system should be adequately represented by the charge distribution Fe(IV)–C(–IV)–Fe(IV), although we reluctantly accept the presence of C(–IV) in the system.

The ΔE_Q values for the complexes III–VI appear to be more sensitive to the nature of the N-base than the δ values and show a decreasing trend that is in remarkable agreement with the sequences observed for the μ-oxo and μ-nitrido analogues (Table I), being also comparable with the total variation within each series. It should also be noticed that the ΔE_Q values measured for the μ-carbido adducts are markedly lower than the value obtained for I and close to the value found for II.

It is particularly significant that the decreasing sequence of the ΔE_Q values, VI (4-mepy) > IV (py) > V (pip) > III (1-meim), is systematically reproduced within each of the other two groups of the μ-nitrido and μ-oxo adducts. We believe that this reproducibility is primarily allowed by the already described structural similarities shared by the three series of complexes and listed in points i–iv. Nevertheless, as the ΔE_Q values depend not only on the electric field gradient generated by the ligands but also on the symmetry of the internal distribution of d electrons at the Fe metal, the spin state and ground state of the latter should also be taken into account for comparison. As regard to the spin state, the following available information has to be considered. (1) The μ-oxo–Fe(III) (d⁵) adducts have all been assigned a low-spin configuration mainly on the basis of EPR, Mössbauer, and magnetic susceptibility data.[5] (2) X-ray crystallography on the μ-carbido 1-meim adduct III and its μ-oxo analogue provide average Fe–N(Pc) and Fe–N(1-meim) bond distances close to

those of the low-spin Fe(II) (d⁶) species [PcFe(N-base)₂],[6,9,12] thus suggesting a low-spin state for the mentioned dimers. (3) ¹H NMR spectra of III in CDCl₃ at room temperature have the typical appearance of essentially diamagnetic systems, with sharp and narrow peaks. (4) Room-temperature magnetic susceptibility measurements on some of the μ-nitrido and μ-carbido adducts gave the following values of the magnetic moment per metal atom: μ_{eff} = 1.02 μ_B for [{(py)PcFe}₂N](PF₆); 0.99 μ_B for [{(pip)-PcFe}₂N](PF₆); 1.08 μ_B for IV; 0.83 μ_B for III. These low values of the magnetic moment, in combination with the fact that the former μ-nitrido complexes also give ¹H NMR spectra suggestive of diamagnetic species, reinforce the hypothesis of low-spin states for these d⁴ systems. In summary, then, there seems to be consistent experimental support for the assignment of a low-spin configuration to all the d⁵ (Fe(III)) and d⁴ (Fe(IV)) N-base adducts under examination.

The definition of the ground state of the present complexes is certainly not facilitated by the low paramagnetism observed and must wait for further information, including magnetic field dependent Mössbauer spectra.

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Contribution from the Laboratoire de Synthèse, Structure et Réactivité des Molécules Phosphorées, Unité Associée au CNRS No. 454, and Laboratoire de Physique Quantique, Unité Associée au CNRS No. 505, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France

Electronic Structure and Relative Stability of Isomers of HPX₂, HPXY, and ClPX₂ (X, Y = O, S)

S. Mathieu,[†] J. Navech,[†] and J. C. Barthelat*,[‡]

The electronic structure and relative stability of many possible isomers of HPX₂, HPXY, and ClPX₂ (X, Y = O, S) are investigated by means of ab initio calculations including polarization functions and electron correlation. For both HPO₂ and HPS₂ series, the three most stable isomers are in the following order: phosphine X=P—X—H (¹A′) < phosphorane H—P(X)₂ (¹A₁) < phosphirane H—P—X—X (¹A′) corresponding to relative energies 0, 15, and 105 kcal·mol⁻¹ (HPO₂) and 0, 4, and 17 kcal·mol⁻¹ (HPS₂). In contrast with HPO₂ series in which only two isomers are found to be stable, for HPS₂ other structures such as (thiosulfinyl)phosphine H—P=S=S (¹A′) can be expected as thermodynamically accessible compounds. The substitution of hydrogen by a chlorine atom reverses the thermodynamical ordering, and chlorophosphorane is calculated to be 19.2 and 49.2 kcal·mol⁻¹ more stable than the corresponding phosphines for the ClPS₂ and ClPO₂ series, respectively. This result emphasizes the prominent role of electronic effects of the substituent, which place chlorophosphorane as the most stable structure in agreement with experiment. In the HPOS mixed phosphine, the structural preference is in favor of the thiono form by 7.5 and 4.2 kcal·mol⁻¹ for cis and trans conformers, respectively. This result appears to be almost entirely governed by the σ-electronic effects in contrast with the corresponding mixed amines in which the π-effects favored the NO double bond. Finally, vibrational frequencies have been calculated for some low-lying structures and are found to be in excellent agreement with available experimental data.

1. Introduction

Recently, there is increasing interest in the molecular structure and chemical reactivities of compounds involving heavy atoms of group 15 with low coordination number. They are often proposed as reactive intermediates[1] or as ligands to transition-metal fragments.[2]

Although phosphorus and arsenic lie just below nitrogen in the periodic table, it is well-known that their abilities to form multiply bonded compounds are very dissimilar.[3] Among the various possible isomers of the RMX₂ type where M represents an atom of group 15 and X = O, S, Se, only a few of them are experi-

mentally isolated, particularly for phosphorus.

The chemistry of nitrogen is characterized by the important classes of nitro compounds and nitrites whereas the corresponding sulfur analogues are hitherto unknown. Compounds of the type RNS₂ are known to exist as *N*-thiosulfinylamines.[4] Moreover, recently, Nonella, Huber, and Ha[5] succeeded in the preparation of all the possible unbranched isomers of HNSO by energy-se-

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†Unité Associée au CNRS No. 454, Université Paul Sabatier.
‡Unité Associée au CNRS No. 505, Université Paul Sabatier.

lective photolysis under matrix-isolated conditions.

By comparison, the knowledge of phosphorus-containing compounds RPX_2 is far from being so extensive. Until now, the three isolated molecules belong to the class of the tricoordinated planar phosphorane
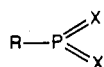

structure.[6] Five years ago, Navech, Majoral, and Kraemer[7] and Appel, Knock, and Kunze[8] simultaneously synthesized the first stable dithiophosphorane (R = 2,4,6-tri-*tert*-butylphenyl) by two different ways. The same bulky substituent group was used by Yoshifuji, Shibayama, and Inamoto[9] in order to isolate a thermally stable diselenophosphorane. In 1983, a similar molecule with two P=O double bonds was postulated as the reactive intermediate by Caminade, El Khatib and Koenig.[10] At that time, $ClPO_2$ was produced by a photochemical reaction between O_3 and POCl in a rare-gas matrix.[11] Very recently, infrared spectroscopic evidence for *cis*-OPOH trapped in solid argon was reported by Withnall and Andrews.[12] To our knowledge, no arsenic-containing compounds of the $RAsX_2$ type have yet been reported in the literature.

