UDC 541.6:543.422:547.24

ANOMERIC EFFECT AND THEORETICAL VIBRATIONAL SPECTRA COMPARED TO THE EXPERIMENT IN 2-CHLORO-1,3,2-DIOXAPHOSPHORINANE-2-OXIDE, -SULFIDE, AND -SELENIDE. I. ANOMERIC EFFECT AND STRUCTURES

© 2011   **W. Förner*, H.M. Badawi**

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

2-Chloro-1,3,2-dioxaphosphorinane-2-oxide, -sulfide, and -selenide are studied at the DFT/B3LYP level and several *ab initio* methods using a 6-311G** basis set. Our energy optimizations by all these methods show that for oxide DFT and *ab initio* methods are not much different, while for the sulfide and the selenide the DFT relative energies are higher by about a kcal/mol as compared to those of MP2, MP3, MP4(SDTQ)//MP2, and CCSD(T)//MP2 (//MP2 indicates that a single-point calculation based on the MP2 optimized geometry is performed). However, regardless of rather large relative energies, that does not change the fact that in all three cases the conformational equilibrium mixture contains more than 95 % of the lowest, *chair*-equatorial conformer (this indicates that the P=X bond is in equatorial position). This one and the next higher conformer (*chair*-axial) are confirmed to be real conformers (energy minima) in all cases. The energetically much higher *twist* and *boat* forms are probably just stationary states and local maxima because in many cases, geometry optimizations do not converge to them. Only for MP2 and the selenide do all optimizations converge to the desired stationary state. The relative energies could all be explained in terms of anomeric effects and ring strains. The decreasing covalent character of the P=X bond, with X changing from O to S and to Se, shows itself in the increasing bond lengths and the decreasing strength of anomeric effects.

K e y w o r d s: anomeric effect, 2-chloro-1,3,2-dioxaphosphorinane-2-oxide, -sulfide, and -selenide, DFT/B3LYP, 6-311G** basis set.

INTRODUCTION

We are very much interested in the structural and spectroscopic (vibrational infrared (IR) and Raman) spectra in five and six membered hetrocycles containing oxygen, sulfur and/or phosphorus atoms. Recently the other groups and also we have studied the five-membered sulfur- containing sulfolane and sulfolene [1—6]. To gain information about the structures of the two molecules, rotational microwave [3, 4], vibrational IR, Raman [1, 2], and electron diffraction studies [5] have been applied. The conformation of the five-membered sulfolane ring could not be determined clearly by electron diffraction [5]. In a more recent microwave study of the molecule [3] the data appeared to be compatible with two different situations: a near planar structure with a small barrier to the fully planar structure or pseudorotation with the bent form lowest in energy. From the microwave spectra of the ground and five excited states of the ring-puckering vibration of sulfolene it could be deduced that the ring puckering has a double minimum potential with a small barrier of about 286 cal/mol to the planarity of the ring [4]. Our MP2 calculations on the same system [6] confirmed that the symmetric potential function of the ring-puckering vibration has a double minimum and a small barrier of 193 cal/mol in good agreement with the experiment (DFT gave a flat minimum corresponding to the planar structure).

---

* E-mail: forner@kfupm.edu.sa

Furthermore and most recently we turned our attention to the corresponding five-membered ring system of dioxaphospholane oxide and sulfide because of their interesting structural and chemical properties [7—15]. We found that in this system, the five-membered ring is highly strained and the possible puckered structures (axial or equatorial) turned out to be not the minima on the potential hypersurface. In order to remove ring strains and the unfavorable lone-pair repulsions between two oxygen atoms in the ring, the stable structure has to be a twisted one. Also the anomeric effect is not able to compete with the lone-pair repulsions to stabilize a puckered conformer [16].

