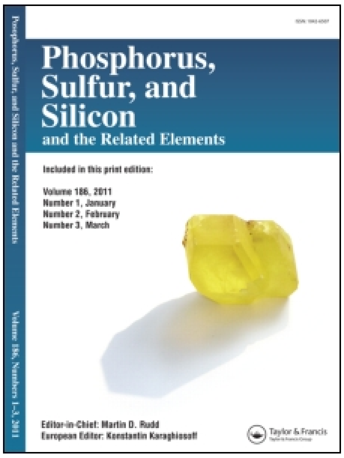

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THE ELECTRONIC STRUCTURE AND BONDING IN THE THIOPHOSPHORYL CATION PS^+

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A CNDO/2—SCF—MO treatment of PS^+ cation is carried out with and without 3d orbitals on phosphorus and sulfur. The CNDO/2 Wiberg bond index suggests an essentially triple bond, in accordance with the bond order of 2.94 "experimentally" determined from the observed infrared spectrum. Conditions for stabilizing this unusual cation by coordination can be inferred from these calculations.

INTRODUCTION

In view of our interest in the electronic structure of thiophosphorus compounds, especially in the peculiarities of the phosphorus-sulfur bonds[1] we turned to investigating one of the simplest systems containing this bond—the thiophosphoryl cation PS^+. Despite the simplicity, the electronic structure of this molecular ion may provide useful general information about the interaction of phosphorus and sulfur orbitals, relevant to understanding the bonding in their inorganic and organometallic derivatives.

In addition, the PS^+ cation is of theoretical interest, aroused by a comparison with the much more investigated homologues, NO^+ and NS^+. The salts of NS^+ cation can be generated by reaction of NSF with strong Lewis acids and isolated as $NS^+PF_6^-$ or $NS^+AsF_6^-$ salts.[2,3] Much more interesting was the finding that this cation can coordinate as a ligand in such complexes as $Mo(NS)(S_2CNR_2)_3$,[4-6] $C_6H_5Cr(NS)(CO)_2$,[7] $M(NS)Cl_3L_2$, M = Ru, Os, L = PPh_3, $AsPh_3$.[8] This makes it somewhat analogous to NO^+ ligand. The partial replacement of a second row element in NO^+ with a third row element, to give NS^+ and then full replacement to give PS^+ raises the question of what role can the d orbitals play in the description of the electronic density in these diatomic species.

The PS^+ cation, discussed here is not stable and no compounds containing it are known; however, it can be detected by spectroscopic methods when phosphorus sulfide (PS) is ionized in gaseous phase.[9-11]

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CALCULATIONS

In order to obtain some information about the PS^+ cation, we resorted to the semiempirical SCF–MO calculations, at the CNDO/2 level,[12] using the parameters given by Santry and Segal.[13] Due to divergencies encountered at some PS bond lengths, the PARAMOL-2 program of Zhogolev and Volkov[14] was modified following the method of Mehrotra[15] and Maslov.[16] According to these authors, at each iteration step, the Fock matrix F is replaced by $F + F'$, where $F' = b(E - P)$, P is the usual density matrix, E is the unity matrix and b is a convenient positive number. It may be shown[15] that, when convergence is reached, the F and F′ matrixes have the same eigenvalues and eigenvectors for the first n double occupied molecular orbitals. In all these calculations we used a value of 2 a.u. for b, and the SCF process was interrupted when ΔE was smaller than 10^{-4} a.u.

We are fully aware that the CNDO/2 method, though still frequently used in the literature, is not the most reliable of the available procedures for MO calculations. However, with a careful and critical examination of the results given by the CNDO/2 method, it can provide preliminary information which may be useful to have, before an ab initio approach would be used for a more accurate investigation.

RESULTS AND DISCUSSION

Taking into account the number of available 3d orbitals for extending the basis set, the following four cases were considered:

	P	S
A	3s, 3p	3s, 3p
B	3s, 3p, 3d	3s, 3p
C	3s, 3p, 3d	3s, 3p, 3d
D	3s, 3p	3s, 3p, 3d

The first step was to establish the optimal interatomic distance, by computing the energy minima vs. the PS bond length. Figure 1 summarises the results of the total energy dependence on the bond length for each chosen orbital basis.

