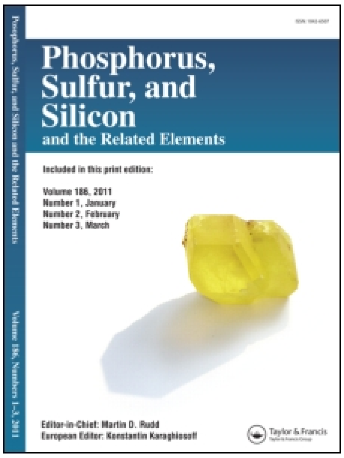

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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**To cite this Article** Silaghi-dumitrescu, Ioan and Haiduc, Ionel(1982) 'BONDING IN ORGANOPHOSPHORUS DITHIO ACIDS. A CNDO/2 CALCULATION OF ELECTRONIC STRUCTURE', Phosphorus, Sulfur, and Silicon and the Related Elements, 12: 2, 205 — 212

**To link to this Article: DOI:** 10.1080/03086648208077448

**URL:** http://dx.doi.org/10.1080/03086648208077448

*Phosphorus and Sulfur*, 1982, Vol. 12, pp. 205–212
0308-664X/82/1202-0205/$06.50/0

# BONDING IN ORGANOPHOSPHORUS DITHIO ACIDS. A CNDO/2 CALCULATION OF ELECTRONIC STRUCTURE

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(*Received February 2, 1981; in final form August 17, 1981*)

A CNDO/2 study on the compounds $(CH_3O)_2P(S)SH$ (A), $(CH_3O)_2PSS^-$ (A′), $(C_3H_7O)_2P(S)SH$ (B), $(CH_3)_2P(S)SH$ (C) and $(CH_3)_2PSS^-$ (C′) is reported. For A and A′ both sp and spd basis was employed, but, for C and C′ only an spd basis was used. The inclusion of the phosphorus 3d orbitals into the basis set has three important consequences: (a) the lowering of the total energy of the system; (b) the decrease of the electronic charge on the phosphorus atom; and (c) the increase of the P—S bond order.

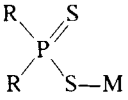
The ratio of the P—(S) and P—SH bond orders agrees well with the force constant ratio $f_{P=S}/f_{P-S}$ only when spd basis is employed, suggesting that, for a correct description of the electronic density in the molecule, the 3d orbitals on the phosphorus should be included in the basis set.

The P—S bond length for C′ derived by a parabolic fitting is in a good agreement with the experimental X-ray data.

## INTRODUCTION

The electronic structure of the phosphorus-sulfur bond in inorganic and organic monothio-derivatives has been the subject of a large number of molecular orbital investigations.[1] On the contrary, the phosphorus dithio-derivatives have not been studied as frequently from this point of view, and to our knowledge, only a few molecular orbital calculations have been reported on such compounds.[2]

This paper is a part of a larger program devoted to the study of the structural behavior of $R_2PS_2^-$ moiety (R being an alkyl or alkoxy group) in certain circumstances. Thus, we are particularly interested in defining the conditions governing the ability of $R_2PS_2^-$ ligands to act as monodentate (I), bidentate (II-symmetric, or asymmetric-III) or bridging (IV), by interaction with an electron acceptor M: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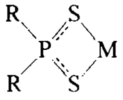
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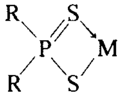
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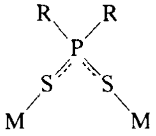
IV

There are confirmed examples for all structural types I–IV established by X-ray diffraction in various classes of compounds.[3]

Another aim of the program is to extract information about the force constants of the P—E bonds from MO characteristics and to correlate them with the values obtained from normal coordinate analysis.[4] There is some hope for this prospect, largely due to recent CNDO-force method calculations by P. Pulay *et al.*[5]

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## CALCULATIONS

(a) Concerning the parameters used in the calculations, we have to emphasize the fact that we have not attempted to obtain absolute values of the molecular parameters calculated, but rather their relative values in the series of molecules investigated; thus, from this point of view, any parametrization is as good as another.