These observations turned our attention to the corresponding six-membered ring compounds such as 2-chloro-1,3,2-dioxaphosphorinane-2-oxide, -sulfide, and -selenide, which have far less strains in their rings, and thus, the anomeric effect in them should be able to stabilize a puckered conformer over the twisted one, while we expect that the strength of the anomeric effect should decrease when going down the chalcogenide group. The vibrational spectra of all three molecules are published in the literature [17, 18], so we could compare our theoretical ones with them and also provide a much better assignment of normal modes to the observed lines than the simple force field based one in [17, 18] using a DFT PED (potential energy distribution) calculation, as outlined in the following part of this paper. Our basic aims in this investigation are the prediction and explanation (assignment of experimentally found lines to normal modes) of the vibrational spectra of the title molecules and a detailed study of the conformational equilibrium in the six-member rings as compared to our previous investigation of the five-member ones described in this part of the paper.

Dioxaphosphorinane compounds are also important by themselves due to their antitumor activity [19], and further, they can plasticize and stabilize plastics like polyvinyl chloride [20]. Such compounds can react with amines, ammonia, alcohols, phenols, and thiophenols to yield esters that are very useful, e.g. as pesticides, plasticizers, lubricants, hydraulic fluids, dyeing assistants, and additives to oil and gasoline [21]. Also substituted dioxaphosphorinanes act as useful pesticides, intermediates for the preparation of plasticizers for synthetic resins, corrosion inhibitors, petroleum additives, and floating agents [22].

AB INITIO AND DFT CALCULATIONS

The Gaussian-98 program [23] running on an IBM RS/6000 model S85 Unix server was used to carry out DFT/B3LYP and MP2 calculations using a 6-311G** basis set. We optimized the possible stationary structures; however, because the energies of the *twist*, *boat*, and planar forms are so high that they play no role in the conformational equilibrium mixture at 25 °C, we did calculate the vibrational frequencies only for the two *chair* forms: equatorial and axial. It turned out that the equatorial form (equatorial refers to the P=X group) is by more than a kcal/mol lower than the axial one, both in DFT and MP2. Thus in the conformational equilibrium, only the *chair*-equatorial conformer is abundant (to more than 95 %) in all molecules and thus is the only one that is included in the spectra calculations. The *chair*-axial form is a global minimum in all three molecules, indicated by the fact that all frequencies are real. For the *twist* and *boat* forms we did not calculate the frequencies, so we do not know whether they are real conformers or just stationary states, i.e. maxima of the potential energy along one or more of the normal coordinates. Only for the selenide and MP2 we were able to obtain all the stationary states in a set of calculations, while specially with DFT many of the iterations converged to another state than the desired one. In the case of selenide, e.g. the DFT optimization meant to yield the *boat*-axial state, actually converged to the *chair*-equatorial conformer, and thus we suspect that *boat*-axial is in fact not a stable conformer, but a local maximum.

THE ANOMERIC EFFECT

The result of our calculations is that for all three molecules the most stable conformer is the *chair*-equatorial (equatorial refers to the position of the P=X bond) one, with the next higher conformer, *chair*-axial being more than 2 kcal/mol higher in energy (according to our DFT calculations); only in MP2 for the selenide it is only 1.3 kcal/mol higher in energy. Therefore only for these two conformers and with DFT we showed that they are global minima on the potential energy hypersurface by a frequency calculation (harmonic approximation) and to be sure that all vibrational frequencies are real. The relative free

Table 1

Geometrical parameters, rotational constants, and total dipole moments for chair-equatorial 2-chloro-1,3,2-dioxaphosphorinane-2-oxide, -sulfide and -selenide as calculated using the DFT/B3LYP *method with a* 6-311G** *basis set in Born-Oppenheimer approximation*

