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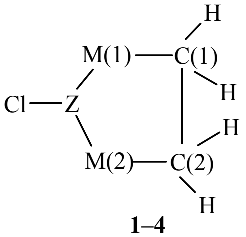
ELECTRONIC AND SPATIAL STRUCTURE OF FIVE-MEMBERED OXYGEN- OR SULFUR-CONTAINING CYCLIC PHOSPHORUS AND ARSENIC COMPOUNDS BASED ON QUANTUM-CHEMICAL CALCULATIONS

V. P. Feshin, E. V. Feshina, and L. I. Zhizhina

We have carried out nonempirical quantum-chemical calculations for five-membered heterocyclic molecules containing O or S atoms and also P or As atoms in the ring, using RHF/6-31G(d) and MP2/6-31G(d) methods with full optimization of their geometry. We have studied their electronic and spatial structure and the characteristics of the interaction between atoms in the molecules.

Keywords: five-membered oxygen- or sulfur-containing cyclic phosphorus and arsenic compounds, quantum chemical calculations, electronic and spatial structure.

For oxygen-containing compounds **1** and **2**, the ^{35}Cl NQR frequencies at 77 K are significantly lower than for the corresponding sulfur-containing analogs **3** and **4** (Table 1) [1, 2], which indicates higher electron densities on the Cl atoms in **1** and **2**. This is explained by the fact that the sulfur atom is leas capable of p_π–σ conjugation than the oxygen atom [2]. We hypothesize that such a ratio of the NQR frequencies and electron densities for these oxygen- and sulfur-containing compounds is because of polarization of the Z–Cl bonds due to the action of the charge on the S or O atom directly through the field, as in other compounds containing a nonlinear triatomic group Y–Z–M or Y–Z=M (see, for example, [3-6]). The negative charge on the oxygen atoms in molecules **1** and **2** should be significantly higher than on the sulfur atoms in molecules **3** and **4**, which also should lead to the observed ratio of electron densities on the Cl atoms and the NQR frequencies for these compounds.



1–4

1 Z = P, M(1) = M(2) = O; **2** Z = As, M(1) = M(2) = O; **3** Z = P, M(1) = M(2) = S;
4 Z = As, M(1) = M(2) = S

Institute of Technical Chemistry, Urals Branch of the Russian Academy of Sciences, Perm 614990; e-mail: cheminst@mpm.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 629-634 April, 2006. Original article submitted May 11, 2004.

TABLE 1. Experimental (ν_{exp}) ^{35}Cl NQR Frequencies of Compounds **1-4** at 77 K and Calculated (ν_{calc}) NQR Frequencies Using the RHF/6-31G(d) and MP2/6-31G(d) Methods

Compound	ν_{exp}, MHz	ν_{calc}, MHz (RHF)	ν_{calc}, MHz (MP2)
1	19.858 [1]	19.957	20.876
2	20.676 [2]	20.737	21.522
3	24.807 [1]	25.684	25.807
4	21.701 [2]	24.739	24.882

In order to study the electronic and spatial structure of the molecules of compounds **1-4** and the interaction of the atoms in them, we carried out nonempirical quantum-chemical calculations for these molecules by the RHF/6-31G(d) and MP2/6-31G(d) methods, with full optimization of their geometry, using the program GAUSSIAN 94W [7]. The origin of the coordinate system was selected to be at the location of the nucleus of the Cl atom. Its *z*-axis is directed along the Cl–Z bond.

The basic geometric parameters of the molecules of **1-4** were obtained as a result of optimization of their geometry by the RHF/6-31G(d) method (Table 2) and the MP2/6-31(d) method (Table 3). As we see, these parameters, obtained by methods of different levels, are insignificantly different, and likewise for the charges on the atoms (Table 4) and the populations of the valence *p*-orbitals of the Cl atoms and their components (Table 5). According to the results of optimization of the geometry for molecules **1-4**, they all have a similar structure.

The sum of the angles at the P atom is somewhat greater than for the As atom. At the P atom, in the molecules of compound **1** it is ~295° and in compound **3** it is ~302°, while for the As atom in compound **2** it is ~289° and in compound **4** it is ~293°. The P and As atoms have a pyramidal electronic structure. The dihedral atoms ClZM(1)C(1) in all the studied molecules are close in magnitude, and likewise for ClZM(2)C(2).

The angles ClZO(1)C(1) are optimal for polarization of the Cl–Z bonds under the action of the unshared electron pairs of the O(1) atom directly through the field, but not for p_π–σ conjugation. The latter is simply impossible for such a molecular geometry. The angles ClZO(2)C(2) are somewhat less favorable for such polarization (see, for example, [8]).

