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An ab initio Study of the Electronic and Steric Structure of Cl_2ZX Molecules (Z = P and As)

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Abstract — The electronic and steric structure of the Cl_2ZX molecules [Z = P and As, X = C_2H_5, $N(CH_3)_2$, and OCH_3] was examined by RHF/6-31G(d) and MP2/6-31G(d) calculations. The data on the electron distribution at the Cl atoms are compared with the published ^{35}Cl NQR data. The main reason for a decrease in the NQR frequency of the molecules with X = $N(CH_3)_2$ and OCH_3 as compared to the ethyl-substituted compounds is an increase in the population of the 3*p* components of their $p_z(p_\sigma)$ orbitals. With X = $N(CH_3)_2$, electron distribution at two Cl atoms differs significantly.
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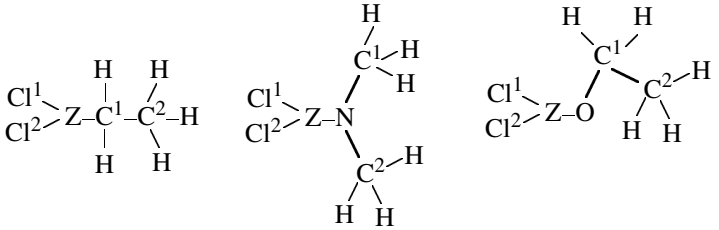
The electron density at the Cl atoms in the molecules of Cl_2PAlk series is slightly lower than in $ClP(Alk)_2$, as should be expected taking into account the electron-acceptor properties of these atoms. For example, the mean ^{35}Cl NQR frequency at 77 K of $Cl_2PC_2H_5$ (Table 1) is higher than that of $ClP(C_2H_5)_2$ (25.08 MHz [1]), and that of $Cl_2PC_4H_9$ (25.8 MHz [1]) is higher than that of $ClP(C_4H_9)_2$ (25.67 MHz [1]). However, in compounds of the $ClPX_2$ and Cl_2PX series, such electron-withdrawing substituents X as $N(Alk)_2$ and OAlk substantially increase the electron density at Cl as compared to X = Alk. In going from mono- to dichloro compound with such substituents, the electron density at the Cl atoms decreases substantially. For example, the ^{35}Cl NQR frequency of $ClP(NMe_2)_2$ (ν^{77} 18.508 MHz [1]) is much lower than the average frequency in the NQR spectrum of Cl_2PNMe_2 (Table 1), and that of $ClP(OMe)_2$ (ν_m^{154} 19.460 MHz [1]) is much lower than for Cl_2POMe (ν^{77} 23.670 MHz [1]). The same is true for the related arsenic compounds. For example, the ^{35}Cl NQR frequency at 77 K of $ClAs(C_2H_5)_2$ (ν^{77} 24.22 MHz [2]) is slightly lower than the mean NQR frequency for $Cl_2AsC_2H_5$ (Table 1). Electron-withdrawing substituents X = $N(Alk)_2$ and OAlk increase the electron density at Cl atoms in the molecules of $ClAsX_2$ and Cl_2AsX series. For example, the ^{35}Cl NQR frequency of $Cl_2AsOC_2H_5$ is noticeably lower compared to $Cl_2AsC_2H_5$ (Table 1). The mean ^{35}Cl NQR frequency of Cl_2AsNMe_2 given in [4] (ν_m^{77} 20.08 MHz) is also lower and even seems unrealistically low. Abnormally low NQR frequencies of the latter compounds were attributed to the p,σ conjugation of the lone pair of the N or O atom with the As–Cl bond [2, 4]. However, analysis of the experimental data and results of ab initio quantum-chemical calculations of the molecules of the $ClPX_2$ [5] and $ClAsX_2$ [6] series, as well as of numerous organic and other organoelement molecules, shows that the anomalous effect of heteroatoms M on the electron density in the geminal Z–Y bonds of nonlinear triatomic groups Y–Z–M and Y–Z=M is mainly due to the polarization of these bonds under the action of the charge on the M atom directly through field (see, e.g., [7, 8]).