	Oxide (X=O)	Sulfide (X=S)	Selenide (X=Se)		Oxide (X=O)	Sulfide (X=S)	Selenide (X=Se)
	Bond lengths (Å)				Rotational constants (GHz)		
$P_1=X_7$	1.459	1.904	2.058	A	2.16128	1.76739	1.64467
P_1-Cl_8	2.076	2.105	2.112	B	1.29888	1.05766	0.69531
P_1-O_2	1.598	1.605	1.611	C	1.21076	0.90535	0.60998
O_2-C_4	1.454	1.456	1.457				
	Bond angle (deg.)				Total dipole moment (D)		
$X_7P_1Cl_8$	113.4	115.6	115.9	μ_t	6.79	6.34	5.99

energies (273.15 K, 1 atm) of the *chair*-axial conformers are 2.66 kcal/mol for the oxide, 2.08 kcal/mol for the sulfide and 2.01 kcal/mol for the selenide (DFT). Thus, in a conformational equilibrium mixture of these two conformers there would be 98.9 % of the *chair*-equatorial conformer for the oxide, 97.1 kcal/mol for the sulfide, and 96.8 % for the selenide. This agrees with the experimental results [17, 18], where no vibrational spectral lines of increasing intensity with increasing temperature could be found, and so it was concluded that there exists no conformational equilibrium mixture. Thus, in the spectral calculations we used the *chair*-equatorial conformer alone.

Table 1 shows some of the geometrical parameters of that conformer for the three molecules as calculated using the DFT method and gradient optimization in Born-Oppenheimer approximation and Fig. 1, *a* gives atom numbering.

As expected, most of the parameters do not change too much between the title oxide, sulfide, and selenide; however, also as expected, the P=X bond length increases from 1.459 Å in the oxide to 1.904 Å in the sulfide and to 2.058 Å in the selenide. The rotational constants decrease as the weight of X increases, and the total dipole moments of the molecules decrease as the electronegativity of X decreases.

In the case of the oxide and the sulfide, many attempts to locate stationary structures by optimization failed, and only in the case of the selenide optimized with MP2, we were able to obtain stationary states in all attempts, namely the conformers, *chair*-equatorial and *chair*-axial, and further a *twist* form and two
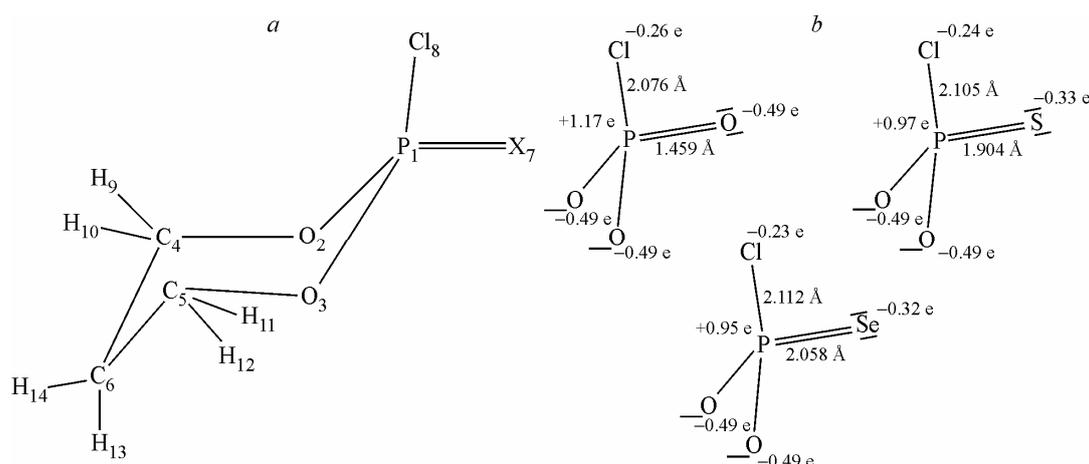

Fig. 1. (*a*) Sketch of *chair*-equatorial 2-chloro-1,3,2-dioxaphosphorinane-2-oxide (X=O), -sulfide (X=S), and -selenide (X=Se) and atom numbering, where equatorial refers to the position of the P=X bond. (*b*) Mulliken charges (units of the electronic charge e) as well as the P—Cl and P=X bond lengths in *chair*-equatorial 2-chloro-1,3,2-dioxaphosphorinane-2-oxide (X=O), -sulfide (X=S), and -selenide (X=Se)

