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SPECIAL FEATURES OF THE GEOMETRY OF THE 2,2,2,4,4,4-HEXACHLORO-1,3-DIMETHYL-1,3-DIAZA-2,4-DIPHOSPHETANE MOLECULE AND ITS ELECTRON DISTRIBUTION ACCORDING TO DATA OF *ab initio* CALCULATIONS*

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The results of a nonempirical calculation of the 2,2,2,4,4,4-hexachloro-1,3-dimethyl-1,3-diaza-2,4-diphosphetane ($Cl_3PNCH_3)_2$ molecule by the RHF 6-31G(d) method are in agreement with the data of X-ray structural analysis of this compound. Calculated ^{35}Cl NQR frequencies for axial and equatorial chlorine atoms are close to the experimental values. The population of the orbitals of the lone electron pairs and the p_σ orbitals of the equatorial Cl atoms were significantly lower than those of the axial atoms. Among the MO there was no MO corresponding to a three-center bond involving a P atom and axial Cl and N atoms.

Keywords: 2,2,2,4,4,4-hexachloro-1,3-dimethyl-1,3-diaza-2,4-diphosphetane, nonempirical calculations, ^{35}Cl NQR parameters, molecular structure.

The special features of the structure of phosphoranes and the character of their electron distribution is of considerable interest in theoretical chemistry. Previously we studied such compounds by ^{35}Cl NQR (see for example [1]), X-ray emission spectroscopy [2], and quantum chemistry [3]. Of the phosphoranes only the PCl_5 molecule was studied by us quantum chemically. It was shown that the lone electron pairs of its equatorial Cl atoms, which orbital axes of symmetry are perpendicular to the equatorial plane of the molecule, participate in a multicenter bond with its axial fragment. The asymmetry of the electron distribution of the equatorial Cl atoms in PCl_5 is caused mainly not by these lone electron pairs but by other orbitals which axes of symmetry lie in the equatorial plane of the molecule [3]. To study further the special features of the geometry and electron distribution of compounds with a pentacoordinated phosphorus atom we have carried out a nonempirical quantum chemical calculation of the 2,2,2,4,4,4-hexachloro-1,3-dimethyl-1,3-diaza-2,4-phosphetane (**1**) molecule with complete optimization of its geometry with the restricted Hartree–Fock (RHF) method in a split-valence basis 6-31G(d) with the GAUSSIAN 94W program [4]. The choice of this molecule for investigation was determined by the special features of its structure, and also by the fact that there are X-ray structural data [5,6], and parameters of the ^{35}Cl NQR spectrum [7,8] for it in the literature, with which the calculated values may be compared.

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* This work is dedicated to dear Mikhail Grigorievich Voronkov, who revealed to me the way into science and accompanied me on this way. *V. P. Feshin*.

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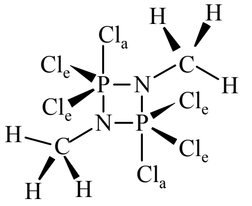

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The results of the optimization of the molecule of **1** by the RHF/6-31G(d) method are in agreement with the data of X-ray structural analysis (Table 1), which confirms the correctness of the calculation carried out. In the individual molecule, as in the crystal, the four-membered $(PN)_2$ ring is planar. According to the calculation the PNPN and NPNP dihedral angles in this molecule are equal to 0°. The coordination polyhedron of each of its phosphorus atoms has the structure of a slightly distorted trigonal bipyramid. The axial P–Cl and P–N bonds are longer than the corresponding equatorial ones. The bonds of the nitrogen atoms lie in the plane of the ring. The sum of the angles between these bonds is equal to 360.0° for each of them. In difference to the crystal all the equatorial chlorine atoms in the individual molecule are equivalent. Judging by the results of the calculation, the isolated molecule of **1** has C_{2h} symmetry, i.e. a second order axis of symmetry, and a plane of symmetry in which are located the P and N atoms of the four-membered ring, the P–Cl_a and the C–N bonds, and one of the C–H bonds of each of the NCH_3 groups. The negative charges on the equatorial Cl atoms (-0.133 e) are significantly lower than on the axial atoms (-0.312 e).

We have estimated the ^{35}Cl NQR frequencies and the asymmetry parameters of the electric field gradient (EFG) in place of the disposition of the Cl atom nucleus in the **1** molecule by a procedure proposed previously using the population of the 3*p*-components of the valence *p*-orbitals of the Cl atoms (Table 2) (see for example [9,10]). For the axial Cl atoms the calculated ^{35}Cl NQR frequency was 26.199 MHz, but the asymmetry parameter of the EFG for ^{35}Cl nuclei was 2.5%, and for the equatorial atoms 30.875 MHz and 20.7% respectively. The calculated NQR frequencies are close to those measured in crystalline compound **1** at 77 K, *viz*. 25.828, 30.015, and 30.360 MHz [7,8]. Regretably the asymmetry parameters of the EFG at the ^{35}Cl nuclei of this compound were not determined. However these values have been measured for other compounds with a pentacoordinated phosphorus atom. For example, the asymmetry parameter for the equatorial Cl atom of $(C_6H_5)_2PCl_3$ was 28.5±2.0%, and for the axial atoms 2.5±1.5% [1]. For other chlorine-containing compounds with a pentacoordinated phosphorus atom the asymmetry parameters of the axial Cl atoms were close to zero, but for the equatorial atoms they have a large value.

