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Gas-Phase Molecular Structure of 2-Halo-1,3-dihetero-2-phospholanes

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Abstract — The molecular structure of 2-chloro-1,3-dithia-2-phospholane was determined using gas-phase electron diffraction and *ab initio* calculations. The heteroring in the molecule has an asymmetric structure like a symmetric P-*envelope* twisted about the C–C bond with an axial P–Cl bond. Geometric parameters of the molecule and mean vibration amplitudes were determined. The molecular structure of 2-chloro-1,3-oxathia-2-phospholane was predicted. The molecule in the gas phase has two conformers [twisted C(O)- and C(S)-*envelope*] with an axial P–Cl bond.

2-Chloro-1,3-dioxa- and 1,3-dithia-2-phospholanes were the first studied 1,3-dihetero-2-phospholanes. It was found that their heteroring has the shape of a symmetric P-*envelope* with an axial P–Cl bond [1, 2]. In the both cases structural analysis was performed on the basis of intensity curves alone, and no independent methods were invoked. Later the molecular structure of 2-chloro-1,3-dioxa-2-phospholane was reinvestigated by spectral methods to find that the experiment is better fitted by an asymmetric model of the molecule [3].

Later the results of spectral studies [4] and molecular mechanics calculations [5] of 2-chloro-1,3-dithia-2-phospholane were published, from which it followed that the heteroring is not symmetric. This prompted us to reinvestigate the structure of 2-chloro-1,3-dithia-2-phospholane and to consider in general the structures of 1,3-diheterophospholanes.

In the present work we used the intensity curves recorded in [2] at nozzle-to-plate distances of 50 and 19 cm. Density measurements of diffraction patterns were performed anew using up-to-date equipment. Preliminary we performed *ab initio* calculations for different models of the heteroring (C_1, C_s, and C_2 symmetry) at the HF/6-31G*, MP2/6-31G*, and B3PW91/6-31G* levels [6]. Vibration amplitudes and perpendicular amplitude corrections were calculated from the HF/6-31G* theoretical force field by the Hedberg–Mills program. Structural parameters were refined by the least-squares method on the basis of experimental intensity curves (Fig. 1) in the terms of r_α structure; refined values were transformed to r_a parameters. Theoretical intensity curves were calculated with tabulated scattering factors [7].

Structural analysis. As follows from the *ab initio* calculations, the only stable conformation with the relative energy $E = 0$ is an asymmetric form (C_1) with axial location of the P–Cl bond (Fig. 2). Less stable conformations have the heterorings of C_s (ΔE = 2.53 kcal/mol) and C_2 (ΔE = 2.74 kcal/mol) symmetry. The results the *ab initio* calculations we used in structural analysis. For the independent geometric parameters we used $P^2–S^3$, $S^3–C^4$, $C^4–C^5$, $C^5–S^1$, and C–H bond lengths, PS^3C^4, $S^3C^4C^5$, and SCH bond angles, and $PS^3C^4C^5$, $S^3C^4C^5S^1$, and PSCH torsion angles. As seen from the *ab initio* results, the P–S and

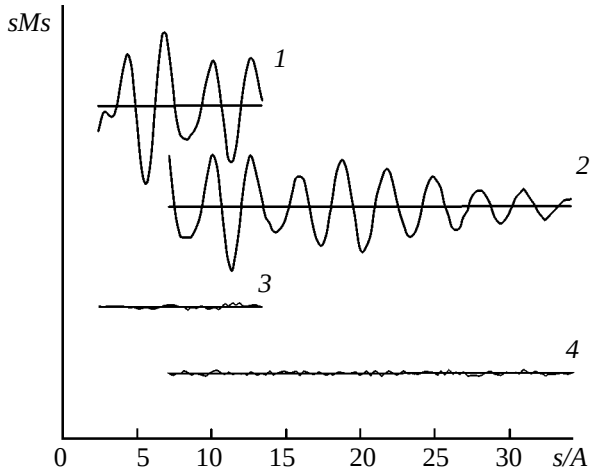

Fig. 1. (*1*, *2*) Experimental $sM(s)$ curves and (*3*, *4*) $\Delta sM(s)$ curves.