We decided to focus our attention on the RPX_2 series with R = H or Cl. This choice was essentially motivated by the particular interest of the dithiophosphorane molecule as a dithiophosphonylating agent.[13,14] The present work is a systematic theoretical study of the structure, relative stability and bonding of all the possible isomers of the RPX_2 series, namely, phosphorane
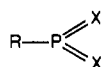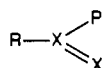

phosphine X=P—X—R (cis and trans conformers), phosphirane
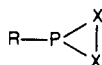
, phosphinidene P—X—X—R (singlet and triplet states), X-hypervalent species R—P=X=X (cis and trans conformers), and two more exotic compounds of phosphine type
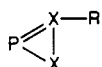
or phosphinidene type

We performed the main part of the study on hydrogenated model compounds with X = O and S. Next, we studied the influence of a chlorine substitution by performing less complete calculations with R = Cl.

The recent ab initio study performed by Nakamura, Takahashi, Okazaki and Morokuma[15] on the corresponding nitrogen analogues of the HPX_2 series allows by comparison a good rationalization of our results.

In addition, some mixed compounds HPXY with X, Y = O, S were also considered in order to analyze the preference of

Table I. SCF-Calculated or Experimental Geometrical Parameters (Å and deg) for RPX_2 Tricoordinated Phosphoranes (C_{2v} Symmetry)

compd	PX	∠XPX	PR	ref
HPO_2	1.432	135.0	1.398	this work
	1.435	136.0	1.420^a	25
	1.435	134.3	1.380	26
$ClPO_2$	1.428	135.1	1.980	this work
	1.441	135.0	1.986	11
HPS_2	1.889	134.1	1.404	this work
$Ar–PS_2{}^b$	1.900	126		8
$ClPS_2$	1.879	133.2	2.018	this work

^{a} Assumed value. ^{b} Experimental values obtained from X-ray diffraction study (Ar = 2,4,6-tri-*tert*-butylphenyl).

phosphorus to form a double bond with oxygen or sulfur in this class of molecules. In the last few years, an increasing effort has been devoted to the synthesis of mixed compounds such as glycerothiophosphocholine derivatives[16] coupled with the need for chiral thiophospholipids required for metabolism investigations. Recently, a new method of synthesis of thiolophospholipids based on thiono–thiolo isomerization of readily accessible thiophospholipids was reported.[17] The thiono–thiolo isomerization of trialkylthiophosphates $(RO)_3PS$ first investigated by Pishchimuka[18] in 1912 calls attention to the preference of phosphorus to form a double bond with oxygen rather than with sulfur. We here consider HPOS as the simplest model to analyze this preference in the case of low coordinated compounds.

Finally, vibrational spectra on some phosphoranes and phosphiranes were calculated and compared with experiment, when available.

2. Computational Details

Restricted Hartree–Fock (RHF) and spin-unrestricted Hartree–Fock (UHF) calculations were carried out by using the PSHONDO algorithm,[19] which is derived from the standard HONDO program package.[20] The PSHONDO algorithm is modified to include nonempirical pseudopotentials according to the technique of Durand and Barthelat.[21,22]

Valence atomic basis sets of four Gaussian orbitals have been optimized for the ground state of each atom by using pseudopotential RHF calculations. Two different basis sets were used. The first one is contracted in a double-ζ (DZ) form for each atom. Adding a 3d polarization function set to oxygen (η = 0.85), phosphorus (η = 0.57), sulfur (η = 0.54), and chlorine (η = 0.65) defines the DZd basis set. The second basis set is a triple-ζ (TZ) contracted set augmented with polarization functions on all atoms, including a set of p functions on hydrogen (η = 0.9). This basis set is designated herein as TZP.

Geometry optimizations were carried out at the SCF level with the DZd basis sets by using a direct gradient technique.[23] The convergence threshold for the gradient components was fixed at 5×10^{-3}. The triplet states of the phosphinidene species were optimized at the UHF level (in all cases, the value of $\langle S^2 \rangle$ remains within 1.5% of $S(S + 1)$).

Valence-shell configuration interaction (CI) calculations were performed at the SCF-optimized geometries according to the CIPSI algorithm.[24] A variational zeroth-order wave function was built up from an iterative selection of the most important determinants, the remaining ones being taken into account through a second-order Möller–Plesset perturbation. In the final step, we included in the zeroth-order wave function all determinants having a coefficient larger than 0.02 in the first-order wave function. Under these conditions, the subspaces which are variationally treated include about 45 determinants while the number

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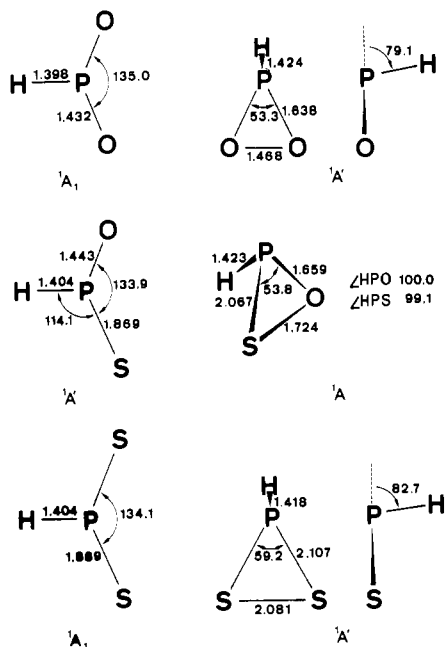(26) Lohr, L. L.; Boehm, R. C. *J. Phys. Chem.* **1987**, *91*, 3203.

Figure 1. SCF-optimized geometries (in Å and deg) for phosphorane and phosphirane structures.

of determinants involved in the perturbation treatment ranges from 2 × 10^6 (DZd basis set) to 5 × 10^6 (TZP basis set).

For dioxo and dithiophosphorane, we also used the CASSCF method to examine the validity of a one-determinant description.

3. Equilibrium Geometries

The geometries were optimized at the SCF/DZd level under symmetry constraints except for the nonsymmetrical molecules. Vibrational frequency calculations for the HPS$_2$ isomers were performed to make certain that the given symmetry does correspond to a real minimum on the potential energy surface (vide infra). Moreover, the planar form of some HPO$_2$ and HPOS isomers has been checked through an out-of-plane deformation calculation.

3.1. Phosphorane and Phosphirane Structures. The SCF optimized geometries of the phosphorane and phosphirane structures in their closed-shell ground states are shown in Figure 1.

All the phosphoranes present a planar form (C_{2v} symmetry for HPO$_2$ and HPS$_2$, C_s symmetry for HPSO). This geometry supports the familiar model of a three-center, four-electron π-system similar to the allylic system.

Our SCF calculated equilibrium geometries for the RPX$_2$ series are successfully compared with some other theoretical or experimental determinations in Table I. All these results are consistent with a large XPX bond angle (ca. 135°) except that for the aryl-substituted dithiophosphorane (126°). However, in the latter case, the geometry is obtained from X-ray diffraction analysis on a single crystal. Note that this structure determination leads to a torsion angle of the aryl group to the PS$_2$ plane of about 80°. This geometry prevents any conjugation between the π-system of the aryl group and the π electrons of PS$_2$. Under these conditions, HPS$_2$ may be considered as a reasonable model for this compound.