Total reference energies, E (*in* H)*, for the chair-equatorial conformer and relative energies* (*to chair-equatorial*)*, ΔE* (*in* kcal/mol)*, for the chair-axial conformer of* 2-*chloro*-1,3,2-*dioxaphosphorinane*-2-*oxide, -sulfide, and -selenide using* MP2, MP3, MP4-SDTQ, *and* (*where possible*) CCSD(T) (DFT *with* DFT *optimized geometries, including the Gibbs free energy G* (*in* H) *and the relative Gibbs free* energy ΔG (*in* kcal/mol)) *where all calculations, except* DFT*, were performed with the* MP2 *optimized geometries. For the selenide also relative energies of the other extrema determined by the* DFT *and* MP2 (*no frequency calculation possible on our computer*) *method are given*

Method		Oxide	Sulfide	Selenide
Chair-equatorial				
MP2	*E*	–1143.379034	–1465.943981	–3468.204562
MP3	*E*	–1143.404426	–1465.984594	–3468.243930
MP4-SDTQ	*E*		–1466.051674	–3468.311014
CCSD(T)	*E*	–1143.470190	–1466.046793	–
DFT	*E*	–1145.374122	–1468.331998	–3471.668500
DFT	*G*	–1145.304992	–1468.266148	–3471.604690
Chair-axial				
MP2	Δ*E*	3.17	1.43	1.27
MP3	Δ*E*	3.02	1.48	1.39
MP4-SDTQ	Δ*E*	3.12	1.45	1.27
CCSD(T)	Δ*E*	2.96	1.39	–
DFT	Δ*E*	3.19	2.33	2.20
DFT	Δ*G*	2.66	2.08	2.01
Selenide				
		DFT	MP2	
Twist	Δ*E*	3.88	3.69	
Boat-equatorial	Δ*E* [a]	4.05	5.55	
Boat-axial	Δ*E* [b]	–6.88		

[a] This calculation (DFT) exceeded the maximum of 80 search steps for a local minimum; non-converged parameter: maximum displacement being 0.0026 and thus larger than the 0.0018 required for convergence.
[b] This optimization (DFT) converged to the *chair*-equatorial conformer.

boat forms. In one of the *boat* forms, the DFT optimization exceeded the maximum possible number of 80 search steps and the calculation stopped. In the case of *boat*-axial and DFT, the optimization converged to the *chair*-equatorial conformer. In Table 2, we list the energies, however, for the selenide we are unable to perform frequency calculations with MP2 in a system containing heavy atoms such as phosphorus, chlorine, and selenium, so we were unable to characterize the exact nature of the *twist* and two *boat* forms (in MP2 also for the *chair* forms); however, they are stationary states, but so high in energy that they do not need to be considered.

In order to get a better feeling about the reliability of the DFT relative energies, in Table 2 we list as reference points the total energies of the *chair*-equatorial conformers of the three molecules together with the relative energies of the *chair*-axial conformers calculated with several *ab initio* methods such as MP2, MP3, MP4(SDTQ)//MP2 (single, double, triple, and quadruple excitations), CCSD(T)//MP2 (coupled cluster singles-doubles with triple excitations approximated). Note that //MP2 indicates that a single-point calculation was performed by the method given before the //MP2, based on the MP2 optimized geometry. However, for MP3, MP4(SDTQ)//MP2, and CCSD(T)//MP2 we had to perform the calculations on our IBM workstation with the MP2 optimized geometries, while in the case of the selenide, even the CCSD(T) single point calculation is too large.