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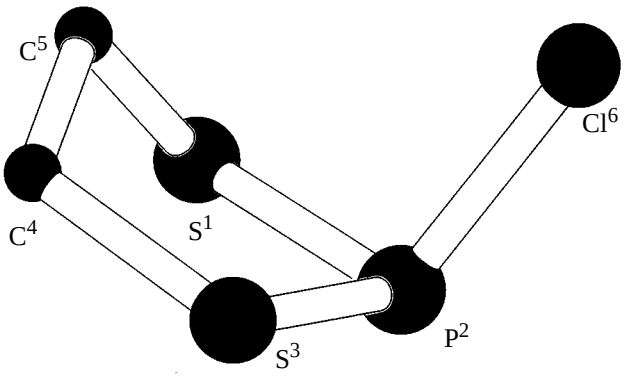

Fig. 2. Conformation of 2-chloro-1,3-dithia-2-phospholane.

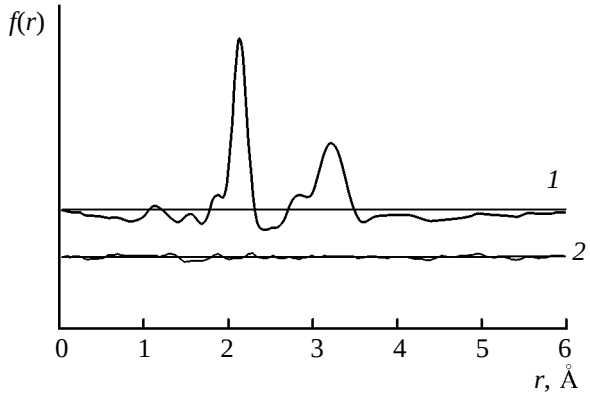

Fig. 3. (*1*) Radial distribution curve and (*2*) $2\Delta[f(r)_{exp} - kf(r)_{calc}]$ curve for 2-chloro-1,3-dithia-2-phospholane.

P–Cl bond lengths are nearly equal, and their independent refinement may cause large uncertainties because of a strong (near 100%) correlation. Therefore, in the structural analysis we used the difference d(PCl) = r(P–Cl) – $r(P^2–S^3)$, whose value was taken from the *ab initio* calculations. The same can be said about the C–S bond lengths. Their difference, according to the calculations, is 0.013 A. The latter was used in the structural analysis.

On the radial distribution curve $f(r)$ (Fig. 3) calculated with a "normal" artificial temperature factor (b 0.0025) we firmly identified peaks at r 1.12, 1.50, 1.83 (shoulder), 2.10 and 3.15 Å, which were unambiguously assigned to the C–H, C–C, C–S, P–S, P–Cl distances and the doublet S···S and S···Cl, respectively. On the "sharpened" $f(r)$ curve (b 0.00001) these peaks are better defined. Moreover, additional peaks at 2.35 (S···H) and 2.75 (C···S) Å appeared. Their positions agree well with an asymmetric model of the molecule.

Table 1 compares the refined geometric parameters of 2-chloro-1,3-dithia-2-phospholane (C_1 conformer with an axial P–Cl bond) and calculation results. Whereas the latter unambiguously rule out symmetric shapes of the heteroring (C_s or C_2), we still performed structural analysis for these models. The R factors for these models proved remarkably higher (14.6 and 7.4%, respectively) than for the asymmetric shape. Thus, we can conclude with assurance that 2-chloro-1,3-dithia-2-phospholane has a single stable conformation in the gas phase. This conclusion is confirmed by spectral analysis of 2-chloro-1,3-dithia-2-phospholane at various temperatures (–50 to 19°C) and in crystal [4]. Furthermore, all stretching vibration lines in the Raman spectra are polarized, implying an asymmetric five-membered ring. It should also be noted that in going from liquid to crystal the intensities of the lines remain unchanged. This proves the absence of conformational equilibrium.

In structural analysis strong emphasis is placed on mean vibration amplitudes u_{ij}. In the first steps we used calculated values. In the final step they were refined as independent parameters. Table 2 compares the observed and calculated vibration amplitudes and the perpendicular amplitude corrections K_{ij}. Vibration amplitudes were refined in groups. As follows from the correlation matrix, a number of amplitudes correlate with certain geometric parameters. This first of all relates to u(P–S) and, naturally, to u(P–Cl), since the latter was refined in a group with u(P–S). It is seen from Table 2 that the calculated amplitudes fairly well fit experimental. Note that the torsion angle SCCS correlates with the bond angle SCC and the torsion angle $PS^2C^4C^5$.