All along this work, the calculated PX bond length will be interpreted as a measure of the multiplicity of the bond. For the sake of comparison, typical values that correspond to formally single and double bonds have been optimized with the same basis sets in model compounds such as HP=X and H$_2$P—XH. The P=X bond is shorter than the single bond by 11.3% for oxygen compounds (1.463 vs 1.650 Å) and by 10% for sulfur compounds (1.912 vs 2.124 Å). The calculated PX bond lengths and the Mulliken net charges on P and X atoms for HPXY phosphoranes are listed in Table II. It is clear from this table that the PX bonds in phosphoranes are slightly shorter than the corresponding double bonds calculated in H—P=X. This shortening (2.5% for HPO$_2$ and 1.2% for HPS$_2$) can be explained by the presence of a second

Table II. SCF-Calculated P–X Bond Lengths (Å) and Mulliken Net Charges on Phosphorus and the X Atom for HPX$_2$ and HPXY Phosphorane Structures (X, Y = O, S).

	bond lengths		net charges		
compd	PO	PS	P	O	S
HPO	1.463		+0.552	−0.528	
HPO$_2$	1.432		+0.948	−0.530	
HPOS	1.443	1.869	+0.649	−0.536	−0.230
HPS$_2$		1.889	+0.263		−0.205
HPS		1.912	+0.172		−0.209

Table III. σ and π Mulliken d-Orbital Population on the Central Phosphorus Atom at the SCF/TZP Level for Phosphorane Structures

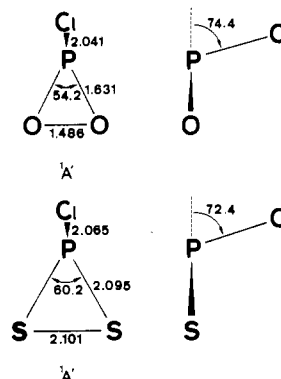|	d population on P		
compd	σ	π	tot.
HPO$_2$	0.354	0.137	0.491
HPOS	0.269	0.104	0.373
HPS$_2$	0.188	0.068	0.256
ClPO$_2$	0.362	0.162	0.524
ClPS$_2$	0.206	0.089	0.294

Figure 2. SCF-optimized geometries (in Å and deg) for substituted-chlorine phosphirane structures.
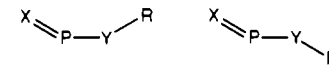
X atom bonded to phosphorus, leading to an increase of the positive net charge on phosphorus that strengthens the P=X bond dipole. Obviously, this effect is all the more important as the electronegativity of the atom added to HP=X is strong. On the other hand, a similar shortening is obtained by using electronegative substituents such as chlorine (see Table I).

In the case of nitrogen analogues, the calculations of Nakamura et al.[15] led to a N—O bond in HNO$_2$ shorter by 2.1% than that of CH$_3$NO while the N—S bond in HNS$_2$ is longer by 3.8% than that of HN=S. This different behavior of the nitrogen compounds is to be attributed to a different ordering of the relative electronegativities of oxygen and sulfur compared with that of nitrogen or phosphorus (O > N > S > P). This point will be discussed again in a later section.

As for the phosphirane structures (see Figure 1), they are nonplanar and all the bonds are normal single bonds. The calculated X–X bond lengths can be compared with the experimental ones, 1.463 Å for O–O in H$_2$O$_2$[27] and 2.061 Å for S–S in H$_2$S$_2$.[28] Note that the less constrained cycle is the dithiaphosphirane for which all the cyclic angles are close to 60°. The optimized geometries of substituted chlorophosphiranes are reported in Figure 2. The σ-attracting effect of the chlorine substitution leads to a slight shortening of the cyclic P–X bond and therefore to a lengthening of the X–X bond by 0.02 Å. The nature of the bonding between phosphorus and chlorine in the substituted phosphirane (Figure 2) and phosphorane (Table I) compounds can be deduced from the P–Cl bond length. Whereas in phosphirane, chlorine has only a σ attracting effect, a small p$_\pi$–d$_\pi$ back-bonding from Cl to P can be infered from the population of phosphorus 3d orbitals in phosphorane (see Table III). Al-

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Table IV. SCF-Optimized Geometries (Å and deg) for Phosphine Isomers XPYH (X, Y = O, S) and Chlorine-Substituted Isomers in Their $^1A'$ Ground State

	PX	PY	YR	∠XPY	∠PYR
s-cis-OPOH[a]	1.449	1.604	0.965	110.0	115.8
	(1.450)	(1.602)	(0.956)	(109.4)	(114.4)
s-trans-OPOH[a]	1.442	1.609	0.960	108.7	113.2
	(1.443)	(1.605)	(0.951)	(108.7)	(113.9)
s-cis-OPSH	1.454	2.105	1.341	108.5	96.9
s-trans-OPSH	1.452	2.106	1.339	107.3	94.7
s-cis-SPOH	1.898	1.612	0.963	109.8	115.7
s-trans-SPOH	1.886	1.622	0.961	108.3	111.6
s-cis-SPSH	1.903	2.098	1.338	110.0	99.0
s-trans-SPSH	1.900	2.098	1.339	107.2	95.4
s-trans-OPOCl	1.439	1.653	1.671	106.0	115.3
s-trans-SPSCl	1.898	2.114	2.031	104.2	100.5

[a] Optimized geometries obtained at the HF/6-31G + d level by Lohr and Boehm[26] are given in parentheses.
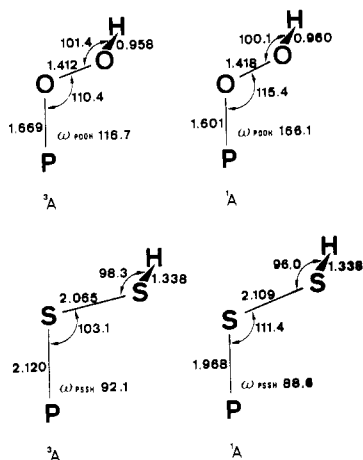
Figure 3. SCF-optimized geometries (in Å and deg) for singlet and triplet phosphinidene PXXH (X = O, S).

though a certain amount of p_π–d_π back-bonding from X to P can be observed from the π-type d population on phosphorus in HPX_2, the increase of this population in the Cl-substituted phosphoranes clearly indicates a contribution of a p-type lone pair on Cl. The appearance of this p_π–d_π back-bonding from Cl to P is responsible for the shortening of the P–Cl bond when going from dioxaphosphirane (2.041 Å) to dioxophosphorane (1.980 Å), leading to a stronger P–Cl bond in phosphorane. This unusually strong PCl bond was already reported and analyzed by Ahlrichs et al.[11] from IR spectroscopy studies of $ClPO_2$ in solid argon.

3.2. Phosphine Structures. The geometrical parameters of the phosphine isomers that can be described as X=P—YR (X, Y = O, S; R = H, Cl) are gathered in Table IV. In each case, the cis and trans conformers are found to be planar.

As is also observed for phosphoranes, the P=X bond is slightly shorter than the normal double bond, due to the replacement of hydrogen in X=P—H by a more electronegative substituent YH, which increases the net atomic charge on phosphorus. The P-Y bond is close to a typical single bond. However, this bond is also shorter than that optimized in H_2P—YH (Y = O, S) by a few percent, e.g. 2.8% for cis-O=P—OH and 1.2% for cis-S=P—SH. This gives evidence for a slight conjugation of the π lone pair of Y with the π system of the P=X bond (vide infra). It can be noticed that this shortening of the P—Y single bond disappears in the chlorine-substituted phosphine.