The calculations have been performed within the CNDO/2 SCF-MO scheme, with the parameters given by Santry and Segal.[6] The computer program PARAMOL 2 has been taken from Zhogolev and Volkov[7] and modified by us: (a) to suit the operating system of the Roumanian-made Felix C-256 computer, and (b) to overtake the divergency difficulties, using the "levels shift" method of Saunders[8] in the elegant manner suggested by Maslov.[9]

The following molecules and ions have been investigated: $(CH_3O)_2P(S)SH$ (A); $(CH_3O)_2PSS^-$ (A′); $(C_3H_7O)_2P(S)SH$ (B); $(CH_3)_2P(S)SH$ (C); and $(CH_3)_2PSS^-$ (C′).

(b) In the calculations we have used 1*s* for hydrogen and 2*s*, 2*p* Slater-type valence orbitals for carbon and oxygen atoms. Concerning the phosphorus and sulfur orbitals, both *sp* and *spd* bases may be used. Since many spectroscopical data[10] suggest a partial double character for the P—S bond, the *sp* basis seems to be inadequate. Ab initio[11] and CNDO/2[12] treatment of $SPF_3$ and $SP(NH_2)_3$ respectively, revealed that the phosphorus-sulfur bond can be accurately described by using only the phosphorus 3d orbitals and neglecting those on sulfur, while CNDO/2 calculations on $SPF_{3-n}Cl_n$[13] with *spd* orbitals on both P and S lead into difficulties in rationalizing the results obtained.

However, from all three calculations, a small $\sigma$ and a larger $\pi$ contribution of P 3d orbitals to the phosphorus-sulfur bond can be inferred. We have employed only the phosphorus 3d orbitals which could have importance in $\pi$ bonding, namely $3d_{z^2}$ and $3d_{x^2-y^2}$.[14]

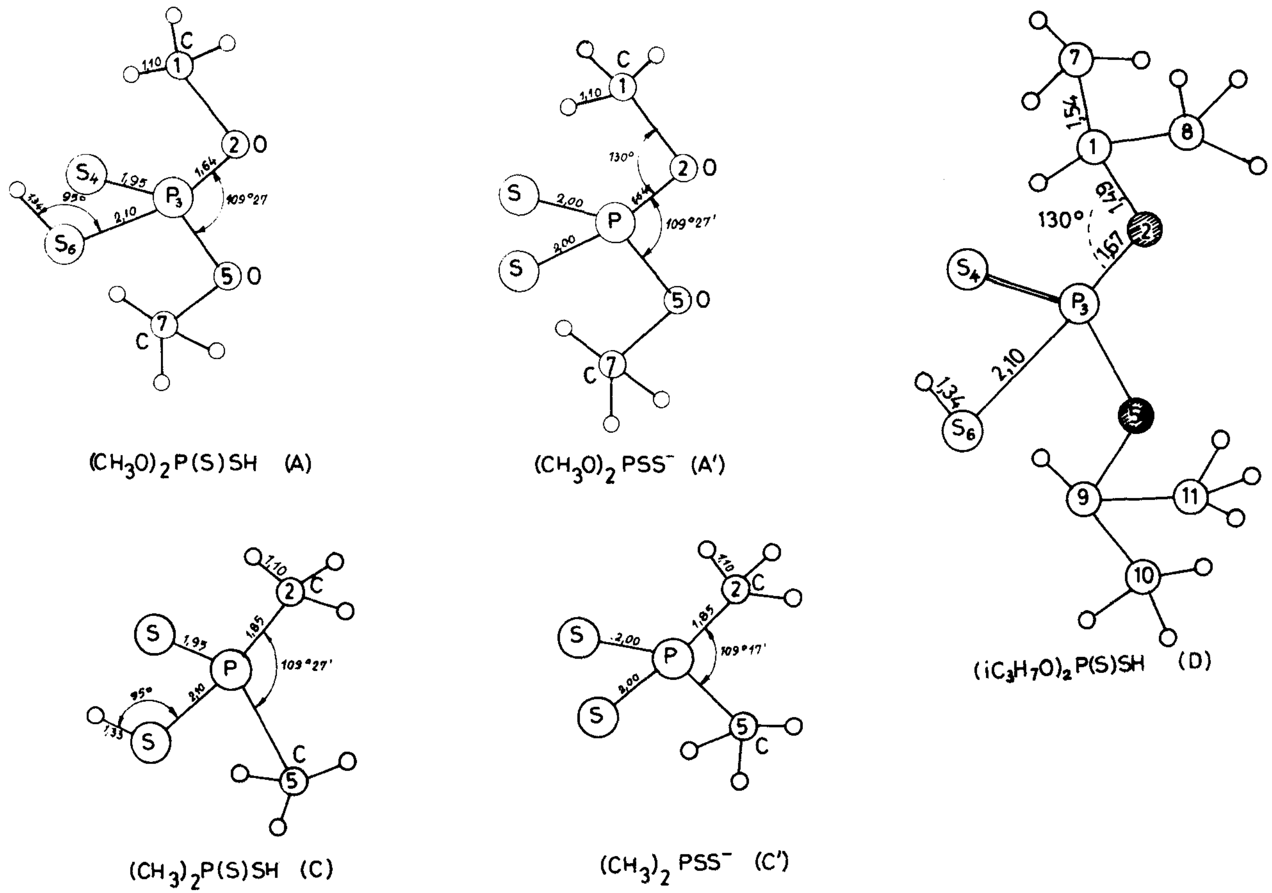
(c) No experimental geometries are known for the compounds listed above (excepting A′[15]) so we have started the calculations with the assumed geometries shown in Figure 1. For C′ a partial optimization of the geometry has been undertaken.