Z = P (**I**), As (**II**) Z = P (**III**), As (**IV**) Z = P (**V**), As (**VI**)

To gain more insight into factors responsible for the trends observed in the electron density at Cl atoms and ^{35}Cl NQR frequencies of the compounds containing a Cl–Z–M group in going from one compound to another and to examine the electronic and steric structure of such molecules, we performed ab initio quantum-chemical calculations of molecules of the Cl_2ZX series with Z = P and As (**I**–**VI**) by the RHF/6-31G(d) and MP2/6-31G(d) methods with complete geometry optimization using GAUSSIAN 94W program [9]. To correctly estimate the population of valent *p* orbitals of Cl^1 and Cl^2 atoms and their components, each molecule was calculated twice, with the coordinate origin placed at the first and second Cl atoms. The Z axis is directed along the corresponding Cl–Z bond.

All the molecules studied have a pyramidal structure. The sum of the bond angles at the Z atom is considerably smaller than 360°, and at the As atom (~297°) it is noticeably smaller than at the P atom (~303°) (Tables 2, 3). As judged from the dihedral angles, RHF and MP2 calculations give essentially similar structure for the molecules of **I**–**VI**. In molecules of **III** and **IV**, the N atom is also pyramidal: in **III**, the sum of bond angles at N is 356.79° (RHF) or 351.68° (MP2); in **IV**, 350.44° (RHF) or 344.36° (MP2). In agreement with the smaller size of P compared to As, the corresponding bond lengths involving the P atom are shorter and its bond angles, larger compared to the As analogs. According to calculations, in each molecule of **I**, **II**, **V**, and **VI** the Cl^1–Z and Cl^2–Z bond lengths are equal (in Tables 2 and 3, only one value is given), as well as the Cl^1ZX and Cl^2ZX bond angles. Charges on both Cl atoms are also the same (Table 4). In the molecules of **III** and **IV**, these bond lengths, bond angles, and charges on Cl atoms (Table 4), as well as the populations of their valence *p* orbitals, differ noticeably (Table 5). The molecules of **III** and **IV** were also calculated by the RHF/6-31G(d) method in the transition states with the planar configuration of the N atom (sum of its bond angles 360°). This allowed us to estimate from calculation results the barriers to inversion of N atoms in the two latter molecules as the difference between the total energies of the molecule in the ground and transition states. For **III**, the barrier is 0.103 kcal mol^{-1}, and for **IV**, 0.672 kcal mol^{-1}.

Previously (see, e.g., [7, 10, 11]) we attained reasonable agreement between the experimental ^{35}Cl NQR frequencies of organic and organoelement compounds and the frequencies calculated with equation given below [12] and populations of 3*p* components of the valent Cl *p* orbitals found by RHF, B3LYP, and MP2 calculations in the split valence 6-31G(d) basis set. This agreement allows us to make a more comprehensive and reliable analysis of the experimental NQR data on the orbital level.

Table 1. Mean experimental (ν_{exp}) ^{35}Cl NQR frequency at 77 K of compounds **I**–**VI** and the frequencies (ν_{calc}) estimated from the results of RHF/6-31G(d) and MP2/6-31G(d) calculations

Molecule	ν_{exp}, MHz	ν_{calc}, MHz (RHF)	ν_{calc}, MHz (MP2)
I	25.842 [1]	25.820	25.803
II	24.482 [3]	25.398	25.418
III	23.896 [1]	25.432, 23.624	26.101, 23.378
IV	20.08 [4]	25.524, 22.942	25.834, 23.058
V	23.504 [1]	23.671	24.254
VI	23.02 [2]	23.712	24.205

$$\nu = e^2Q_{at}/2h[(N_x + N_y)/2 - N_z](1 + \eta^2/3)^{1/2},$$

where ν is the NQR frequency; e^2Qq_{at}, atomic quadrupole coupling constant obtained from calculation of the Cl_2 molecule by the corresponding method; *h*, Planck constant; η, parameter of asymmetry of the electric field gradient at the nucleus of the indicator atom; and N_x, N_y and N_z, populations of the valence p_x, p_y, and p_z orbitals of this atom, respectively.

