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Features of the Molecular Structure of Compounds of $(Cl_3PNAr)_2$ Series (Ar = C_6H_4Z, Z = H, Cl) by Quantum-Chemical Calculations and the Data of ^{35}Cl Nuclear Quadrupole Resonance

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Abstract—A series of dimeric molecules $(Cl_3PNAr)_2$ where Ar = C_6H_4Z, Z = H or Cl in 2–4 positions, was calculated by the RHF/6-31G* method with the full geometry optimization. A specific nature of the intramolecular steric orientation of aryl groups was revealed, therewith in the case Ar = C_6H_4Cl-2 short nonvalent contacts were founf between the *ortho*-chlorine atom and PCl_3 group manifested in the peculiarity of geometric parameters and NQR spectroscopy data of this compound. The correlation of the ^{35}Cl NQR frequencies of P–Cl bonds with the values of the charges on the chlorine atoms obtained by quantum-chemical calculations of the molecules was analyzed.

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The dimeric compounds $(Cl_3PNAr)_2$ where Ar = C_6H_5 (**I**), $C_6H_4Cl^2$ (**II**), $C_6H_4Cl^3$ (**III**) and $C_6H_4Cl^4$ (**IV**) was studied previously by the method of nuclear quadrupole resonance (NQR) of ^{35}Cl nuclei [1, 2] that provided information on their structural and dynamic properties in the crystalline state. The existence of the thermally activated positional exchange of one axial and two equatorial chlorine atoms bound to the pentacoordinated phosphorus atom of the molecular fragment PCl_3 was discovered (the rearrangement of the trigonal twist type [3]), and the effect of this motion on the spin-lattice relaxation of the nuclei in *ortho*-position of the aryl radicals in the compounds **I–IV** was stated [1]. In [1] the presence of nonvalent interactions in the spatial structure of the molecules **I–IV** was noted, but the relevant geometric characteristics were not considered quantitatively. Of particular interest is the manifestation of nonvalent intramolecular contacts in the dimer **II** where the nuclear quadrupole spin-lattice relaxation of the ^{35}Cl nuclei of the atoms Cl^2 is modulated by the exchange motions of the P–Cl bonds [1, 2].

The purpose of this study was to establish by quantum-chemical calculations the structural parameters of molecules **I–IV** and the features of the spatial orientation of aryl moieties. The study was aimed also at the quantitative determination of nonvalent interatomic contact in the dimer **II** of the $C_6H_4Cl^2$ group with the dynamically active PCl_3 group, which affects the data of ^{35}Cl NQR spectroscopy of the atoms Cl^2 [1].

The quantum-chemical calculations were performed by the nonempirical RHF/6-31G* method using the program Gaussian 03W [4], with full geometry optimization of the molecules **I–IV**. The results of the calculations are listed in Tables 1 and 2, including the typical bond lengths and torsion angles of the molecules, while other geometrical parameters are not considered, since they are almost of standard values. Simultaneously, the charges of the chlorine atoms in the P–Cl bonds were obtained by the calculations for the subsequent correlation with the corresponding ^{35}Cl NQR frequencies (Table. 3). On the whole, the data of the nonempirical calculations showed the complete

Table 1. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecules of dimeric compounds $(Cl_3PNC_6H_4Z)_2$, Z = H, Cl^2, Cl^3, and Cl^4, calculated by RHF/6-31G* method[a]

Parameter	Z = H	Z = Cl^2	Z = Cl^3	Z = Cl^4
		Bond, *d*		
P–Cl_a	2.140	2.143	2.136	2.137
P–Cl_e^1	2.040	2.033	2.038	2.039
P–Cl_e^2	2.040	2.034	2.038	2.039
P–N_a	1.803	1.817	1.806	1.805
P–N_e	1.645	1.650	1.646	1.646
N–C^1	1.433	1.428	1.431	1.430
C^x–Cl^x	–	1.736	1.741	1.740
		Angle, ω		
PNP	100.8	101.4	101.0	101.0
NPN	79.2	78.6	79.0	79.0
Cl_aPN_a	174.3	173.2	174.1	174.2
Cl_aPN_e	95.1	94.6	95.1	95.1
$Cl_aPCl_e^1$	90.4	91.1	90.5	90.5
$Cl_aPCl_e^2$	90.4	90.0	90.5	90.5
$Cl_e^1PCl_e^2$	111.7	109.7	111.8	111.8
$Cl_e^1PN_a$	92.8	94.0	92.7	92.8
$Cl_e^2PN_a$	92.8	92.6	92.7	92.8
$Cl_e^1PN_e$	123.9	123.0	123.9	123.9
$Cl_e^2PN_e$	123.9	126.9	123.9	123.9
PN_aC^1	128.7	128.5	128.6	128.6
PN_eC^1	130.5	130.1	130.4	130.4
NC^1C^2	120.0	122.7	119.6	120.2
NC^1C^6	120.1	119.1	120.2	120.2
$C^2C^1C^6$	119.9	118.2	120.2	119.6
$C^1C^2X^2$	119.7	122.0	120.5	119.9
$C^1C^6X^6$	119.8	118.7	119.9	119.9