The PS bond length varies from 1.91 Å (3d orbitals only on sulfur—case D) to 1.99 Å (when no 3d orbitals are used in calculations—case A). It can be noticed that the inclusion of all 3d orbitals (C) does not cause a large decrease in bond length compared to case A (1.961 Å versus 1.966 Å). No experimental PS^+ bond length is known and the validity of these results can be evaluated only indirectly. Thus, to get an idea about the reliability of the CNDO/2 derived bond lengths we used the observed IR frequency of 844.6 cm^{-1} [11,17] which gives a force constant of 6.617 mdyne/Å. Now, by means of the well known Gordy's formula[18] $f_{PS} = 1.67\, N_{PS}(X_P X_S/R^2)^{3/4} + 0.30$, the interatomic distance R can be estimated by taking for X_P and X_S the Pauling electronegativities. Table I includes the values of calculated force constants over a reasonable range of bond orders N_{PS} and bond lengths R.

These data show that force constants close to the experimental one are obtained only when the bond order has a value lying somewhere around 3 and the bond

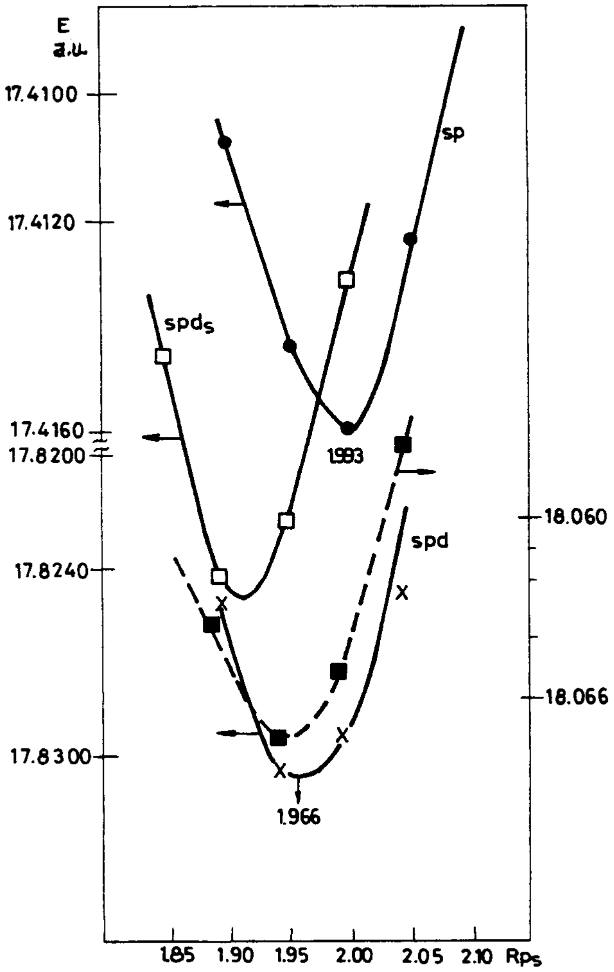

FIGURE 1 Total energy dependence on R_{PS} and basis set ●—case A (sp); ■—case B (spd$_P$); ×—case C (spd$_{S+P}$); □—case D (spd$_S$).

TABLE I

PS$^+$ force constants* as a function of R_{PS} and bond order N

N \ R_{PS}	1.85	1.90	1.95	2.00	2.05	2.10
1.50	3.65	3.52	3.40	3.29	3.17	3.07
2.00	4.77	4.60	4.43	4.27	4.13	4.00
2.50	5.89	5.67	5.47	5.27	5.09	4.92
3.00	7.00	6.74	6.50	6.27	6.05	5.85
3.50	8.12	7.81	7.53	7.26	7.01	6.77

*Experimental value: 6.517 mdyne/Å.