Fig. 2. Sketches of the two possible stabilizing MO interactions (anomeric effect) in *chair*-equatorial 2-chloro-1,3,2-dioxaphosphorinane-2-oxide (X=O), -sulfide (X=S), and -selenide (X=Se).
(*a*) σ^* (P—Cl) — (lone pair) lp(O) interaction,
(*b*) π^* (P=X) — (lone pair) lp(O) interaction
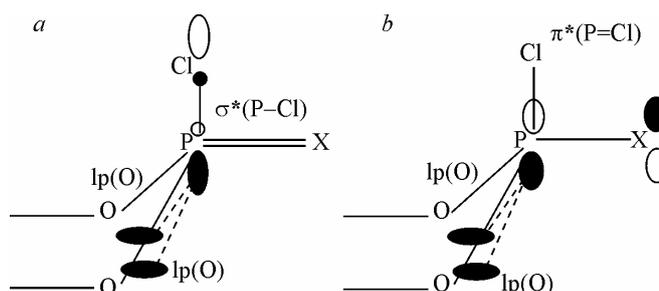
Obviously, in the case of the oxide, DFT agrees fairly well with the *ab initio* results, while for the sulfide and the selenide the DFT values are higher by almost a kcal/mol than the *ab initio* ones. However, this discrepancy does not invalidate our conclusion that the *chair*-equatorial conformer is by far the most abundant one and that a conformational mixture of different forms contains almost only the lowest conformer.

Most easy to explain are the high energies of the *boat* forms of the molecules, because in the *boat* structures the ring strains are simply far too large. In a corresponding five-membered ring system (dioxaphospholane) we found that the *twist* form is the only stable conformer and that no puckered conformers exist [16]. The reason for that is the small five-membered ring in which ring strains in puckered structures easily overcome any anomeric effect and in addition, in puckered structures there would be repulsive interactions between the lone pairs at the in-ring oxygen atoms. In our much larger six-membered rings, both the ring strains (in the *chair* conformers) and the repulsions between lone pairs at in-ring oxygen atoms (larger distance between them) in puckered conformers are still present, but are much smaller, while here ring strains in a *twist* form become larger. The two low energy conformers, the puckered ones are stabilized by anomeric effects, especially the *chair*-equatorial one.

In the *chair*-equatorial conformer, the P=X bond is in the equatorial position, and the P—Cl bond is in an axial one. For the P—Cl bond that gives rise to the usual anomeric stabilization of the conformer: as shown in Fig. 2, *a* the antibonding, empty σ^* orbital of the P—Cl bond can overlap with the two filled lone pairs at the in-ring oxygen atoms.

T a b l e   3

Overcomplete set of internal coordinates for 2-chloro-1,3,2-dioxaphosphorinane-2-oxide (X=O), -sulfide (X=S), and -selenide (X=Se) according to atom numbering given in Fig. 1, a (note that our PED (Potential Energy Distribution) program automatically identifies and removes redundant internal coordinates from both the internal coordinate and the symmetry coordinate lists)

No.	Coordinate		Definition	No.	Coordinate		Definition	No.	Coordinate		Definition
1	P_1O_3	stretch	R_1	15	$O_2P_1O_3$	bend	α_1	28	$O_3P_1Cl_8$	bend	v_{14}
2	P_1O_2	stretch	R_2	16	$C_4O_2P_1$	bend	α_2	29	$O_2C_4H_9$	bend	v_{31}
3	O_2C_4	stretch	R_3	17	$C_6C_4O_2$	bend	α_3	30	$C_6C_4H_9$	bend	v_{32}
4	C_4C_6	stretch	R_4	18	$C_5C_6C_4$	bend	α_4	31	$O_2C_4H_{10}$	bend	v_{33}
5	C_5C_6	stretch	R_5	19	$C_6C_5O_3$	bend	α_5	32	$C_6C_4H_{10}$	bend	v_{34}
6	O_3C_5	stretch	R_6	20	$C_5O_3P_1$	bend	α_6	33	$C_4C_6H_{13}$	bend	v_{41}
7	P_1X_7	stretch	r_1	21	$H_9C_4H_{10}$	bend	β_3	34	$C_5C_6H_{13}$	bend	v_{42}
8	P_1Cl_8	stretch	r_2	22	$X_7P_1Cl_8$	bend	β_1	35	$C_4C_6H_{14}$	bend	v_{43}
9	C_4H_9	stretch	r_5	23	$H_{14}C_6H_{13}$	bend	β_4	36	$C_5C_6H_{14}$	bend	v_{44}
10	C_4H_{10}	stretch	r_6	24	$H_{12}C_5H_{11}$	bend	β_5	37	$C_6C_5H_{11}$	bend	v_{51}
11	C_6H_{13}	stretch	r_7	25	$X_7P_1O_2$	bend	v_{11}	38	$O_3C_5H_{11}$	bend	v_{52}
12	C_6H_{14}	stretch	r_8	26	$X_7P_1O_3$	bend	v_{12}	39	$C_6C_5H_{12}$	bend	v_{53}
13	C_5H_{11}	stretch	r_9	27	$O_2P_1Cl_8$	bend	v_{13}	40	$O_3C_5H_{12}$	bend	v_{54}
14	C_5H_{12}	stretch	r_{10}								