Thus, the combined analysis of electron diffraction data and MO calculations showed that the 2-chloro-1,3-dithia-2-phospholane molecule in the gas phase has an asymmetric conformation with an axial P–Cl bond. This bond is close in length to that in 2-chloro-1,3-dioxa-2-phospholane [3] but considerably longer than in PCl_3 (2.043(3) Å [8]) or Cl_2PSMe (2.038(6) Å [9]). It can be concluded that the P–Cl bonds in fragments $\begin{matrix} X \\ X \end{matrix}\!\!>$P–Cl (X = O, S) are lengthened equally but to a lesser extent than the P–Cl bonds in 1,3-oxaza- and 1,3-diaza-2-phospholanes (2.17 Å) [10, 11]. The P–S bond lengths in 2-chloro-1,3-dithia-2-phospolane (2.081 and 2.117 Å) are close to those in phosphorodichloridite Cl_2PSMe [2.082(12) Å], phosphorodibromidite Br_2PSMe (2.116(16) Å [9]), phosphorodifluoridite F_2PSGeH_2 (2.115(8) Å [12]), sulfide $(F_2P)_2S$ (2.132(4) Å [13]), and trimethyl phosphorotrithioite (2.115(4) Å [14]). The P–S bond lengths in different compounds are close to the sum of the co-

Table 1. Geometric parameters of 2-chloro-1,3,2-dithiaphospholane

Parameter[a]	Experiment		Calculation		
	r_a	r_α	HF/6–31G	MP2/6–31G	B3PW91/6–31G
Bond, Å					
d(PCl)	–0.015		–0.015	–0.010	0.001
P^2–Cl	2.103] (14)	2.100	2.096	2.103	2.130
P^2–S^3	2.117]	2.115	2.111	2.113	2.129
P^2–S^1	2.081(28)[b]	2.080	2.097	2.098	2.113
C^4–S^3	1.836(5)	1.823	1.837	1.833	1.843
C^5–S^1	1.816	1.810	1.824	1.821	1.832
d(CS)	–0.013		–0.013	–0.012	–0.011
C^4–C^5	1.514(11)	1.503	1.521	1.516	1.516
C–H	1.121(16)	1.103	1.089	1.089	1.094
Bond angle, deg					
SPCl	102.9(4)		102.7	102.8	102.9
SPS	96.7(5)[b]		96.6	96.7	96.3
$P^2S^3C^4$	102.0(7)		101.1	100.4	100.8
$S^3C^4C^5$	112.1(8)		111.8	111.4	111.4
$C^4C^5S^1$	112.1		110.0	109.5	109.6
d(SCC)	0.0		–1.8	–1.9	–1.8
HCS	107.6(45)			107.0	
Torsion angle, deg					
$P^2S^3C^4C^5$	–17.9(32)		–18.7	–20.2	–22.0
$S^3C^4C^5S^1$	42.7(31)		47.0	50.2	50.2
$C^4C^5S^1P^2$	–45.2(32)[b]		–50.4	–53.1	–51.8
$C^5S^1P^2S^3$	27.5(31)[b]		31.9	33.2	31.1
$S^1P^2S^3C^4$	–8.9(32)[b]		–11.3	–11.5	9.3
$ClP^2S^3C^4$	96.0(34)[b]		93.2	93.0	95.7
$ClP^2S^1C^5$	–77.4(33)[b]		–72.8	–71.5	–73.7
$H^7C^4S^3P^2$	–142		–140	–141	–142
$H^8C^4S^3P^2$	103		103	101	100
$H^9C^5S^1P^2$	71		72	72	71
$H^{10}C^5S^1S^2$	–169		–170	–173	–172
R Factor, %	5.26				

[a] *d*(PCl) = *r*(P^2–S^3) – *r*(P–Cl), *d*(CS) = *r*(S^3–C^4) – *r*(S^1–C^5), *d*(SCC) = ∠($S^3C^4C^5$) – ∠($S^1C^5C^4$). [b] Dependent parameters.

valent radii of P and S atoms (2.12 A), unlike P–O bond lengths. The P–O bond lengths in oxygen-containing cyclic compounds vary, according to electron diffraction data, in the range 1.62–1.64 Å [15] (the sum of the covalent radii of O and P atoms is 1.85 Å). It is to be noted that the P–S bonds in 2-chloro-1,3-dithia-2-phospholane and the $ClP^2S^3C^4$ and $ClPX^1C^5$ torsion angles in the *gauche* fragments (Table 1) are different though the differences are close to the experimental uncertainties. Of interest in this connection are the X-ray diffraction results for 2,2'-(ethylenedithio)bis(1,3-dithia-2-phospholane) where both the dithiaphospholane rings have an asymmetric shape and endocyclic P–S bonds differ by 0.02 Å [16].

