually unchanged. A linear dependence between the ^{35}Cl NQR frequencies in tetrahedral cations of pentavalent phosphorus and isoelectronic silicon compounds was found. This made it possible to estimate the field constant of the NQR frequency, $d\nu/dE_z$, for the Cl atom participating in the P—Cl bond, which appeared to be about 20% smaller than the known value of the field constant for the chlorine atom participating in the Si—Cl bond. Thus, it is believed that the polarizability of chlorine atom participating in the P—Cl bond is lower than that of the chlorine atom participating in the Si—Cl bond. Linear dependences between the ^{35}Cl NQR frequencies of Cl atoms in the P—Cl bond on the sum of the Taft constants were found for the same series of compounds. A linear dependence was found between the ^{35}Cl NQR frequencies in the molecular forms of aryl-containing compounds of pentavalent phosphorus and in those of their ionic forms. The slope of this dependence for axial Cl atoms is much steeper than for equatorial ones.

The sequence of shifts of the ^{35}Cl NQR frequencies for compounds p-ClC_6H_4X (X = $SiCl_3$, PCl_4, $[PCl_3]^+$) indicates that electron-acceptor properties of the substituents increase in the order $SiCl_3 < PCl_4 < PCl_3^+$. Changes in the ^{35}Cl NQR frequencies of Cl atoms of the chloromethyl groups in compounds $[(ClCH_2)_{4-m}(CH_3)_mP]^+Cl^-$ are pure additive.

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