3.3. Phosphinidene Structures. The geometries of the singlet and triplet PXXH (X = O, S) phosphinidene isomers are displayed in Figure 3. All molecules are found to be nonplanar. The main factor governing their geometries is the conjugation of a lone pair
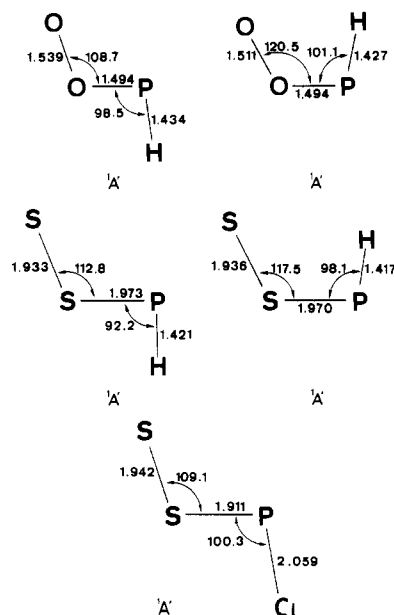

Figure 4. SCF-optimized geometries (in Å and deg) for closed-shell X-hypervalent species HPXX (X = O, S).

of the neighboring X atom with the orbitals of the phosphinidene end. In the singlet states, a π orbital on terminal P is empty and allows a full delocalization of the X lone pair
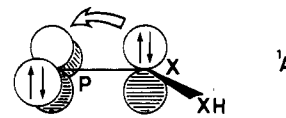
This leads to P–X bond lengths shorter than typical single-bond lengths (3% for X = O and 7.3% for X = S) giving an important more than single-bond character to this bond.

In the triplet states, the previously invoked delocalization is not favorable since it involves a three-electron, two-center interaction
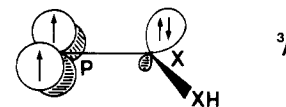
In triplet dioxophosphinidene, the P–O bond length is found to be ~0.02 Å longer than a P–O single-bond length. In triplet dithiophosphinidene, the P–S bond length is very close to that of a P–S single bond.

3.4. X-Hypervalent Species. The geometries for the closed-shell X-hypervalent isomers are reported in Figure 4. All these isomers are found to be planar.

The superoxophosphine is characterized by a very long O–O bond length, 1.511 Å in cis-HPOO and 1.539 Å in trans-HPOO. This can be easily explained by considering this closed-shell molecule as formed during the interaction between the triplet phosphinidene PH and the O_2 molecule. The highest occupied MO of O_2 in its ground state is a π^* MO containing two electrons. The delocalization of the two unpaired electrons of PH in this π^* MO leads to a significant lengthening of the O–O bond, which takes a value of the same order of magnitude as that in O_2^{2-}, i.e. 1.49 Å.[29] As expected, the PO bond length is then close to that of a P=O double bond.

Another possibility consists in the interaction between a PH phosphinidene and a O_2 molecule in two different spin states, leading to an open-shell diradical structure. We have only studied the resulting triplet diradical. Under these conditions, the molecule takes a nonplanar form with one unpaired electron located at phosphorus and the other one on the terminal oxygen atom. The
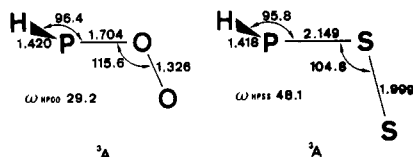
(29) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders Company: Philadelphia, PA, 1977.

Figure 5. UHF-optimized geometries (in Å and deg) for the triplet diradical structures of the HPXX isomers.
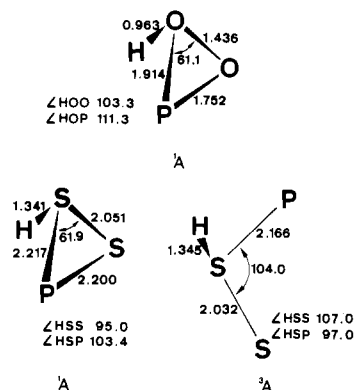
Figure 6. SCF-optimized geometries (in Å and deg) for some exotic isomers.

Table V. Relative Energies (kcal·mol⁻¹) for HPO₂ Isomers

isomer	state	SCF		CI	
		DZd	TZP	DZd	TZP
s-cis-HOPO	¹A′	0.0	0.0	0.0	0.0
s-trans-HOPO	¹A′	4.0	4.4	4.1	3.9
HP(O)₂	¹A₁	14.9	16.7	15.1	15.0
HPOO	¹A′	100.4	106.1	101.5	104.8
POOH	³A	97.4	103.8	115.1	
POOH	¹A	128.5	134.4	130.9	
HPOO	³A	106.8		135.0	
HOOP	¹A	146.9	153.5	152.2	
s-cis-HPOO	¹A′	146.9	153.1	153.1	
s-trans-HPOO	¹A′	147.7	153.7	155.6	

Table VI. Relative Energies (kcal·mol⁻¹) for HPS₂ Isomers

isomer	state	SCF		CI	
		DZd	TZP	DZd	TZP
s-trans-HSPS	¹A′	0.0	0.0	0.0	0.0
s-cis-HSPS	¹A′	0.3	0.2	0.2	0.1
HP(S)₂	¹A₁	8.2	6.0	5.7	3.6
HPSS	¹A′	12.7	12.7	17.5	16.7
s-trans-HPSS	¹A′	41.7	42.1	28.9	28.8
s-cis-HPSS	¹A′	41.5	42.3	28.9	28.9
PSSH	³A	14.5	16.2	33.5	
HPSS	³A	21.4		41.8	
PSSH	¹A	39.9	41.1	44.7	
HSSP	¹A	52.3	54.1	58.7	
HS(S)P	³A	49.3	50.6	72.0	

corresponding geometry optimized at the UHF level is shown in Figure 5. In that case, only one of the two unpaired electrons of PH is delocalized in the π* MO of O₂ and the lengthening of the O–O bond is less marked than precedently. The calculated O–O bond length, 1.326 Å, is close to the experimental value in O₂⁻, i.e. 1.32 Å.[29] Consequently, the P–O bond is slightly longer (by ca. 0.05 Å) than a formal single bond.

Sulfur analogues also present a similar open-shell triplet diradical structure with a nonplanar geometry and a S–S bond between a single and a double bond. Nevertheless, the corresponding closed-shell isomer appears to be quite different from its oxygen analogue due to the well-known hypervalent capacity of the sulfur atom. Both the P–S and S–S bonds in the cis and trans isomers are close to double bonds (see Figure 4) with a slight lengthening of about 2% for the S–S bond and 3% for the P–S bond. This suggests a small contribution of the two following structures, S=S⁺—P⁻—H and S⁻—S⁺=P—H, for the thiosulfinylphosphine.

3.5. Some Highly Hindered Structures. These structures contain at once two unfavorable factors such as hypervalency, a three-membered cycle, or unsaturation of phosphorus. The geometries of some of them are reported in Figure 6.