[a] The numbering of atoms is shown in Fig. 1.

identity of the two parts in the isolated dimeric molecules of each investigated compound **I–IV**. This identity is maintained in crystalline state, as follows from the ^{35}Cl NQR spectra: six chlorine atoms in the P–Cl bonds of the molecule give three resonance signals [1, 2]. Note that calculations of dimers **I–IV** using the methods B3LYP/6-31G* and MP2/6-31G* did not lead to significant difference in the molecular geometric parameters compared with those obtained by the RHF/6-31G* method.

As seen from Tables 1 and 2, all the molecules **I–IV** in the free state contain a flat four-member ring $(PN)_2$ with zero dihedral angles PNPN and NPNP, and virtually the same plane contains simultaneously the

Table 2. Principal torsional angles (τ, deg) in the molecules $(Cl_3PNC_6H_4Z)_2$, Z = H, Cl^2, Cl^3, and Cl^4, calculated by RHF/6-31G* method[a]

Angle τ	Z = H	Z = Cl^2	Z = Cl^3	Z = Cl^4
PNPN	0	0	0	0
NPNP	0	0	0	0
$NPNC^1$	180	180	180	180
Cl_aPN_eP	180	178	180	180
$Cl_aPN_eC^1$	0	2	0	0
$Cl_e^1PN_aP$	–124	–123	–124	–124
$Cl_e^2PN_aP$	124	127	124	124
$Cl_e^1PN_eP$	86	87	86	86
$Cl_e^2PN_eP$	–86	–85	–86	–86
$PN_eC^1C^2$	89	83	90	90
$PN_eC^1C^6$	–90	–97	–89	–90
$PN_aC^1C^2$	–90	–97	–90	–90
$PN_aC^1C^6$	90	83	90	90
$NC^1C^2X^2$	–1	–5	–1	–1
$NC^1C^6X^6$	1	3	1	1

[a] The numbering of atoms is shown in Fig. 1.

Table 3. Average ^{35}Cl NQR frequencies (ν_{av}, MHz) at 77 K of axial (Cl_a) and equatorial (Cl_e) chlorine atoms in the P–Cl groups of dimeric compounds $(Cl_3PNR)_2$ [2, 8] and atomic charges (*q*, au) of these atoms calculated by RHF/6-31G* method

R	Bond	ν_{av}	$-q$
CH_3	P–Cl_a	25.828	0.312
	P–Cl_e	30.188	0.133
CH_2CH_2Cl	P–Cl_a	26.312	0.302
	P–Cl_e	30.522	0.123
C_6H_5	P–Cl_a	26.364	0.294
	P–Cl_e	30.674	0.137
$C_6H_4Cl^2$	P–Cl_a	26.809	0.292
	P–Cl_e	30.989	0.119
$C_6H_4Cl^3$	P–Cl_a	26.926	0.286
	P–Cl_e	30.799	0.130
$C_6H_4Cl^4$	P–Cl_a	26.650	0.287
	P–Cl_e	30.519	0.132

atoms P and N, and the C^1 atoms and P–Cl_a bonds with a small deviation by 2° of the latter in **II** (schematic image of the molecules **I–IV** is shown in Fig. 1). The coordination of the bonds of atoms N and C^1 is also planar, as evidenced by the value of the sum of angles between the bonds of each of these atoms equal 360° (Fig. 1 and Table 1). The position of benzene rings of molecules **I**, **III**, and **IV** is perpendicular to the plane of the four-membered ring $(PN)_2$, which differs by 7°

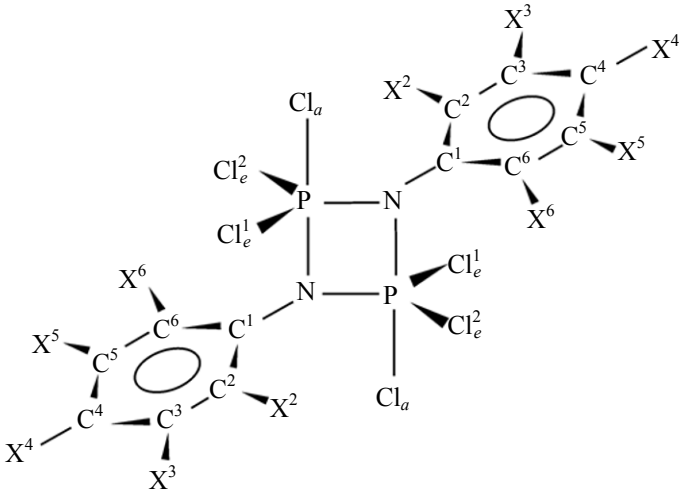

Fig. 1. A model of molecular structure $(Cl_3PNC_6H_4Z)_2$, Z = H, Cl-2, Cl-3, and Cl-4 with numbering of the atoms. Cl_a and Cl_e are axial and equatorial chlorine atoms, X^2–X^6 are the H and Cl atoms at the respective substitution in the benzene ring.