Symmetry coordinates (*not normalized*) *for* 2-*chloro*-1,3,2-*dioxaphosphorinane*-2-*oxide* (X=O), -*sulfide* (X=S), *and* -*selenide* (X=Se)

Species	Description	Symmetry coordinate
A′	γ-CH$_2$ antisym. stretch	$S_1 = r_5 - r_6 - r_9 + r_{10}$
	γ-CH$_2$ sym. stretch	$S_2 = r_5 + r_6 + r_9 + r_{10}$
	δ-CH$_2$ antisym. stretch	$S_3 = r_7 - r_8$
	δ-CH$_2$ sym. stretch	$S_4 = r_7 + r_8$
	P=X stretch	$S_5 = r_1$
	P—Cl stretch	$S_6 = r_2$
	ring deformation	$S_7 = R_1 + R_2 - 2R_3 + R_4 + R_5 - 2R_6$
	ring deformation	$S_8 = R_1 + R_2 - R_4 - R_5$
	ring breathing	$S_9 = R_1 + R_2 + R_3 + R_4 + R_5 + R_6$
	γ-CH$_2$ deformation (scissor)	$S_{10} = 4\beta_3 - v_{31} - v_{32} - v_{33} - v_{34} + 4\beta_5 - v_{51} - v_{52} - v_{53} - v_{54}$
	γ-CH$_2$ rock	$S_{11} = v_{31} + v_{32} - v_{33} - v_{34} - v_{51} - v_{52} + v_{53} + v_{54}$
	γ-CH$_2$ wag	$S_{12} = v_{31} - v_{32} + v_{33} - v_{34} - v_{51} + v_{52} - v_{53} + v_{54}$
	γ-CH$_2$ twist	$S_{13} = v_{31} - v_{32} - v_{33} + v_{34} + v_{51} - v_{52} - v_{53} + v_{54}$
	δ-CH$_2$ deformation (scissor)	$S_{14} = 4\beta_4 - v_{41} - v_{42} - v_{43} - v_{44}$
	δ-CH$_2$ rock	$S_{15} = v_{41} + v_{42} - v_{43} - v_{44}$
	PXCl deformation (scissor)	$S_{16} = 4\beta_1 - v_{11} - v_{12} - v_{13} - v_{14}$
	PXCl rock	$S_{17} = v_{11} + v_{12} - v_{13} - v_{14}$
	ring antisym. deformation	$S_{18} = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$
	ring sym. puckering	$S_{19} = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6$
	ring antisym. puckering	$S_{20} = \alpha_1 + \alpha_2 + \alpha_3 - \alpha_4 - \alpha_5 - \alpha_6$
	ring sym. deformation	$S_{21} = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$
A″	γ-CH$_2$ antisym. stretch	$S_{22} = r_5 - r_6 + r_9 - r_{10}$
	γ-CH$_2$ sym. stretch	$S_{23} = r_5 + r_6 - r_9 - r_{10}$
	γ-CH$_2$ deformation	$S_{24} = 4\beta_3 - v_{31} - v_{32} - v_{33} - v_{34} - 4\beta_5 + v_{51} + v_{52} + v_{53} + v_{54}$
	γ-CH$_2$ rock	$S_{25} = v_{31} + v_{32} - v_{33} - v_{34} + v_{51} + v_{52} - v_{53} - v_{54}$
	γ-CH$_2$ wag	$S_{26} = v_{31} - v_{32} + v_{33} - v_{34} + v_{51} - v_{52} + v_{53} - v_{54}$
	γ-CH$_2$ twist	$S_{27} = v_{31} - v_{32} - v_{33} + v_{34} - v_{51} + v_{52} + v_{53} - v_{54}$
	δ-CH$_2$ wag	$S_{28} = v_{41} - v_{42} + v_{43} - v_{44}$
	δ-CH$_2$ twist	$S_{29} = v_{41} - v_{42} - v_{43} + v_{44}$
	PXCl wag	$S_{30} = v_{11} - v_{12} + v_{13} - v_{14}$
	PXCl twist	$S_{31} = v_{11} - v_{12} - v_{13} + v_{14}$
	ring deformation	$S_{32} = R_1 - R_2 + R_3 - R_4 + R_5 - R_6$
	ring deformation	$S_{33} = R_1 - R_2 + R_4 - R_5$
	ring deformation	$S_{34} = R_1 - R_2 - 2R_3 - R_4 + R_5 + 2R_6$
	ring antisym. deformation	$S_{35} = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$
	ring twisting	$S_{36} = \alpha_2 + \alpha_3 - \alpha_5 - \alpha_6$