Table 3 compares the geometric parameters of 2-chloro-1,3-dihetero-2-phospholanes. The heteroring in the oxygen derivative is fattened compared with that in the dithiaphospholane analog. This may be due to the different values of *r*(P–O) and *r*(P–S) and of the POC and POS bond angles (120–116 Å and 100°C) in acyclic structures (see, for example, [15]). The molecules have similar structures. If one takes as a base the X^1PX^3 plane, than in the dioxaphospholane ring the C^4 and C^5 atoms deviate from this plane (experimental data) by –0.40 and –0.62 Å, while in the dithiaphospholane ring, by –0.26 and –0.83 Å. Both molecules have the Cl atom axial. In other words, the conformation of the heterorings is P-*envelope*

Matrix of correlation coefficients for the molecular model of C_1 symmetry for 2-chloro-1,3,2-dithiaphospholane

	P–S	C–S	C–C	C–H	PS^3C^4	SCC	SPCl	HCS	$\tau(S^3–C^4)$	τ(C–C)	u(PS)	u(CC)	u(CH)	u(SCl)	u(CCl)	u(CS)	u(SH)
P–S	100																
C–S	–1	100															
C–C	–11	15	100														
C–H	0	–2	18	100													
PS^3C^4	–83	5	24	–2	100												
SCC	3	–35	–60	–16	11	100											
SPCl	–59	8	10	–3	61	7	100										
HCS	13	–18	–8	–12	–4	31	–19	100									
$\tau(PS^3C^4C^5)$	–20	–17	–27	–1	18	55	4	37	100								
τ(SCCS)	–3	24	40	12	–22	–94	–10	–36	–67	100							
u(PS)	–93	5	12	0	78	–5	54	0	21	4	100						
u(CC)	–25	–1	3	–6	22	0	13	3	5	0	27	100					
u(CH)	–3	–4	13	2	4	–8	0	8	0	5	5	3	100				
u(SCl)	–29	0	4	1	37	14	1	18	–22	–8	35	13	4	100			
u(CCl)	4	–3	–5	–6	–4	–4	31	–5	–3	4	–5	0	0	2	100		
u(CS)	0	3	3	0	–3	–3	8	–20	–12	7	3	4	0	3	0	100	
u(SH)	–14	5	7	–2	28	12	20	–51	–7	–15	0	–3	–4	–6	3	24	100

twisted about the C–C bond; therewith, the torsion angles τ(C–C) differ more than 2 times (Table 3).

The structural similarity of the 1,3-dioxa- and 1,3-dithiaphospholane heterorings allows us to suppose that the 1,3-oxathia-2-phospholane ring, too, has the same structure. Here two conformations are possible [let us label them C(O) and C(S)], with different deviations of C^5 and C^4 from the O–P–S plane. No structural data for 2-chloro-1,3-oxathia-2-phospholane are available in literature. Based on the IR and Raman spectral evidence, Shagidullin *et al.* [4] proposed that in the liquid phase there is an equilibrium between two idealized C(O)-*envelope* forms with axial and equatorial locations of the P–Cl bond. In essence, the proposed C^5-*envelope* conformation is consistent with the *ab initio* geometry of this molecule: The C^5OPS torsion angle equals 13° (Table 3). The fact that the *ab initio* geometries of 2-chloro-1,3-dioxa- and 1,3-dithia-2-phospholane molecules agree well with experimental data lets us to predict the structure and conformations of 2-chloro-1,3-oxathia-2-phospholane by theoretical methods. Table 3 presents the results of such calculations at the MP2/6-31G* level (note that the same results were obtained at the HF/6-31G* and B3PW91/6-31G* levels). The C(S) and C(O) conformers have equal energies (within 0.1 kcal/mol) and dipole moments. In the C(S) conformer the C^4 and C^5 atoms are deviate from the O–P–S plane by 0.90 and 0.29 Å and in the C(O) conformer, by 0.12 and 0.70 Å, i.e. twisted P-*envelope* conformations are realized. Both conformers have the P–Cl bond axial. Its length, as it follows from the *ab initio* results (2.10 Å) almost equals that in 2-chloro-1,3-dithia-2-phospholane.