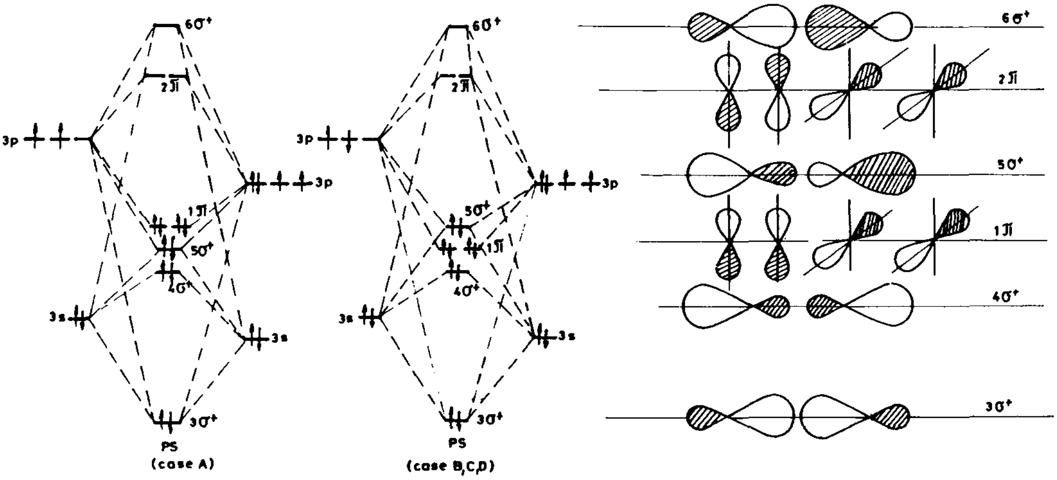

FIGURE 2 The MO diagram for PS^+ cation. To maintain the clarity the 3d orbitals are not explicitly drawn. Their influence is "felt" by $5\sigma^+ - 1\pi$ inversion (see the text).

lengths varies between 1.90 and 1.95 Å. There is no other combination of R and N_{PS} values leading to an acceptable force constant. Since case A produces a too long phosphorus–sulfur equilibrium distance, it can be assessed that a relatively correct PS^+ bond length can be obtained only by including in the basis set the 3d orbitals on P or/and S atoms.

The second step was to determine the molecular orbitals, bond orders and other data which can be derived from these, at the optimum bond lengths. The molecular orbitals sequence is shown in Figure 2 (for the sake of simplicity, the contribution of 3d orbitals is not shown explicitly).

Five electron pairs supplied by the valence shells of the two atoms are shared by three σ^+ type orbitals and one double degenerate πMO. One of the σ^+ ($3\sigma^+$) and the 1πMO have clear bonding character, while $4\sigma^+$ and $5\sigma^+$ have slightly antibonding and slightly bonding nature, respectively. Hence, the expected bond order is 3. Thus the bond order suggested by the experimental force constant is supported by a simple counting of the electron pairs involved in bonding.

An alternative picture of the electronic distribution is offered by using an Edminston-Ruedenberg localization.[19] The result is that besides a sigma and two π bonds, two electron pairs appear highly localized on sulfur and phosphorus, respectively (see Figure 3).

The density matrix P affords another approach to the bond order, using the definition of Wiberg,[20] Borisov[21] and Armstrong *et al.*[22]: $W_{AB} = \Sigma_{i \in A} \Sigma_{j \in B} P_{ij}^2$. These values reflects almost a triple bond, in a remarkable agreement with the predictions based on electron pairs counting and the bond order deduced from the PS^+ force constant through Gordy's formula. It is noticeable that Siebert's empirical formula[23] corrected by Goubeau,[24] relating force constants and bond orders, practically gives the same bond order -2.94. This might have an important computational

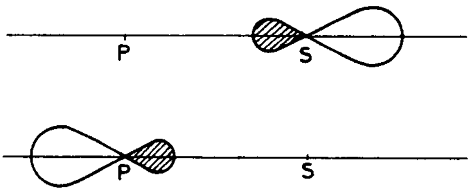

FIGURE 3 Localized electron pairs on sulfur (the lowest MO) and phosphorus (the highest occupied MO).