We may hypothesize that the patterns seen in the change in electron density on the Cl atom, the bond lengths Z–Cl, etc. as the orientation of the unshared electron pairs of the S atom changes relative to the Z–Cl bond in the Cl–Z–S group will be the same as in the case of the O atom in the Cl–Z–O group [8]. Therefore the above discussion for oxygen-containing molecules is also valid for the sulfur-containing analogs.

As expected, the negative charges on the O atoms in the molecules of compounds **1** and **2** are significantly higher than on the S atom in compound **3**. In the molecule of compound **4**, the S atom has a small positive charge (Table 4). In accordance with the non-inductive effect of the M atom on the Y atom in the groups Y–Z–M and Y–Z=M (see, for example, [3-6]), a significant negative charge on the O atom (M = O) leads to an increase in the electron density of the Cl atom (Y = Cl) and a decrease in electron density on the P atom (Z = P) in the molecule of compound **1** and the As atom (Z = As) in the molecule of compound **2** compared with the molecules of compounds **3** and **4** respectively (Table 4). The negative charge on the O atom in the molecule of compound **2** is somewhat higher than in the molecule of compound **1**.

In accordance with the indicated pattern, other conditions being equal, this should lead to a higher electron density on the Cl atom and a lower ^{35}Cl NQR frequency for the molecule of compound **2**. However, in fact the negative charge on the Cl atom in this molecule is somewhat lower than in the molecule of compound **1**, and its experimental and calculated ^{35}Cl NQR frequency is higher. This is due to the fact that polarization of the Y–Z bond in the Y–Z–M bond not only depends on the charge on the M atom but also is inversely proportional

TABLE 2. Bond Lengths (*d*), Bond Angles (α), and Torsion Angles (β) in Molecules of Compounds **1-4**, Calculated by the RHF/6-31G(d) Method

Compound	Bond	*d*, Å	Angle	α, deg	Angle	β, deg
1	Cl–P	2.107	Cl–P–O(1)	100.32	Cl–P–O(1)–C(1)	-75.44
	P–O(1)	1.612	Cl–P–O(2)	100.23	Cl–P–O(2)–C(2)	86.30
	P–O(2)	1.612	P–O(1)–C(1)	112.50	P–O(1)–C(1)–C(2)	-27.66
	O(1)–C(1)	1.421	P–O(2)–C(2)	114.46	P–O(2)–C(2)–C(1)	0.93
	O(2)–C(2)	1.422	O(1)–C(1)–C(2)	105.66	O(1)–C(1)–C(2)–O(2)	16.04
	C(1)–C(2)	1.539	O(2)–C(2)–C(1)	106.37		
2	Cl–As	2.219	Cl–As–O(1)	99.31	Cl–As–O(1)–C(1)	-75.56
	As–O(1)	1.744	Cl–As–O(2)	98.41	Cl–As–O(2)–C(2)	96.28
	As–O(2)	1.746	As–O(1)–C(1)	111.02	As–O(1)–C(1)–C(2)	-34.89
	O(1)–C(1)	1.416	As–O(2)–C(2)	113.36	As–O(2)–C(2)–C(1)	-15.52
	O(2)–C(2)	1.418	O(1)–C(1)–C(2)	106.54	O(1)–C(1)–C(2)–O(2)	31.54
	C(1)–C(2)	1.531	O(2)–C(2)–C(1)	107.65		
3	Cl–P	2.096	Cl–P–S(1)	102.52	Cl–P–S(1)–C(1)	-72.68
	P–S(1)	2.097	Cl–P–S(2)	102.72	Cl–P–S(2)–C(2)	93.08
	P–S(2)	2.111	P–S(1)–C(1)	96.86	P–S(1)–C(1)–C(2)	-50.40
	S(1)–C(1)	1.824	P–S(2)–C(2)	101.11	P–S(2)–C(2)–C(1)	-18.63
	S(2)–C(2)	1.837	S(1)–C(1)–C(2)	110.05	S(1)–C(1)–C(2)–S(2)	46.95
	C(1)–C(2)	1.522	S(2)–C(2)–C(1)	111.85		
4	Cl–As	2.219	Cl–As–S(1)	99.69	Cl–As–S(1)–C(1)	-71.05
	As–S(1)	2.209	Cl–As–S(2)	99.81	Cl–As–S(2)–C(2)	92.98
	As–S(2)	2.222	As–S(1)–C(1)	96.32	As–S(1)–C(1)–C(2)	-51.90
	S(1)–C(1)	1.826	As–S(2)–C(2)	100.50	As–S(2)–C(2)–C(1)	-23.34
	S(2)–C(2)	1.836	S(1)–C(1)–C(2)	110.80	S(1)–C(1)–C(2)–S(2)	52.51
	C(1)–C(2)	1.521	S(2)–C(2)–C(1)	112.63		