4. Relative Stability and Bonding

4.1. HPX₂ Isomers. Relative energies at different levels of calculation for all SCF/DZd-optimized geometries of HPX₂ isomers (X = O, S) are gathered in Tables V and VI. In all cases, the X=P—X—H phosphine structure is found to be the most stable isomer. Earlier theoretical works[26,30] on some HPO₂ isomers have already reported this structure to be more stable than the phosphorane or phosphirane structure. This theoretical prediction is now confirmed by the recent spectroscopic identification of cis-O=P—OH as photolysis product of an oxygen atom–PH₃ reaction.[12] However, the few available experimental works on the R-substituted compounds led to a phosphorane structure with R = Cl[11] and R = 2,4,6-tri-tert-butylphenyl.[7] As expected, the R substituent plays a qualitative role in the thermodynamical stability, and we will show later the influence of a chlorine substitution on the energy ordering of the various isomers. For sulfur-containing molecules, other low-lying structures (lower than 30 kcal·mol⁻¹) may be considered as thermodynamically stable. In oxygen analogues, the possibility of several stable isomers is reduced to the phosphine and phosphorane structures. For all these

low-lying structures, we improved our description by using a triple-ζ + polarization basis set at the CI level. Both basis set expansion and electron correlation treatments do not lead to substantial modifications of the energetic ordering. Note that the electron correlation effects are more important for the multiply bonded structures.[31] This results in an appreciable lowering of the hypervalent structures, i.e. the phosphorane and the HPXX isomers, in the case of sulfur compounds.

It is well-known that the usual valence of atoms of group 15 is three and that of atoms of group 16 is two. However, among the studied HPX₂ isomers, X and P are in various valence states according to the number of valence electrons involved in bonding. The resulting structures may be classified as usual valent species when X and P are in their usual valence states and as hyper- or hypovalent species for the cases in which X or P is in the corresponding unusual valence state. We propose to analyze the bonding nature of each type of structures according to this classification.

4.1.1. Usual-Valent Structures. Phosphorus and oxygen (or sulfur) are in their usual valence states only in phosphine and phosphirane isomers. The most stable of these two structures (phosphine) corresponds to an hydrogen atom strongly bonded to the most electronegative X atom. Independently of this electron factor, the formation of the X–X bond in the phosphirane structure leading to a three-membered ring introduces a geometrical constraint. Consequently, in both HPX₂ series, phosphirane is found to be energetically higher than phosphine due to these electronic and geometrical effects.

The energy difference between phosphine and phosphirane is much more pronounced for oxygen- than for sulfur-containing compounds, 101.5 kcal·mol⁻¹ vs 17.5 kcal·mol⁻¹, respectively. This difference is due to the relative covalent radii and electronegativities of oxygen and sulfur with respect to phosphorus.

At this point, we will focus our attention on the phosphine previously described as X=P—Y—H (X, Y = O, S). Figure 7 shows the π orbitals of phosphine compared with those of the three-center, four-electron π-system of phosphorane already studied in π-isoelectronic structures such as diiminophosphorane[25] and bis(methylene)phosphorane.[32] The valence electron structure

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(31) Trinquier, G.; Barthelat, J. C.; Satgé, J. *J. Am. Chem. Soc.* **1982**, *104*, 5931.
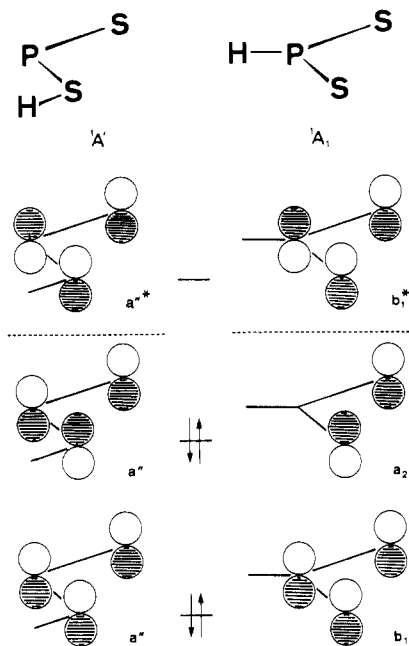
Figure 7. π molecular orbitals of phosphine and phosphorane structures.

Table VII. Net Charges on Terminal Atoms, Interatomic Distances (Å), and Stabilization Energies (kcal·mol⁻¹) for cis-X=P—Y—H (X, Y = O, S)

		$q(X)$	$q(H)$	$d(XH)$	ΔE(cis/trans)
X = O	Y = O	−0.57	+0.40	2.57	3.9
	Y = S	−0.55	+0.19	2.73	0.3
X = S	Y = O	−0.31	+0.40	2.83	3.6
	Y = S	−0.25	+0.18	3.00	−0.1

of the phosphine in its $^1A'$ ground state is $(1a')^2(2a')^2(3a')^2$-$(4a')^2(5a')^2(1a'')^2(6a')^2(2a'')^2(7a')^2(3a'')$. The frontier orbitals are formed by σ-type (HOMO) and π-type (LUMO) orbitals. Furthermore, the slight conjugation of the π lone pair of Y with the π-bonding system leads to some analogy with the phosphorane π-electronic structure. The a'' bonding and antibonding orbitals of phosphine correspond to the b_1 and b_1^* orbitals of phosphorane. A qualitative difference between these two systems appears in the nature of the highest π occupied orbital. This orbital, which is doubly occupied in both structures, is nonbonding in the phosphorane and bonding on P–X and antibonding on P–Y in the phosphine. These features of both phosphine and phosphorane π-systems allow a good understanding of the dynamic UV spectra registered during the alcoholysis of (2,4,6-tri-*tert*-butylphenyl)-dithiophosphorane. We are studying this reaction by means of a kinetical and theoretical approach, and our results will be described in a subsequent paper.[33]

The cis and trans conformers of dithiophosphine are quasi degenerate in energy whereas a slight stabilization of about 4 kcal·mol⁻¹ is calculated for the cis form of dioxophosphine. In an attempt to find a simple explanation for this preference, we show the net charges obtained by Mulliken population analysis and the distance between terminal atoms for the cis form in Table VII. The comparison of HPX₂ with HPXY (X, Y = O, S) cis phosphines reveals that cis/trans stabilization increases with the electrostatic attraction between H and the terminal atom. For a given terminal atom X, the cis/trans stabilization is actually observed when the net charge on H is strong.

For both HPX₂ phosphines, we investigated cis–trans isomerizations by rotation around the P–Y bond, keeping the geometry frozen at the trans form. The isomerizations occur with rotational barriers of 11.3 kcal·mol⁻¹ for dithiophosphine and of 13.5

Table VIII. Valence Energy Levels (eV) for the HPXY (X, Y = O, S) Phosphorane Structures Calculated with the TZP Basis Set

HPO₂ (C_{2v})		HPOS (C_s)		HPS₂ (C_{2v})	
π	a_2	−13.79	n_σ(S)	a'	−11.05	π	a_2	−10.06
n_σ	b_2	−14.17	π	a''	−11.24	n_σ	b_2	−10.50
n_σ	a_1	−14.19	n_σ(O)	a'	−13.32	n_σ	a_1	−10.95
π	b_1	−16.37	π	a''	−15.39	π	b_1	−13.25
	b_2	−17.10		a'	−15.89		b_2	−14.48
	a_1	−18.11		a'	−17.37		a_1	−15.99
	a_1	−21.89		a'	−21.20		a_1	−20.62
	b_2	−36.86		a'	−28.24		b_2	−26.51
	a_1	−38.51		a'	−37.52		a_1	−29.55

kcal·mol⁻¹ for dioxophosphine and the corresponding angles are 88.9 and 84.3°, respectively.