By the same procedure we calculated the ^{35}Cl NQR frequencies of the molecules studied (Table 1). According to RHF and MP2 calculations, the populations of the corresponding valence *p* orbitals of both Cl atoms in the molecules of **I**, **II**, **V**, and **VI** and of the components of these orbitals are the same. Therefore, only one NQR frequency is given for them. In the molecules of **III** and **IV**, these values differ substantially for the Cl^1 and Cl^2 atoms (Table 5). Therefore, two NQR frequencies are given for them (Table 1). The calculated ^{35}Cl NQR frequencies, in particular, those obtained from RHF/6-31G(d) calculations, are close to the experimental values. Therefore, in the analysis of factors responsible for variations in the NQR frequency in going from one molecule to another, we primarily took into account results of calculations by this particular method. The experimental NQR frequencies of **IV** (ν^{77} 19.50, 20.270, and 20.463 MHz [4]) are much lower than those estimated from the results of the quantum-chemical calculations of this molecule (Table 1). The calculated ^{35}Cl NQR frequencies of **III**–**VI** are fairly close to each other. The experimental NQR frequencies of **III** and **V** are also close, whereas the NQR frequencies of **IV** given in [4] are much lower than those of **VI** (Table 1). Probably, the experimental ^{35}Cl NQR frequencies of **IV** were measured in [4] incorrectly.

Table 2. Bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the molecules of **I**–**VI**, according to RHF/6-31G(d) calculations

Molecule	Bond	*d*, Å	Bond deg	ω, deg	Torsion deg	τ, deg
I	Cl–P	2.068	$ClPC^1$	100.61	$Cl^1PC^1C^2$	52.13
	P–C^1	1.847	Cl^1PCl^2	101.72	$Cl^2PC^1C^2$	–52.08
	C^1–C^2	1.529	PC^1C^2	119.85		
II	Cl–As	2.192	$ClAsC^1$	98.80	$Cl^1AsC^1C^2$	50.41
	As–C^1	1.948	Cl^1AsCl^2	99.20	$Cl^2AsC^1C^2$	–50.41
	C^1–C^2	1.527	AsC^1C^2	118.91		
III	Cl^1–P	2.072	Cl^1PN	101.77	Cl^1PNC^1	53.55
	Cl^2–P	2.094	Cl^2PN	103.90	Cl^2PNC^1	–48.18
	P–N	1.655	Cl^1PCl^2	98.29	Cl^1PNC^2	–147.92
	N–C^1	1.455	PNC^1	125.50	Cl^2PNC^2	110.34
	N–C^2	1.459	PNC^2	117.09		
			C^1NC^2	114.20		
IV	Cl^1–As	2.188	Cl^1AsN	99.32	Cl^1AsNC^1	52.02
	Cl^2–As	2.216	Cl^2AsN	101.79	Cl^2AsNC^1	–47.63
	As–N	1.788	Cl^1AsCl^2	97.40	Cl^1AsNC^2	–164.12
	N–C^1	1.454	$AsNC^1$	122.98	Cl^2AsNC^2	96.23
	N–C^2	1.458	$AsNC^2$	114.23		
			C^1NC^2	113.23		
V	Cl–P	2.080	ClPO	102.12	Cl^1POC^1	51.12
	P–O	1.582	Cl^1PCl^2	99.24	Cl^2POC^1	–51.24
	O–C^1	1.435	POC^1	130.24	POC^1C^2	179.75
	C^1–C^2	1.513	OC^1C^2	107.69		
VI	Cl–As	2.198	ClAsO	100.62	Cl^1AsOC^1	49.90
	As–O	1.720	Cl^1AsCl^2	97.48	Cl^2AsOC^1	–49.88
	O–C^1	1.425	$AsOC^1$	128.49	$AsOC^1C^2$	179.97
	C^1–C^2	1.514	OC^1C^2	107.72		

Table 3. Bond lengths (*d*), bond angles (ω) and torsion angles (τ) in the molecules of **I**–**VI**, according to MP2/6-31G(d) calculations