to the square of the distance between these charges and the electron cloud of the Y–Z bond (see, for example, [3, 9]). Since the volume of the As atom is greater than the volume of the P atom, this distance for the molecule of compound **2** is greater than for the molecule of compound **1**, which also leads to the observed ratio of the electron densities of the Cl atoms and the ^{35}Cl NQR frequencies for the molecules of compounds **1** and **2**. The ratio of the charges on the M and Cl atoms in the molecules of compounds **3** and **4** corresponds to the above-indicated pattern (Table 4).

Earlier (see, for example, [3, 10, 11]) we obtained satisfactory agreement between the experimental ^{35}Cl NQR frequencies and the frequencies calculated from Eq. (1) [12]

$$\nu = (e^2Qq_{\text{ат}}/2h)[-N_z + (N_x + N_y)/2](1 + \eta^2/3)^{1/2} \qquad (1)$$

with populations (N) of the 3*p*-components of the valence *p*-orbitals of the Cl atoms, found in the nonempirical quantum-chemical calculations for organic and heteroorganic molecules by different methods. This agreement allows us to interpret the experimental ^{35}Cl NQR spectra in greater depth.

We analogously calculated the ^{35}Cl NQR frequencies for the studied molecules of compounds **1-4** (Table 1). The values of the frequencies calculated for the molecules of compounds **1** and **2** (especially using the RHF/6-31G(d)) method) practically agree with the experimental values. The calculated and experimental

TABLE 3. Bond Lengths (*d*), Bond Angles (α), and Torsion Angles (β) in Molecules of Compounds **1-4**, Calculated by the MP2/6-31G(d) Method

Compound	Bond	*d*, Å	Angle	α, deg	Angle	β, deg
1	Cl–P	2.107	Cl–P–O(1)	100.89	Cl–P–O(1)–C(1)	-72.74
	P–O(1)	1.649	Cl–P–O(2)	100.55	Cl–P–O(2)–C(2)	91.98
	P–O(2)	1.649	P–O(1)–C(1)	108.97	P–O(1)–C(1)–C(2)	-37.94
	O(1)–C(1)	1.450	P–O(2)–C(2)	112.35	P–O(2)–C(2)–C(1)	-10.65
	O(2)–C(2)	1.451	O(1)–C(1)–C(2)	105.01	O(1)–C(1)–C(2)–O(2)	29.86
	C(1)–C(2)	1.539	O(2)–C(2)–C(1)	106.34		
2	Cl–As	2.225	Cl–As–O(1)	100.00	Cl–As–O(1)–C(1)	-73.22
	As–O(1)	1.784	Cl–As–O(2)	98.36	Cl–As–O(2)–C(2)	98.35
	As–O(2)	1.787	As–O(1)–C(1)	107.57	As–O(1)–C(1)–C(2)	-41.09
	O(1)–C(1)	1.447	As–O(2)–C(2)	110.57	As–O(2)–C(2)–C(1)	-20.89
	O(2)–C(2)	1.448	O(1)–C(1)–C(2)	106.32	O(1)–C(1)–C(2)–O(2)	39.91
	C(1)–C(2)	1.523	O(2)–C(2)–C(1)	107.87		
3	Cl–P	2.104	Cl–P–S(1)	102.52	Cl–P–S(1)–C(1)	-71.53
	P–S(1)	2.097	Cl–P–S(2)	102.83	Cl–P–S(2)–C(2)	92.97
	P–S(2)	2.113	P–S(1)–C(1)	95.66	P–S(1)–C(1)–C(2)	-53.05
	S(1)–C(1)	1.822	P–S(2)–C(2)	100.49	P–S(2)–C(2)–C(1)	-20.13
	S(2)–C(2)	1.834	S(1)–C(1)–C(2)	109.49	S(1)–C(1)–C(2)–S(2)	50.03
	C(1)–C(2)	1.518	S(2)–C(2)–C(1)	111.28		
4	Cl–As	2.227	Cl–As–S(1)	99.50	Cl–As–S(1)–C(1)	-69.84
	As–S(1)	2.216	Cl–As–S(2)	99.44	Cl–As–S(2)–C(2)	93.16
	As–S(2)	2.230	As–S(1)–C(1)	94.99	As–S(1)–C(1)–C(2)	-54.31
	S(1)–C(1)	1.825	As–S(2)–C(2)	99.50	As–S(2)–C(2)–C(1)	-25.39
	S(2)–C(2)	1.834	S(1)–C(1)–C(2)	110.16	S(1)–C(1)–C(2)–S(2)	56.15
	C(1)–C(2)	1.517	S(2)–C(2)–C(1)	112.29		