4.1.2. Hypervalent Structures. A major difference between the 2p-block and 3p-block atoms is their ability to be involved in hypervalent structures. The reasons invoked for the limit of four electron pairs (octet rule) for second-row elements such as nitrogen are the small size of these atoms, their high electronegativity, and the lack of low-lying 3d orbitals.[34]

However, theoretical studies always show a very small occupation of the 3d valence AO's of phosphorus for molecules such as PCl₅ and PCl₆⁻ for instance.[35] As can be seen in Table III, the 3d-orbital populations on phosphorus are ranging in phosphorane structures from 0.5 (HPO₂) to 0.3 electron (HPS₂). This reveals a small but evident 3d-orbital contribution. However, this contribution plays an essential role for the determination of equilibrium geometries. For instance, carrying out geometry optimization of dithiophosphorane without d functions abnormally lengthens the PS bond by 0.15 Å. Moreover, the separation into σ and π 3d populations shows that the main occupation occurs in the σ d orbitals with a significant proportion, 72.1% and 73.4% for HPO₂ and HPS₂, respectively. This can be explained by a delocalization of the X lone pairs onto the phosphorus vacant σ d orbitals. This result emphasizes that the phosphorus 3d orbitals play a prominent role to improve the σ-bonding system. Therefore, it seems to be difficult to consider the availability of d orbitals as a quantitative estimation of trends to hypervalency. It may be noticed that Schoeller and Niemann[32] have also observed a negligible contribution of phoshorus d orbitals in the π bond description of bis(methylene)phosphorane.

Valence energy levels for the HPXY (X, Y = O, S) phosphorane structures are given in Table VIII. The nature of the MO's in both HPO₂ and HPS₂ compounds is analogous. The highest MO's correspond to n_σ lone pairs and π orbitals. The details of the composition of the σ-type orbitals have already been analyzed by Schoeller and Lerch.[25] The frontier orbital is a π-type orbital for HPO₂ and HPS₂. Note the n_σ/π inversion for the mixed HPOS compound. According to Koopmans' theorem, the corresponding orbital energies could be compared with experimental ionization potentials, if available. As expected in the HPX₂ compounds, the π frontier orbital is raised in energy with decreasing electronegativity of X.

The size and electronegativity of the atoms remain the most important factors governing the trends to hypervalency. It seems then reasonable to classify oxygen, nitrogen, sulfur, and phosphorus in the following order with respect to this trend: O < N < ≪ S < P. In good agreement with this classification, phosphoranes are found to be the most stable of all the hypervalent structures. The closed-shell X-hypervalent species are higher in energy than their corresponding phosphorus hypervalent isomers by about 23 and 140 kcal·mol⁻¹ in HPS₂ and HPO₂ series, respectively (see Tables V and VI).

The MO's of the (thiosulfinyl)phosphine H—P=S=S are quite similar to that of dithiophosphorane showing the typical three-center, four-electron π-system. However, the small contribution of the resonance hybrid S=S⁺—P⁻—H ↔ S⁻—S⁺=P—H, in

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Table IX. Relative Energies (kcal·mol⁻¹) for HPOS Isomers

		SCF		CI	
isomer	state	DZd	TZP	DZd	TZP
s-cis-HOPS	$^1A'$	0.0	0.0	0.0	0.0
s-trans-HOPS	$^1A'$	3.5	4.0	3.8	3.6
s-cis-HSPO	$^1A'$	6.1	9.5	5.7	7.5
s-trans-HSPO	$^1A'$	6.3	9.8	6.1	7.8
HP(O)S	$^1A'$	13.5	15.1	11.7	10.9
HPOS	^1A	49.7	54.7	51.6	

which the inner sulfur atom is not formally tetravalent, shows the slight reluctance of sulfur to be involved in hypervalent structures.

The hypervalency of oxygen is still less evident, and the closed-shell HPOO structure is found to have an oxygen–oxygen antibonding HOMO. Indeed, the triplet diradical structure is energetically more favorable by 18.1 kcal·mol⁻¹. Similarly, the nitroso oxides are known to behave as peroxy radicals.[36] In sharp contrast with this situation, the closed-shell HPSS structure remains more stable than the diradical isomer by 12.9 kcal·mol⁻¹. This result clearly shows the previously mentioned difference between oxygen and sulfur with respect to hypervalency.

4.1.3. Hypovalent Structures. POOH and PSSH phosphinidenes are investigated in their low-lying singlet and triplet states. Both compounds are found to be triplet in their ground state as is usually the case for phosphinidenes.[37] The ^1A–^3A energy gap is greater for POOH than for PSSH, 15.8 vs 11.2 kcal·mol⁻¹. This can be related to the delocalization of a X lone pair onto phosphorus, which is more efficient in the case of sulfur and then stabilizes singlet dithiophosphinidene more strongly than singlet dioxophosphinidene.

It can be noticed that the role of 3d orbitals on phosphorus for both triplet and singlet phosphinidenes is significantly less important than in there hypervalent isomers, since the corresponding populations are about 0.1 electron for POOH and 0.05 electron for PSSH.

4.1.4. Other Very Unstable Structures. These structures, which accumulate unfavorable factors, are strongly unstable and cannot be considered as thermodynamically accessible compounds.

4.2. HPOS Mixed Compounds. Relative energies for HPOS isomers are gathered in Table IX. In this part of our study, we only consider the phosphine, phosphorane, and phosphirane isomers previously calculated as the most stable structures in both HPO₂ and HPS₂ series. We found the following energetical order— phosphine < phosphorane < phosphirane—which is the same as in the HPX₂ series. Of the two isomeric phosphines, the thiono form with a phosphorus–sulfur double bond S=P—O—H is found to be more stable than the thiolo form O=P—S—H by 7.5 and 4.2 kcal·mol⁻¹ for the cis and trans conformers, respectively. In order to analyze the preference of phosphorus to form a double bond with oxygen rather than with sulfur, we must consider the trans conformers. The energy difference between the cis conformers takes into account in addition the effect of the intramolecular electrostatic interaction, which most strongly stabilizes the thiono form (see Table VII). The bond strength between hydrogen and other atoms of the O–P–S fragment appears to be the preponderant factor governing the thermodynamical stability. If we consider the OPS fragment, the relative strengths of the PO and PS double and single bonds is in favor of the O=P—S– arrangment by about 15 kcal·mol⁻¹. However, this may be reversed by the difference between OH and SH bond strengths since OH is more stable than SH by about 20 kcal·mol⁻¹ (see Table X). Therefore, this leads to a relative stabilization of thionophosphine with respect to thiolophosphine in spite of the larger bond strength of the PO double bond vs the PS one. A similar result was already mentioned by Boatz and Gordon[40] in phosphinothioic acid.

Table X. Experimental or Theoretical[a] Bond Energies (kcal·mol⁻¹)

bond	energy	compd	bond	energy	compd
O—H	111[b]	H₂O	N—S	(46.8)[c]	NSH
N—H	93[b]	NH₃	N≡S	(81.5)[c]	HNS
S—H	88[b]	H₂S	P—O	(76)[d]	POH
P—H	78[b]	PH₃	P=O	(118)[d]	HPO
N—O	39[b]	NH₂OH	P—S	(48)[d]	PSH
N=O	142[b]	ClNO	P=S	(74)[d]	HPS

[a] Theoretical values are given in parentheses. [b] Reference 29. [c] From CEPA-SD calculation.[38] [d] Values obtained at the MP2 level with TZP basis set.[39]

Table XI. Relative Energies (kcal·mol⁻¹) for the Most Stable ClPX₂ Isomers (X = O, S)

compd	method	Cl—P(<X)(X)	Cl—P(X)(X) triangle	Cl—X—P=X	Cl—P—X=X
ClPS₂	SCF/DZd	0.0	0.3	14.4	32.1
	CI/DZd	0.0	7.4	19.2	22.9
ClPO₂	SCF/DZd	0.0	74.3	51.6	
	CI/DZd	0.0		49.2	

However, note that the electronic effect of an electronegative substituent could reverse the previous result.