Molecule	Bond	*d*, Å	Bond deg	ω, deg	Torsion deg	τ, deg
I	Cl–P	2.071	$ClPC^1$	99.62	$Cl^1PC^1C^2$	52.33
	P–C^1	1.844	Cl^1PCl^2	102.58	$Cl^2PC^1C^2$	–52.32
	C^1–C^2	1.526	PC^1C^2	118.98		
II	Cl–As	2.196	$ClAsC^1$	97.89	$Cl^1AsC^1C^2$	50.40
	As–C^1	1.953	Cl^1AsCl^2	99.49	$Cl^2AsC^1C^2$	–50.39
	C^1–C^2	1.524	AsC^1C^2	117.73		
III	Cl^1–P	2.070	Cl^1PN	100.34	Cl^1PNC^1	52.38
	Cl^2–P	2.113	Cl^2PN	104.78	Cl^2PNC^1	–49.52
	P–N	1.677	Cl^1PCl^2	98.64	Cl^1PNC^2	–162.00
	N–C^1	1.463	PNC^1	124.00	Cl^2PNC^2	96.51
	N–C^2	1.468	PNC^2	114.47		
			C^1NC^2	113.21		
IV	Cl^1–As	2.191	Cl^1AsN	98.64	Cl^1AsNC^1	50.80
	Cl^2–As	2.229	Cl^2AsN	102.05	Cl^2AsNC^1	–48.88
	As–N	1.815	Cl^1AsCl^2	97.54	Cl^1AsNC^2	–174.34
	N–C^1	1.463	$AsNC^1$	120.78	Cl^2AsNC^2	85.98
	N–C^2	1.470	$AsNC^2$	111.41		
			C^1NC^2	112.17		
V	Cl–P	2.086	ClPO	102.54	Cl^1POC^1	51.18
	P–O	1.618	Cl^1PCl^2	99.12	Cl^2POC^1	–51.28
	O–C^1	1.459	POC^1	125.65	POC^1C^2	179.80
	C^1–C^2	1.510	OC^1C^2	106.92		
VI	Cl–As	2.205	ClAsO	101.21	Cl^1AsOC^1	49.92
	As–O	1.759	Cl^1AsCl^2	97.27	Cl^2AsOC^1	–49.91
	O–C^1	1.452	$AsOC^1$	123.38	$AsOC^1C^2$	180.00
	C^1–C^2	1.511	OC^1C^2	106.72		

As noted above, the ^{35}Cl NQR frequencies of **III**–**VI** are abnormally low as compared to those of **I** and **II**. In these molecules, the electron-withdrawing substituents $N(CH_3)_2$ and OC_2H_5 increase the electron density on the Cl atoms. This could be expected, taking into account the noninductive effect of the M = N and O atom on the electron density of the indicator Y atom in the nonlinear triatomic groups Y–Z–M and Y–Z=M (see, e.g., [7, 8]). According to the data of RHF/6-31G(d) calculations, in going from **I** to **III** and **V**, the half-sum of the populations of the 3*p* components of the valence p_x and p_y orbitals of the Cl atoms slightly decreases, which results in a certain decrease in the NQR frequencies of the two latter molecules. However, the main reason for this decrease is a significant increase in the population of the 3*p* components of the Cl $p_z(p_\sigma)$ orbitals (Table 5). In going from **II** to **VI**, the decrease in the NQR frequency also results primarily from an increase in the population of $p_z(p_\sigma)$-orbital of the Cl atom. In the molecule of **IV**, the NQR frequency of the Cl^2 atom appreciably decreases, mainly for the same reason, whereas the NQR frequency of the Cl^1 atom even sligtly increases owing to a small increase in the half-sum of the populations of the 3*p* components of its p_x and p_y orbitals, with the populations of the $p_z(p_\sigma)$ orbitals remaining unchanged.