## CALCULATED QUANTITIES

The output of the CNDO program cited above includes, in addition to the usual data, the partition of the total energy into the covalent and ionic contribution and also dipole moments and Wiberg bond indices computed by subroutines programmed in our laboratory.

Two papers (2b,2c) containing CNDO/2 calculations on dithiophosphato anions have been published so far. Both of them, however, deal with the interpretation of photoelectron spectra of their Ni and Sn derivatives. Since these authors do not mention the geometrical parameters used in calculations, the energy levels obtained cannot be compared with our results. We stress only that qualitatively our bonding scheme is approximately the same as that obtained by these authors. Particularly, the highest occupied molecular orbitals and the lowest unoccupied ones are in phase and antiphase combinations of the sulfur 3p orbitals, respectively.

For the sake of brevity, the coefficients of the molecular orbitals are not given here. Because the density matrices are more suitable in discussing the bonding features than the molecular-orbital coefficients themselves, we focus attention on them and also on the quantities derivable from them.



$(CH_3O)_2P(S)SH$ (A)

$(CH_3O)_2PSS^-$ (A′)

$(iC_3H_7O)_2P(S)SH$ (D)

$(CH_3)_2P(S)SH$ (C)

$(CH_3)_2PSS^-$ (C′)

FIGURE 1 The geometrical parameters of the molecules investigated. Tetrahedral angles were assumed for the unspecified angles.

TABLE I

Electronic Charge Distribution and Orbital Population for the compounds A, A′, C, C′