4.3. Influence of a Chlorine Substitution. We only considered phosphine, phosphorane, and phosphirane ClPO₂ isomers since hypovalency on phosphorus and hypervalency on oxygen have already shown a great instability in HPO₂. For the ClPS₂ series, we studied, in addition, the (thiosulfinyl)phosphine, because we think that this hypervalent structure, already found in a reasonable energy range for HPS₂ isomers, must be stabilized by the increase of the electrophilic character of phosphorus due to the chlorine substitution. The other structures with chlorine atom bonded to sulfur (or oxygen) are not considered here. They are expected to be still more unstable than their hydrogen analogues since chlorine (unlike hydrogen) prefers to be bonded to an electropositive atom.

Relative energies for these ClPX₂ isomers (X = O, S) calculated with a double-ζ plus polarization basis set are reported in Table XI. The comparison with the HPX₂ series reveals three points: (i) the phosphorane structure appearing to be the most stable isomer in both ClPO₂ and ClPS₂ series; (ii) a relative stabilization of phosphirane with respect to phosphorane structure due to the chlorine substitution; (iii) the important role of correlation energies in predicting the most stable structure, i.e. the phosphorane structure, for the ClPS₂ series.

In good agreement with experiment,[11] the chlorine-substituted phosphorane is the most thermodynamically stable structure, whereas phosphine remains relatively high in energy. The destabilizing effect of chlorine substitution in phosphine is still more important in oxygen compounds than in sulfur compounds in conformity with the fact that chlorine–oxygen interaction is unfavorable compared with the chlorine–sulfur interaction (49 vs 65 kcal·mol⁻¹ for ClO and ClS bond energies[29] in Cl₂O and Cl₂S, respectively) according to the relative electronegativity of oxygen and sulfur.

5. Comparison with the Nitrogen Analogues

Now let us compare our results with the HNO₂ and HNS₂ analogues studied by Nakamura et al.[15] With respect to their thermodynamical stabilities, a similar energy ordering is observed for the nitrogen and phosphorus analogues in the oxygen series. Only nitrite H—O—N=O and nitro
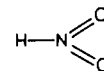
compounds may be considered as thermodynamically stable species. For the other structures, the cyclic dioxaziridine is upper in enegy than the monocoordinated-nitrogen isomers probably due

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Table XII. SCF/DZd Vibrational Frequencies (cm⁻¹) and Zero-Point Energies (kcal·mol⁻¹) for the Three Most Stable Isomers of the HPS₂ Series in Their Ground States[a]

symm	freq	assignt	symm	freq	assignt	symm	freq	assignt
a′	213	PS bend	a₁	247	PS₂ scissor	a″	428	PS₂ a-str
a″	354	torsion	b₁	509	PS₂ wag	a′	450	PS₂ scissor
a′	476	PS str	a₁	573	PS₂ s-str	a′	594	PS₂ s-str
a′	686	PS str	b₂	775	PS₂ a-str	a″	720	PS₂ rock
a′	852	SH bend	b₂	965	PS₂ rock	a′	879	PS₂ wag
a′	2616	SH str	a₁	2387	PH str	a′	2286	PH str
	ZPE = 7.4			ZPE = 7.7			ZPE = 7.8	

[a] A scale factor of 0.9 is used.

to the very constrained nature of the three-membered cycle. Apart from this case, the energetical ordering is identical with that of HPO₂ with the nitrite in its cis form as the most stable structure. On the other hand, the situation is very different for the HNS₂ and HPS₂ analogues. Dithiophosphine appears to be the most stable HPS₂ isomer while *N*-thiosulfinylamine is encountered as the most stable HNS₂ isomer. The comparison reveals that nitrogen behavior is different in both oxygen and sulfur series. The electronegativity ordering O > N > S > P shows that, unlike phosphorus, nitrogen is located between oxygen and sulfur. This ordering can simultaneously explain the differences observed in HNO₂ and HNS₂ series and the similarities in HPO₂ and HPS₂ series. Indeed, in any case, the most stable isomer (H—O—N=O, H—N=S=S, H—O—P=O, and H—S—P=S) corresponds to the strongest bond energy which can be obtained by bonding of hydrogen with the most electronegative atom of the molecule. As an example, the A–H bond energies are 93, 88, and 78 kcal·mol⁻¹ for NH₃, H₂S and PH₃, respectively (see Table X). Therefore, the S–H bond is favorable to stabilize the phosphine structure in HPS₂, whereas the sulfur hypervalent structure is favored in HNS₂ due to the strong value of the N–H energy bond. For both HNO₂ and HPO₂ analogues, the same most stable structure is observed since the O–H energy bond (111 kcal·mol⁻¹ in H₂O) is greater than the N–H and P–H energy bonds.

A major difference between nitrogen and phosphorus and between oxygen and sulfur with respect to hypervalency is clearly illustrated here. In the phosphoranes, PX bonds are found to be slightly shorter than double bonds (vide supra). This situation is also observed in the corresponding nitro compound whereas the NS bond in the dithionitro isomer is between a single and a double bond. This must be interpreted as suggested by the SCF-calculated PX bond lengths.
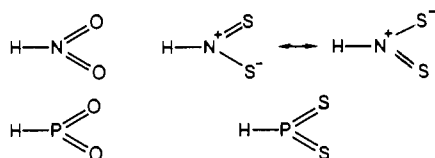
In addition to our classification in terms of intrinsic trends to hypervalency, it appears that the relative electronegativity of the central atom with respect to that of ligand atoms plays a crucial role to allow or prevent hypervalency.

This can be exemplified by the fact that nitrogen seems to accept hypervalency in nitro compounds more easily than in thionitro compounds. For the same reason, sulfur gives hypervalent bonds in nitrogen compounds more easily than in phosphorus analogues. Thus, in contrast with the (thiosulfinyl)phosphine, the inner sulfur atom in *N*-thiosulfinylamine is truly tetravalent.

Another consistent picture of the role of relative electronegativities is given by the monocoordinated nitrogen and phosphorus compounds, i.e. NXXH and PXXH in their singlet states. In such isomers, nitrogen forms with oxygen and sulfur real double and triple bonds, respectively. The resulting structures, N⁻=O⁺—OH and N≡S—S—H, implicate a determining participation of the X lone pair in the NX π-bonding. This delocalization is only

Table XIII. Comparison between Observed and Calculated SCF/DZd Vibrational Frequencies (cm⁻¹) of ClPS

	freq			
symm	calcd	exptl	assignt	scale factor
a′	255.9	229	bend	0.895
a′	510.5	462.4	PCl str	0.906
a′	792.0	716.1	PS str	0.904

partial in phosphorus analogues due to the small electron-attracting effect of phosphorus with respect to nitrogen.