In **III** and **IV**, the Z–Cl^1 and Z–Cl^2 bonds are oriented differently relative to the N–C^1 and N–C^2 bonds (Tables 2, 3) and to the N atom, whose electron distribution is not spherically symmetrical. Therefore, the electron distribution at the Cl^1 and Cl^2 atoms (Tables 4, 5) and their NQR frequencies (Table 1) differ noticeably. This difference is probably due, first of all, to different orientation of the lone electron pair of the N atom relative to the Z–Cl^1 and Z–Cl^2 bonds. Similar influence of the orientation of the lone electron

Table 4. Charges (q) on atoms in molecules of **I**–**VI**, according to RHF/6-31G(d) and MP2/6-31G(d) calculations

Method	Molecule	q_{Cl^1}, e	q_{Cl^2}, e	q_Z, e	q_{C^1}, e	q_{C^2}, e	q_N, e	q_O, e
RHF	**I**	–0.278	–0.278	0.633	–0.583	–0.487	–	–
	II	–0.256	–0.256	0.518	–0.504	–0.486	–	–
	III	–0.289	–0.314	0.772	–0.289	–0.292	–0.721	–
	IV	–0.239	–0.288	0.702	–0.294	–0.300	–0.696	–
	V	–0.314	–0.314	0.905	–0.020	–0.496	–	–0.700
	VI	–0.259	–0.259	0.864	–0.005	–0.494	–	–0.749
MP2	**I**	–0.279	–0.279	0.637	–0.508	–0.488	–	–
	II	–0.258	–0.258	0.522	–0.499	–0.487	–	–
	III	–0.285	–0.324	0.788	–0.299	–0.303	–0.715	–
	IV	–0.238	–0.294	0.710	–0.303	–0.311	–0.685	–
	V	–0.310	–0.310	0.915	–0.025	–0.492	–	–0.717
	VI	–0.258	–0.258	0.860	–0.012	–0.491	–	–0.749

Table 5. Populations of the valence p orbitals of the Cl atoms (ΣNp) and of their $3p$ and $4p$ components in **I**–**VI**, according to RHF/6-31G(d) and MP2/6-31G(d) calculations

Molecule	Orbital	RHF			MP2		
		Np_x, e	Np_y, e	Np_z, e	Np_x, e	Np_y, e	Np_z, e
I	$3p$	1.292	1.283	1.010	1.293	1.282	1.010
	$4p$	0.671	0.669	0.373	0.671	0.669	0.375
	ΣNp	1.963	1.952	1.383	1.964	1.951	1.385
II	$3p$	1.285	1.274	1.007	1.285	1.273	1.006
	$4p$	0.672	0.670	0.386	0.672	0.671	0.387
	ΣNp	1.957	1.944	1.393	1.957	1.944	1.393
III, Cl^1	$3p$	1.287	1.287	1.014	1.290	1.289	1.009
	$4p$	0.673	0.672	0.378	0.671	0.670	0.377
	ΣNp	1.960	1.959	1.392	1.961	1.959	1.386
III, Cl^2	$3p$	1.280	1.279	1.026	1.277	1.278	1.026
	$4p$	0.680	0.678	0.394	0.683	0.681	0.404
	ΣNp	1.960	1.957	1.420	1.960	1.959	1.430
IV, Cl^1	$3p$	1.282	1.280	1.007	1.283	1.280	1.004
	$4p$	0.669	0.666	0.376	0.668	0.666	0.377
	ΣNp	1.951	1.946	1.383	1.951	1.946	1.381
IV, Cl^2	$3p$	1.273	1.269	1.024	1.271	1.269	1.022
	$4p$	0.680	0.678	0.403	0.682	0.679	0.408
	ΣNp	1.953	1.947	1.427	1.953	1.948	1.430
V	$3p$	1.279	1.283	1.027	1.280	1.285	1.022
	$4p$	0.679	0.675	0.391	0.677	0.675	0.391
	ΣNp	1.958	1.958	1.418	1.957	1.96	1.413
VI	$3p$	1.274	1.276	1.020	1.274	1.277	1.016
	$4p$	0.673	0.670	0.387	0.673	0.670	0.388
	ΣNp	1.947	1.946	1.407	1.947	1.947	1.404

pairs of the N and O atoms on the electron distribution at the Cl atoms was demonstrated by quantum-chemical calculations of the $ClCH_2NH_2$ [6] and $ClCH_2OCH_3$ [12] molecules at different rotation angles of amino group around C–N bond and methoxy group around H_2C–O bond, respectively. This influence is probably responsible for the doublet ^{35}Cl NQR spectrum of form **I** of compound **III** (23.135 and 24.450 MHz [1]).

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