TABLE II

Orbital population and Wiberg bond index for PS$^+$

Atoms orbitals	P		S	
	A	C	A	C
3s	1.8754	1.7317	1.8713	1.7682
$3p_y$	0.6673	0.6508	1.3325	0.9327
$3p_z$	0.6673	0.6508	1.3325	0.9327
$3p_x$	1.0632	0.8621	1.1902	1.3035
$3d_{xy}$	—	0.1897	—	0.2267
$3d_{yz}$	—	0.0000	—	0.0000
$3d_{z^2}$	—	0.0352	—	0.0502
$3d_{xz}$	—	0.1897	—	0.2267
$3d_{x^2-y^2}$	—	0.1056	—	0.1452
Charge	0.7266	0.5842	0.2733	0.4159
W_{PS}	2.77	3.50		

consequence: CNDO/2 bond orders used together an appropriate empirical formula could determine in a cheap way the unknown stretching force constants.

Orbital populations are given in Table II.

The positive charge of molecule is distributed between the two atoms, being more localized on phosphorus (A, B, and C), in accordance with the difference of the electronegativities.

The data show that $3d_\pi$ orbitals ($3d_{xy}$ and $3d_{yz}$) have a relatively greater importance than $3d_\sigma$ ($3d_{x^2-y^2}$ and $3d_{z^2}$). This result is supported also by ab initio calculations on another system with a virtual triple PS bond: SPF_3.[25]

In the light of this finding the $5\sigma^+ - 1\pi$ inversion caused by the inclusion of 3d orbitals in the basis set (see Figure 2) is perfectly understandable. Both $3d_\sigma$ and $3d_\pi$ orbitals lead to the lowering of the occupied MOs they are mixed in, but the lowering caused by $3d_\pi$ is larger, consequently the 1π level will be shifted down to $5\sigma^+$. This way the fundamental term of molecule is $^1\Sigma^+$ instead of $^3\Sigma^+$ (if 1π were above $5\sigma^+$), in accordance with the experiment.[17]

SOME CHEMICAL CONSEQUENCES OR POSSIBLE FUTURE OF THIS CATION

The coordination chemistry of the nitrosyl cation NO^+, the formal second row analog of the title compound is well developed.[26,27] If the oxygen atom of the nitrosyl group is replaced by a sulfur atom, the thiazenium cation NS^+ is obtained, and its chemistry is quite well known by now.[2,3] The coordination compounds in which the thiazenium cation NS^+ is coordinated to a metal center are remarkably stable.[4-8] This cation acts as a ligand in a manner similar to NO^+, through the nitrogen atom, the M—N—S angle being almost linear (cca. 172°).[6,7]

As the highest occupied MO in the thiophosphoryl cation PS^+ is an electron pair well localized on the phosphorus atom (Figure 3) and also, vacant, relatively low lying π^* orbitals are available for back donation, the idea of extending the analogy of coordinated nitrosyl and thiazenium cations down to the thiophosphoryl cation becomes very attractive.

There are of course, many factors which could influence the stability of such hypothetical system, containing $M—:P \equiv S:$ units. However, our results suggest two important conditions to be realized in order to stabilize the coordinated PS^+.

(a) Due to the fraction of positive charge localized on phosphorus, the thiophosphoryl cation would be a poor σ donor ligand, so the metallic site has to be a very good acceptor in the M—P direction;

(b) A good π donor metallic centre would decrease the positive charge on phosphorus and thus enhance the donating ability of this ligand. Hence, a possible design of a coordination compound, let say $X_pML_q(PS)$, containing a thiophosphoryl cation woud require:

—a metal M of group VI–VIII, in a low oxidation state as a central ion

—a ligand X trans to PS^+, highly electronegative, able to form mostly σ bonds (a halogen might be well suited in this case)

—ligands L with relatively poor π accepting properties (PR_3, PPh_3, $AsPh_3$ and related compounds) which avoid a large decrease of the π electron density on the metal, thus making it available for bonding with PS^+.

The above considerations challenge the experimental chemist to find the right conditions under which a thermally or photochemically generated PS^+ cation would react with an appropriate transition metal (or organometallic) substrate, to form an isolable complex.

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