A comparison with the HNSO mixed compounds investigated by Nonella et al.[5] gives a satisfactory example for the dissimilar ability of the second- and third-row elements to form multiply bonded compounds. In contrast with the phosphorus analogues, the mercaptoamine HS—N=O is calculated to be more stable than its thiono form, HO—N=S, by 6.5 kcal·mol⁻¹. The energy differences between a double and a single bond are about 103 kcal·mol⁻¹ for NO bonds and 34.7 kcal·mol⁻¹ for NS bonds (see Table X). On the other hand, the corresponding energy differences for phosphorus are 42 and 26 kcal·mol⁻¹, respectively. These values evidence the preponderant role of the strength of double bonds between the second-row atoms for stabilizing the thiolo form in nitrogen compounds, although OH bonding could be preferred to SH bonding.

6. Vibrational Frequencies

Table XII summarizes the SCF/DZd harmonic vibrational frequencies and the associated zero-point energies for the three most stable structures of the HPS₂ series at their optimized geometries. These values have been scaled by an uniform correcting factor of 0.9 since it is well-known that frequencies calculated at the Hartree–Fock level are generally overestimated.[41] This discrepancy arises for two reasons: (i) the calculated frequencies refer to strictly harmonic vibrations; (ii) the SCF approximation tends to slightly overestimate the true harmonic frequencies due to neglect of correlation effects.

We thus determined a set of scale factors by comparing our calculated SCF/DZd vibrational frequencies with the experimental values obtained on ClPS isolated in an argon matrix[42] (see Table XIII). The errors appear to be nearly constant, allowing systematic corrections to be made. Unfortunately, the infrared spectrum of ArPS₂ phosphorane (Ar = 2,4,6-tri-*tert*-butylphenyl) is complicated by the presence of a large substituent and only the experimental 789-cm⁻¹ band may be assigned to the antisymmetric PS stretching vibration.

It can be noted that the calculated zero-point vibrational energies only differ by 0.4 kcal·mol⁻¹, and this does not lead to any change in the energy ordering of the three most stable HPS₂ isomers.

The vibrational frequencies of the chlorine-substituted phosphoranes Cl-PX₂ (X = O, S) are given in Table XIV where they are compared to the available experimental values for ClPO₂.[11] Among the six vibrations exhibited by the planar ClPO₂ molecule

(41) Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 2310.

(42) Schnöckel, H.; Lakenbrink, M. *Z. Anorg. Allg. Chem.* **1983**, *507*, 70.

Table XIV. SCF/DZd Calculated (Scaled) and Experimental Vibrational Frequencies (cm^{-1}) for ClPX$_2$ Phosphoranes

symm	ClPO$_2$ freq		ClPS$_2$ freq calcd	assign
	calcd	exptl[a]		
b$_2$	305	(290)	217	PX$_2$ rock
a$_1$	404	(450)	227	PX$_2$ scissor
b$_1$	406	(400)	252	PX$_2$ wag
a$_1$	579	586	452	PCl str
a$_1$	1142	1143	614	PX$_2$ s-str
b$_2$	1452	1443	779	PX$_2$ a-str

[a] Reference 11. Values in parentheses are estimated values.

(C_{2v} symmetry), only the three stretching vibrations were experimentally observed. Our calculated frequencies for these stretching modes are in excellent agreement with experiment and confirm the experimental attributions. Moreover, the frequencies for the unobserved deformation modes are calculated to be close to their estimated values.

As concerns the ClPS$_2$ molecule, the PCl stretching mode is predicted to be shifted by 134 cm^{-1} with respect to its value in ClPO$_2$. This value is close to that observed for a normal PCl single bond as in ClPS, once more indicating that the p$_\pi$-d$_\pi$ back-bonding from Cl to P is much less pronounced in chlorodithiophosphorane than in chlorodioxophosphorane.

7. Validity of the One-Determinant Description for HPX$_2$ Phosphoranes

Although a single-determinantal wave function leads to a symmetrical structure for the phosphoranes, these typical three-center, four-electron π-systems would be better described by a multiconfigurational wave function. In order to improve our description, we have carried out CASSCF calculations, taking the three π orbitals as active orbitals at the DZd level.

The CASSCF geometry optimization of HPS$_2$ gives a C_{2v} structure with the following parameters: PS, 1.902 Å; PH, 1.402 Å; SPS, 133.3°. In contrast with this result, HPO$_2$ undergoes a geometry change leading to a nonsymmetrical structure of C_s symmetry

$$H-P^+\diagup^{\diagup O_a}_{\diagdown O_b^-}$$

(PO$_a$, 1.432 Å; PO$_b$, 1.461 Å; PH, 1.396 Å; HPO$_a$, 113.2°; HPO$_b$, 111.7°). The PO$_a$ double bond is observed to be enhanced with respect to that in HPO by the presence of the second oxygen atom as in the SCF description. The nature of the PO$_b$ bond can be supposed to be the same as in H$_3$PO (1.470 Å), already analyzed by Boatz and Gordon[40] and described as a strong donor single bond augmented by a noticeable amount of π back-bonding from oxygen to phosphorus. However, the energy stabilization of this nonsymmetrical structure with respect to a C_{2v}-constrained CASSCF optimization is only 1 kcal·mol^{-1}.

It can be noted that for the analogous HNO$_2$ compound the CASSCF gradient optimization performed by Nakamura et al.[15] does not modify the C_{2v} symmetry obtained at the SCF level.

8. Concluding Remarks

The main results of our study of the equilibrium geometries and relative stabilities of HPX$_2$ (X = O, S) isomers can be summarized as follows:

1. Despite the fact that phosphorane-λ^5,σ^3 is the only experimentally isolated structure among the RPX$_2$ (X = O, S, Se) molecules, our calculations predict the phosphine as the most stable HPX$_2$ model compound. This prediction is supported by a recent spectroscopic identification of the HOPO intermediate.[12]

2. Relative electronegativities of the atoms play a crucial role in determining the structure and the thermodynamical stability of the different isomers. Indeed in the chloro-substituted series, the phosphorane-λ^5,σ^3 is found to be the most stable isomer in agreement with experiment.

3. For the mixed compounds, the comparison with nitrogen analogues shows that the π-interaction in such compounds is prominent and the thiolo form of amine is found to be more stable than the thiono form. In sharp contrast, in phosphorus mixed compounds, the σ interaction appears to be the major factor governing the stability leading to the thiophosphine as the most stable form. Thus, the σ electronic effects of the substituent must be considered in order to answer the basic question concerning the preference of phosphorus to form a double bond with oxygen or rather with sulfur. As an example, the substitution of hydrogen by an electronegative atom could logically stabilize the PO double bond in the mixed phosphine.

4. The ability of phosphorus to be involved in hypervalent structures is essentially due to its weak relative electronegativity with respect to oxygen and sulfur, and the availability of 3d orbitals does not seem to be a sufficient factor to allow hypervalency.

The behavior of diselenonitrogen and -phosphorus analogues becomes somewhat predictable because of the close dependence of thermodynamical stability on electronic effects in such compounds. Thus, we propose the (selenoseleninyl)amine H—N=Se=Se, the hydroselenoselenoxophosphine Se=P—Se—H and the diselenoxophosphorane HP(Se)$_2$ among the lowest lying structures in HNSe$_2$ and HPSe$_2$.

All calculations of this work have been carried out from a thermodynamical viewpoint. The kinetic factors which may control the synthesis of phosphorane-λ^5,σ^3 are not considered here. We will extend our study to the monomolecular or bimolecular phosphorane–phosphine isomerization and to the phosphorane dimerization in HPS$_2$ compounds. The latter calls particular attention to the reaction of sulfur with primary phosphines, which leads to the phosphorane in its monomeric or dimeric form.