Table 2. Principal mean vibration amplitudes u_{ij} and perpendicular amplitude corrections K_{ij} (Å)

Parameter	u_{ij}(exp)	u_{ij}(calc)	$K_{ij} \times 10^3$
P–Cl	0.058 (4)	0.055	3
$P–S^3$	0.057	0.053	2
$P–S^1$	0.056	0.052	1
$C^4–S^3$	0.044	0.053	6
$C^5–S^1$	0.043	0.053	13
C–C	0.047 (10)	0.051	6
C–H	0.074 (15)	0.076	18
Cl···S	0.104 (8)	0.095	0
$P···C^4$	0.078	0.068	4
$P···C^5$	0.085	0.075	1
S···S	0.078	0.068	0
$S^1···C^4$	0.079 (7)	0.070	6
$S^3···C^5$	0.077	0.068	4
$Cl···C^4$	0.151 (36)	0.166	–5
$Cl···C^5$	0.166	0.181	–8
$S···H^{7,8}$	0.153 (51)	0.110	25
$S···H^{9,10}$	0.152	0.109	10
$Cl···H^7$	0.249[a]	0.284	–11
$Cl···H^8$	0.107[a]	0.150	3
$Cl···H^9$	0.278[a]	0.277	–17
$Cl···H^{10}$	0.163[a]	0.206	–4

[a] Refined in earlier steps of calculations.

Turning to arsenic analogs of 2-halo-1,3-dihetero-2-phospholanes, we can note that, as deduced by Zaripov *et al.* from electron diffraction data [17, 18], the diheteroarsolane rings in them, too, has an asymmetric structure with an axial As–Hlg bond. However, the conformation of the heteroring in 2-methyl-1,3-

Table 3. Geometric parameters of 2-chloro-1,3-dihetero-2-phospholane

Parameter	Dioxaphospholane		Dithiaphospholane		Oxathiaphospholane (MP2/6–31G**)	
	experiment	HF/6–31G**	experiment	MP2/6–31G**	conformer C(S)	conformer C(O)
Bond, Å						
P–Cl	2.092(4)	2.106	2.103(14)	2.103	2.104	2.101
X^1–P^2	1.608(4)	1.612	2.081(28)[a]	2.098	1.648	1.648
P^2–X^3	1.608	1.612	2.117(14)	2.113	2.113	2.135
X^3–C^4	1.439(8)	1.421	1.836(5)	1.833	1.821	1.828
C^4–C^5	1.550(29)	1.538	1.514(11)	1.516	1.518	1.516
C^5–X^1	1.439(8)	1.423	1.816(5)	1.821	1.450	1.446
Bond angle, deg						
$X^1P^2X^3$	96.3(10)	93.8	96.7(5)[a]	96.7	95.0	94.7
$P^2X^3C^4$	111.4(16)	112.4	102.0(7)	100.4	90.1	93.5
$X^3C^4C^5$	103.4(28)	105.6	112.1(8)	111.4	106.8	107.8
$C^4C^5X^1$	109.4(29)	106.4	112.1	109.5	110.1	107.7
$C^5X^1P^2$	110.5(23)	114.5	98.5(12)[a]	95.6	118.7	114.3
$Cl^6P^2X^1$	99.6(5)	100.2	102.9(4)	102.5	100.7	101.5
$Cl^6P^2X^3$	100.2(5)	100.3	102.9	102.8	102.0	102.0
Torsion angle, deg						
$X^1P^2X^3C^4$	29.5(41)	25.7	–8.9(32)[a]	–11.5	–29.8	3.9
$P^2X^3C^4C^5$	–29.6(71)	–20.2	–17.9(32)	–20.2	41.7	21.6
$X^3C^4C^5X^1$	16.6(90)	16.9	42.7(31)	50.2	–41.0	–45.0
$C^4C^5X^1P^2$	2.3(80)	0.10	–45.2(32)[a]	–53.1	15.5	52.5
$C^5X^1P^2X^3$	–17.8(44)	–14.4	27.5(31)[a]	33.2	12.9	–31.6
$Cl^6P^2X^3C^4$	71.5(41)	75.4	96.0(34)[a]	93.0	72.3	–99.0
$Cl^6P^2X^1C^5$	–83.7(44)	–86.8	–77.4(33)	–71.5	–90.3	71.6

[a] Dependent parameters.

dithia-2-arsolane is *half-chair* (C_2 symmetry). This conformational difference the referees explained by the anomeric effect in the halo derivatives.

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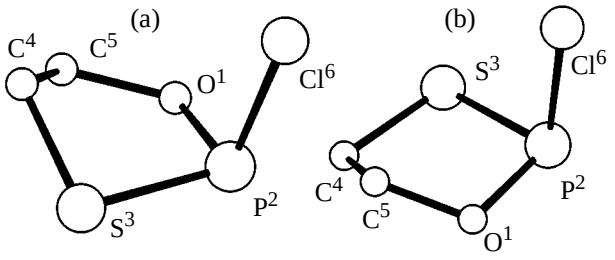

Fig. 4. Conformations of 2-chloro-1,3-oxathia-2-phospholanes: (a) C(S) conformer and (b) C(O) conformer.

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