| | | Compound | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | A | | A′ | | | C | C′ |
| | Atom | *sp* | *spd* | *sp* | *spd* | Atom | *spd* | *spd* |
| 2s | | 1.0677 | 1.0624 | 1.0679 | 1.0637 | | 1.0583 | 1.0705 |
| 2p | $C_1$ | 2.8175 | 2.8280 | 2.8431 | 2.8493 | $C_2$ | 3.0360 | 3.0663 |
| Charge | | 0.1146 | 0.1113 | 0.0887 | 0.0868 | | −0.0945 | −0.1369 |
| 2s | | 1.0675 | 1.0623 | 1.0681 | 1.0639 | | 1.0433 | 1.0580 |
| 2p | $C_7$ | 2.8166 | 2.8255 | 2.8441 | 2.8508 | $C_5$ | 3.0505 | 3.1807 |
| Charge | | 0.1156 | 0.1121 | 0.0876 | 0.0858 | | −0.0939 | −0.1389 |
| 3s | $P_3$ | 1.3311 | 1.2641 | 1.3747 | 1.2927 | $P_3$ | 1.2636 | 1.2771 |
| 3p | | 2.6564 | 2.4750 | 2.6194 | 2.4351 | | 2.8787 | 2.8657 |
| 3d | | — | 0.4355 | — | 0.4514 | | 0.3882 | 0.3883 |
| Charge | | 1.0122 | 0.8235 | 1.0056 | 0.8206 | | 0.4693 | 0.4718 |
| 3s | | 1.8867 | 1.8489 | 1.8953 | 1.8634 | | 1.8804 | 1.8882 |
| 3p | $S_4$ | 4.6014 | 4.5126 | 4.7175 | 4.6789 | $S_4$ | 4.5372 | 4.6941 |
| Charge | | −0.4882 | −0.3616 | −0.6130 | −0.5425 | | −0.4178 | −0.5824 |
| 3s | | 1.8138 | 1.7605 | 1.8953 | 1.8634 | | 1.8147 | 1.8882 |
| 3p | $S_6$ | 4.3452 | 4.3773 | 4.7176 | 4.6789 | $S_6$ | 4.2939 | 4.6941 |
| Charge | | −0.1645 | −0.1379 | −0.6130 | −0.5424 | | −0.1088 | −0.5824 |
| 2s | | 1.6822 | 1.6602 | 1.6892 | 1.6637 | | — | — |
| 2p | $O_2$ | 4.7024 | 4.6741 | 4.7253 | 4.7271 | | — | — |
| Charge | | −0.3548 | −0.3354 | −0.4166 | −0.3910 | | — | — |
| 2s | | 1.6822 | 1.6603 | 1.6892 | 1.6637 | | — | — |
| 2p | $O_5$ | 4.6726 | 4.6775 | 4.7274 | 4.7274 | | — | — |
| Charge | | −0.3553 | −0.3358 | −0.4168 | −0.3912 | | — | — |

## RESULTS AND DISCUSSION

(a) The electron density reflected in the atomic charges and orbital populations given in Table I shows that the most important result of introducing the 3d orbitals is the decrease of the charge on the phosphorus atom, accompanied by an increase in the charge on sulfur and oxygen atoms. The result is a shift of electron density from sulfur and oxygen into the empty 3d orbitals on the phosphorus atom and a more reasonable charge on the phosphorus atom.

In order to check whether or not this shift is neutralized by the normal inclusion of the sulfur 3d orbitals, we have carried out† a set of calculations in which all 3d orbitals have been included in the basis set. The atomic charges for compound C′ are given in Table II.

As can be seen, the enlargement of the basis set does not neutralize nor reverse the direction of the electron flow. On the contrary, it is enhanced, and finally, a quite large negative charge on phosphorus is attained.

The sign of the charges on the atoms in A′ and C′ (excepting the H atoms) is in agreement with those previously reported in the literature for the silver salts of these acids.[2d]

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† At the suggestion of one of the referees

TABLE II

The atomic charges in $(CH_3)_2PSS^-$, calculated with various basis orbitals on phosphorus and sulfur.

| Basis on P | Basis on S | $P_1$ | $S_{2,3}$ | $C_4$ | $C_5$ |
|---|---|---|---|---|---|
| *sp*, | *sp* | .6399 | −.6400 | −.1554 | −.1534 |
| [a]*spd*, | *sp* | .4718 | −.5824 | −.1389 | −.1389 |
| [b]*spd*, | *sp* | −.0907 | −.4482 | −.1115 | −.1055 |
| [b]*spd*, | *spd* | −.3834 | −.4666 | .0295 | .0253 |