TABLE 1. Bond Lengths (d, Å) and Valence Angles (α, deg) in the **1** Molecule, Optimized by the RHF/6-31G(d) Method and X-ray Structural Analysis (XSA) Data [5,6]

Bond	RHF	XSA [5]	XSA [6]	Angle	RHF	XSA [5]	XSA [6]
P–Cl_a	2.144	2.152	2.133	NPN	79.6	81.7	80.5
P–Cl_e	2.044	2.022	2.029	PNP	100.4	98.3	99.5
		2.018	2.023	Cl_aPN_e	94.3	93.8	94.5
P–N_a	1.776	1.776	1.769	Cl_ePN_e	124.3	124.6	124.6
P–N_e	1.634	1.629	1.635			125.2	125.0
N–C	1.461	1.476	1.475	Cl_ePN_a	92.6	93.0	92.9
C–H	1.079	—	—			91.0	92.3
				CN_eP	132.2	134.6	134.6
				CN_aP	127.4	127.0	125.9
				Cl_aPCl_e	90.9	90.3	90.2
						90.4	90.7
				Cl_ePCl_e	111.0	109.8	110.0

TABLE 2. Populations (ΣNp) of the Valence p-Orbitals and Their $3p$- and $4p$-Components of the Axial (Cl_a) and Equatorial (Cl_e) Cl Atoms in the Molecule of **1**, Calculated by the RHF/6-31G(d) Method

Contribution	Cl_a			Cl_e		
	p_x, e	p_y, e	p_z, e	p_x, e	p_y, e	p_z, e
$3p$	1.293	1.288	1.009	1.285	1.330	0.978
$4p$	0.668	0.679	0.394	0.616	0.626	0.321
ΣNp	1.961	1.967	1.403	1.901	1.956	1.299

The satisfactory agreement between the experimental and calculated ^{35}Cl NQR parameters shows the correctness of the calculated electron distribution in the molecule of **1**. The significantly greater length of the axial P–Cl bonds compared with the equatorial, and also the larger negative charge on the axial Cl atoms than on the equatorial is in agreement with the significantly lower ^{35}Cl NQR frequency of the axial Cl atoms compared with the equatorial. Such a relationship of the NQR frequencies of the axial and equatorial Cl atoms in the molecule of **1** is caused by the lower average of the populations of the $3p$-components of the valence p_x- and p_y-orbitals of the axial Cl atoms (1.290 e) and the higher population of the $3p$-component of the p_z-orbital compared with the corresponding values for the equatorial atoms. At the same time the total populations of the p_x-, p_y-, and p_z-orbitals ($N3p + N4p$) of the axial Cl atoms are significantly greater than for the corresponding orbitals of the equatorial atoms (Table 2). The populations of the $3p$-components of the valence p_x- and p_y-orbitals of the axial Cl atoms are close to one another as are the total populations of these orbitals (Table 2). The population of the $3p$-component of the valence p_x-orbital of an equatorial Cl atom is close to the axial value, while that of the p_y-orbital is significantly greater. This also mainly causes the large value of the asymmetry parameter of the EFG at the nuclei of the equatorial Cl atoms.

The quantum chemical calculation for the molecule of **1** was carried out twice to estimate the ^{35}Cl NQR parameters. In one case the origin of coordinates was placed at the axial Cl atom and in the other case at an equatorial Cl atom. In both cases the Z axis coincided with the direction of the appropriate Cl–P bond.

In the system of coordinates with the origin at the nucleus of an equatorial Cl atom the Y axis is perpendicular to the plane in which the equatorial bonds of the phosphorus atom are found. The total population of the p_y-orbitals of the equatorial Cl atoms was significantly less than 2 e. The p_y-orbitals of the phosphorus atoms participating in the formation of the axial P–Cl and P–N bonds were also electron-deficient (0.711 e). The complete population of the p_x-orbitals of the equatorial Cl atoms was even less than that of their p_y-orbitals. The populations of these orbitals were less than those of the corresponding orbitals of the axial Cl atoms (Table 2). All these orbitals are contained in a series of MO, i.e. they participate in the formation of various multicenter bonds. Among them there was no MO corresponding only to a three-center bond involving the phosphorus atom and Cl and N atoms in the axial positions of a trigonal bipyramid.

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