However, one of the lobes of the antibonding, empty π^* orbital of the P=X bond has the right symmetry to overlap also with the same filled lone pair orbitals, yielding additional stabilization as Fig. 2, *b* indicates. This stabilization might be slightly weaker than the one due to the P—Cl bond, because as Hernandez-Laguna et al. [12] point out, e.g. P=O, as the one in our system and also the other P=X bonds tend to be more like a highly polarized triple bond than a conventional double bond. Such distortions might reduce the anomeric-like effect due to the P=X bond. This might explain why the *chair*-axial con-

former is so much higher in energy: because in that conformer, the P—Cl bond can no longer stabilize the systems due to its anomeric effect, while the P=X bond still has a symmetry which allows its anomeric-like effect, also when P=X is in the axial position. However, as mentioned above, the stabilization due to the P=X bond is probably much weaker than that due to the P—Cl bond.

Obviously, the anomeric stabilization in these systems decreases slightly when the electronegativity of X becomes reduced, as indicated in Fig. 1, *b*, where we give the Mulliken charge densities together with P=X and P—Cl bond lengths in the three molecules. Obviously, P—Cl bonds are not changed too much between the three systems, while P=O is much shorter than P=S, which itself is slightly shorter than P=Se. Thus, while the anomeric effect due to the P—Cl bond will be not much different in the three molecules, the decreasing covalent character of the bonding when going from O to S and to Se, will decrease the stabilizing effects of the P=X bond drastically, explaining why the destabilization of the *chair*-axial conformer relative to the *chair*-equatorial one decreases from the oxide to the sulfide and to the selenide.

However, the conformational equilibrium is almost completely on the side of the *chair*-equatorial conformers, and as found experimentally [17, 18], no conformer bands have to be expected in spectra. Most probably, the strongest anomeric stabilization of the *chair*-equatorial conformer results from P—Cl rather than the P=X bonds. This is in contrast to the corresponding five-membered ring system [16], in which the anomeric effect cannot compete with the destabilization due the repulsion between oxygen lone pairs on the atoms on both sides of the phosphorus atoms, leading to a twisted structure in the five-membered ring rather than to a puckered one.

The overcomplete set of internal coordinates we used is given in Table 3, which is constructed based on the *chair*-equatorial minimum, and the symmetry coordinates are listed in Table 4. Note that our program removes automatically redundant internal coordinates from both sets of coordinates. The assignments of vibrational spectra based on that are discussed in the following part of the paper.