[a] only 3d orbitals used
[b] all 3d orbitals used in calculations

The calculation performed on B revealed an unexpected feature: the sign on the hydrogen atom bonded to $S_6$ is negative, like the charge on $S_6$. This fact could support the idea of the $K_a$ dependence on the nature of the organic groups attached to the phosphorus atom. The following ordering of $K_a$ might be expected:

$$(CH_3O)_2P(S)SH < (C_2H_5O)_2P(S)SH < (C_3H_7O)_2P(S)SH$$

However, it should be mentioned that this problem is not entirely solved and experimental results are still contradictory.[16]

Dipole moments are also sensitive to the influence of the 3d orbitals on phosphorus. For the compound A a dipole moment of 1.40 D is obtained when the *spd* basis is employed while the *sp* basis leads to a somewhat greater value (1.66 D). Our calculated value for C (3.26 D) is in a good agreement with the experimental value (3.67 D)[17] and suggests that the electronic distribution is relatively correctly described by the CNDO technique even in molecules containing more than one element of the third period.

(b) Conformational analysis was partially performed on compound A′. We have varied the angle between 1-2-3 and 2-3-4 by 60 degrees. The dependence of the total energy upon this angle is shown in Figure 2.

The relatively small barrier height denotes that one conformer can be easily transformed into another. Therefore, several conformers can be simultaneously present, which may explain the splitting of the P—S bond vibrational bands in the infrared spectrum. The same results have been achieved by Bulgakova and Shagydulyin[18] by normal coordinate analysis.

(c) Most of the phosphorus-sulfur bond lengths lie in the 1.86–2.14 Å range.[19] The extreme values could be ascribed to the classical "double bond" (1.86–1.94 Å) and "single" bond (2.10–2.14 Å), respectively, while the 1.95 to 2.10 Å region corresponds to the fractional "intermediate" bond orders.

As no experimental P—S bond length is available for C′ we have derived a theoretical one, varying it between 1.95 and 2.10 Å. A minimum of the total energy has been observed around 2.0 Å and a parabolic fitting led eventually to the equilibrium value $R_{PS} = 2.013$ Å, in accordance with P—S bond lengths found in many dithiophosphate metal derivatives.[16] It should be noticed that this value is greater than the corresponding P—S bond length for A′ in agreement with the lower electronegativity of the $CH_3$ group than that of $OCH_3$ group. The calculated P—S bond length is well ranged in the intermediate P—S bond region, according to the assumed delocalization of the $\pi$-electron density in the $PS_2$ fragment of the molecule.

(d) Bond orders have been calculated using the definition of Borisov and Semenov,[20] on the basis of Wiberg indexes. The computed bond orders are collected in Table III. From these data, the influence of the 3d orbitals on the phosphorus-