TABLE 4. Charges (*q*) on Cl, C, Z (P, As) and M (O, S) Atoms in Molecules of Compounds **1-4**, Calculated by the RHF/6-31G(d) and MP2/6-31G(d) Methods

Method	Compound	*q*, e					
		Cl	Z	M(1)	M(2)	C(1)	C(2)
RHF	**1**	-0.386	1.081	-0.704	-0.713	-0.058	-0.026
	2	-0.320	1.097	-0.738	-0.751	-0.045	-0.004
	3	-0.284	0.382	-0.015	-0.033	-0.507	-0.470
	4	-0.274	0.265	0.037	0.026	0.498	-0.474
MP2	**1**	-0.373	1.102	-0.719	-0.736	-0.073	-0.015
	2	-0.314	1.094	-0.740	-0.755	-0.055	-0.002
	3	-0.288	0.383	-0.010	-0.028	-0.510	-0.496
	4	-0.278	0.268	0.039	0.029	-0.500	-0.473

NQR frequencies for the molecule of compound **2** are only slightly higher than for compound **1**. The calculated NQR frequency for the molecule of compound **3** is somewhat higher while the frequency for the molecule of compound **4** is significantly higher than the experimental value.

TABLE 5. Populations of Valence *p*-Orbitals of Cl Atoms (ΣNp), Their 3*p*- and 4*p*-Components in Molecules of Compounds 1-4, Estimated By the RHF/6-31G(d) and MP2/6-31G(d) Methods

Compound	Orbital	Np_x, e	Np_y, e	Np_z, e	Np_x, e	Np_y, e	Np_z, e
		RHF			MP2		
1	3*p*	1.270	1.269	1.055	1.273	1.271	1.048
	4*p*	0.692	0.692	0.427	0.689	0.688	0.424
	ΣNp	1.962	1.961	1.482	1.962	1.959	1.472
2	3*p*	1.264	1.268	1.043	1.269	1.265	1.036
	4*p*	0.685	0.689	0.418	0.682	0.683	0.418
	ΣNp	1.949	1.957	1.461	1.951	1.948	1.454
3	3*p*	1.281	1.287	1.008	1.281	1.286	1.006
	4*p*	0.680	0.677	0.382	0.681	0.678	0.387
	ΣNp	1.961	1.964	1.390	1.962	1.964	1.393
4	3*p*	1.273	1.278	1.010	1.272	1.278	1.008
	4*p*	0.681	0.678	0.396	0.681	0.679	0.400
	ΣNp	1.954	1.954	1.406	1.953	1.957	1.408

The calculated ^{35}Cl NQR frequencies for the last two molecules are insignificantly different. The experimental NQR frequencies for these compounds should also be insignificantly different. However, in the literature [2], an experimental ^{35}Cl NQR frequency is given for compound **4** that is significantly lower than for **3** (Table 1). Most likely the ^{35}Cl NQR frequency for compound **4** is given incorrectly in [2].

The satisfactory agreement between the experimental ^{35}Cl NQR frequencies for organic and heteroorganic compounds and the values calculated from the populations of the 3*p*-components of the valence *p*-orbitals of the Cl atoms, including for compounds **1-3**, allows us to analyze the reasons for the changes in the NQR frequencies for compounds **1-4** as we go from one to the other. The increase in the NQR frequency as we go from oxygen-containing and sulfur-containing molecules is due to some extent to the slight increase in the half-sum of the populations of the 3*p*-components of the valence p_x- and p_y-orbitals of the Cl atoms. The major contribution to this increase comes from the significant decrease, as we go from oxygen-containing to sulfur-containing molecules, in the populations of the 3*p*-components of the valence $p_z(p_\sigma)$-orbitals of these atoms (Table 5, Eq. (1)), which is quite consistent with the explanation of the ratio of the ^{35}Cl NQR frequencies for these compounds by polarization of the Z–Cl bonds under the action of the charge on the M atom directly through the field.

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