CONCLUSIONS

Phosphorinanes turned out to be good examples to study the effects of going down in a period of the periodic table. The anomeric effect decreases when going from O to S and to Se in a P=X bond, with the P atom and two neighboring oxygens in a six-membered ring. According to the PED (see the following paper), in all three molecules, there occurs no pseudorotational motion and the conformational equilibrium mixture contains almost only the *chair*-equatorial conformer (to more than 95 %) in agreement with variable-temperature vibrational spectroscopy [17, 18].

REFERENCES

1. *Katon J.E., Feairheller W.R. Jr.* // Spectrochim. Acta. – 1965. – **21A**. – P. 199.
2. *Fini G., Furtonato B.* // Spectrochim. Acta. – 1976. – **32A**. – P. 423.
3. *Alonso J.L.* // J. Mol. Struct. – 1981. – **73**. – P. 71.
4. *Alonso J.L., Lister D.G.* // J. Chem. Soc. Chem. Commun. – 1982. – **2**. – P. 93.
5. *Naumov V.A., Semashko V.N.* // Zh. Strukt. Khim. – 1971. – **14**. – P. 595.
6. *Badawi H.M., Förner W., El-Ali B., Al-Durais A.* // Spectrochim. Acta. A. – 2008. – **70**, N 5. – P. 983 – 990.
7. *Ashani Y., Snyder S.L., Irwin I.B.* // Biochem. – 1972. – **11**. – P. 3518.
8. *Shagidullin R.R., Shakirov I.K., Plyamovatyi K. et al.* // Zh. Obshchei Khim. – 1976. – **46**. – P. 1021.
9. *Amitai G., Ashani Y., Grunfeld Y. et al.* // J. Med. Chem. – 1976. – **19**. – P. 810.
10. *Prasad D.V., Mahadevan V.* // Polymer Bulletin. – 1980. – **3**. – P. 241.
11. *Zaripov N.M., Galiakberov R.M.* // Zh. Struct. Khim. – 1984. – **25**. – P. 143.
12. *Hernandez-Laguna A.A., Sainz-Diaz C.I., Smeyers Y.G. et al.* // J. Phys. Chem. – 1994. – **98**. – P. 1109.
13. *Cserepi-Suucs S., Toth I., Parkanyi L., Bakos J.* // Tetrahed. Asymm. – 1998. – **9**. – P. 3135.
14. *Hager C.D., Sopchik A.E., Bentrude W.G.* // J. Org. Chem. – 2000. – **65**. – P. 2778.
15. *Luo Z., Shi D.* // J. Heterocyc. Chem. – 2006. – **43**. – P. 1021.
16. *Badawi H.M., Förner W., Suwaiyan A.A.* // J. Mol. Struct. (accepted.) – 2008.
17. *Shakirov I.K., Shagidullin R.R.* // Zh. Obshchei Khim. – 1978. – **48**. – P. 508.

18. *Shagidullin R.R., Shakirov I.K., Musyakaeva R.K. et al.* // Izvest. Akad. Nauk SSSR Ser. Khim. – 1981. – **7**. – P. 1535.

19. *Billman J.H., May R.F., Heard J.E.* // J. Pharm. Sci. – 1968. – **57**. – P. 1809.

20. *Hooker* Chemical Corp., Patent GB 853798 19601109, 1960.

21. *Lanham W.M.* Union Carbide Corp., Patent US 2892862 19590630, 1959.

22. *Lanham W.M.* Union Carbide Corp., Patent US 2894016 19690707, 1969.

23. *Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Zakrzewski V.G., Montgomery J.A., Jr. Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Strain M.C., Frakas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G.A., Ayala P.Y., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Cioslowski J., Ortiz J.V., Baboul A.G., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R.L., Fox D.T., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P.M.W., Johnson B.G., Chen W., Wong W., Andres J.L., Head-Gordon M., Replogle E.S., Pople J.A.* Gaussian, Inc., Pittsburgh PA, 1998.