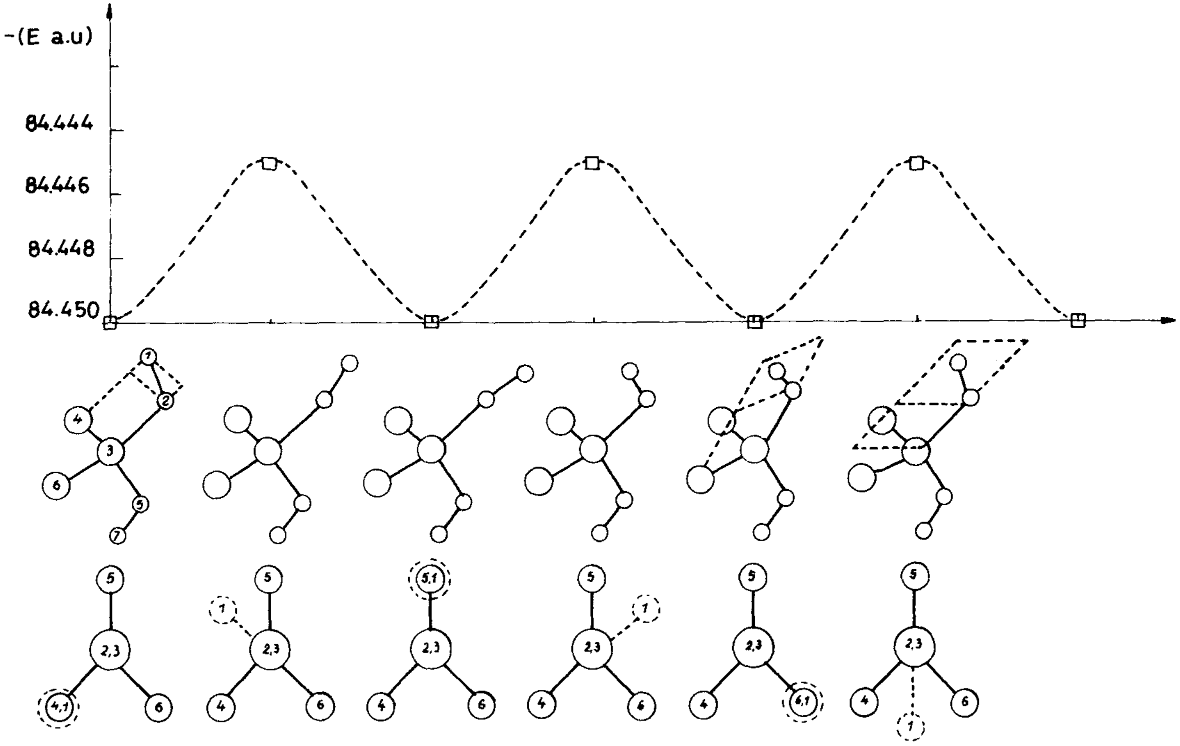

FIGURE 2 The dependence of the total energy of $(CH_3O)_2PS_2^-$ upon the (SPO,POC) dihedral angle

TABLE III

CNDO/2 Bond Orders

| | A | | A | | C | C′ |
|---|---|---|---|---|---|---|
| | *sp* | *spd* | *sp* | *spd* | *spd* | *spd* |
| P=S | 1.0247 | 1.4891 | 1.0233 | 1.3408 | 1.2600 | 1.1782 |
| P—S | 0.9182 | 1.0475 | 1.0233 | 1.3408 | 1.0232 | 1.1782 |
| P—O | 0.8676 | 0.8975 | 0.7465 | 0.7842 | — | — |
| C—O | 0.9746 | 0.9773 | 0.9970 | 0.9983 | — | — |
| P—C | — | — | — | — | 0.9899 | 0.9899 |

sulfur bond is more clear. By allowing the 3d orbitals to participate in bonding, it can be seen (column A′) that a net increase in the PS bond order is achieved. The methoxy groups, as can be expected from the bond lengths, strengthen the PS bonds compared to the methyl groups.

The P=S and P—S bond order ratio calculated in the *sp* basis is 1.11 while in the spd basis it is 1.42. The later is in a good agreement with the ratio of the corresponding force constants ($f_{P=S}/f_{P\text{-}S} = 1.38$) obtained from the vibrational spectrum of $(CH_3O)_2P(S)SCH_3$.[22] For C, the ratio of the bond orders is also close to that of the corresponding force constants ratio: ($W_{P=S}/W_{P\text{-}S} = 1.21$; $f_{P=S}/f_{P\text{-}S} = 1.32$.[23] This result suggests that phosphorus 3d orbitals should be taken into account in describing the phosphorus-sulfur bond.

For the compound C′ the experimental force constants are available[4] from which the bond order can be obtained using Gordy's empirical formula.[24] Again, the agreement with the $W_{PS}$ bond order is satisfactory.

The P—O bond orders are lower than those of the other "single" bonds in the molecules investigated. These relatively low values could be responsible for the lability of the OR groups of the dithiophosphoric derivatives recently reported in the literature.[16,25,26]

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