from the orientation of the plane of benzene ring in the molecule **II** containing a chlorine atom in the *ortho*-position (Table 2).

The latter situation is due to steric repulsion of *ortho*-chlorine atoms in the benzene ring by chlorine atoms in the bonds P–Cl (Fig. 1). Indeed, it follows from the calculations that, while the sum of van der Waals radii of two chlorine atoms is 3.5–3.6 Å [5, 6], in molecule **II** the nonvalent distances between the Cl^2 atom and the neighboring atoms Cl_a and Cl_e^1 are equal to 3.7 and 3.4 Å, respectively. Such close interatomic contacts result is a dynamic effect of the chlorine atoms P–Cl_a and P– Cl_e^1 involved in the exchange motion on the Cl^2 atom. This situation explains the observed in [1] modulation effects in the ^{35}Cl nuclear quadrupole spin-lattice relaxation of the nuclei located

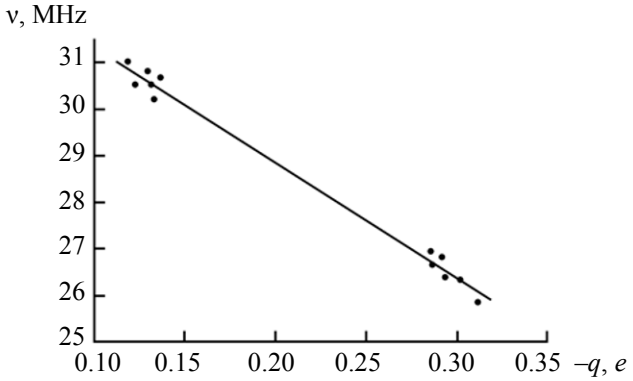

Fig. 2. Correlation between the ^{35}Cl NQR frequencies at 77 K (ν) and the values of negative charges (–*q*) on the chlorine atoms in the P–Cl groups of the dimeric compounds (Table 3). The straight line corresponds to Eq. (1).

in the *ortho*-positions. On the other hand, the static interaction of the atoms Cl^2 with the molecular frame leads to partial deformation of the molecule **II,** which can be seen at comparing its structure with that of dimers **I**, **III**, and **IV**. Thus, according to the data in Tables 1 and 2, molecule **II** differs slightly by its geometric structure from the other molecules of the series, whose structural parameters are almost identical.

At the same time, in the four studied dimers $(Cl_3PNC_6H_4Z)_2$, and in the previously studied molecules $(Cl_3PNCH_3)_2$ and $(Cl_3PNCH_2CH_2Cl)_2$ [2, 7, 8] a common to all these compounds consistency of the ^{35}Cl NQR frequencies of the chlorine atoms in the PCl_3 group was found with the charge distribution in these molecules calculated by the nonempirical RHF/6-31G* method (Table 3). The regular relationship between the ^{35}Cl NQR frequencies and the charges of axial and equatorial chlorine atoms is expressed in correlation shown in Fig. 2 and is described by Eq. (1) with the correlation coefficient $r = -0.995 \pm 0.003$ and standard deviation $s = 0.219$ MHz:

$$\nu(\text{MHz}) = 33.831 - 24.889(-q). \quad (1)$$

The relative standard deviation is less than 1%, which does not exceed the level of influence of crystallographic effects on the NQR frequency shift in the molecular solid state [9]. This situation is significant, since the atomic charges are determined for the molecules in the free state, while the NQR spectra are taken from crystalline compounds. Consequently, the value of standard deviation in the performed

correlation suggests that the correlation of the ^{35}Cl NQR frequencies with the charges on the chlorine atoms of PCl_3 fragment is due to the molecular structure of the dimers. This correspondence shows that the NQR spectroscopy is a high resolution method for the solid state [9]. On the other hand, the high degree of correlation ($|r| = 0.995$) of the data obtained for the investigated dimers by nonempirical calculations and experimentally observed NQR spectra confirms the adequacy of the quantum chemical method used in determining the geometrical parameters of molecules. In general, the integrated approach based on applying the methods of quantum chemistry and NQR spectroscopy demonstrates the possibility of a more complete analysis of the structural features of compounds.

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