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An *ab initio* LCAO-MO-SCF Study of the Electronic Structure of Phosphirane and Thiirane

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Wave functions have been determined for the C_2H_4PH and C_2H_4S cyclic molecules, using (951/52/3) and (95/52/3) uncontracted Gaussian basis sets for each molecule. From Mulliken population analyses and electron-density plots, it is shown that the valence orbitals of C_2H_4PH and C_2H_4S are closely related and that these are similar to the respective orbitals of cyclopropane.

Für die zyklischen Moleküle C_2H_4PH und C_2H_4S wurden mit den nichtkontrahierten Basissätzen ((951/52/3) und (95/52/3)) von Gaußfunktionen Wellenfunktionen bestimmt. Die Mullikenschen Populationsanalysen sowie Diagramme der Elektronendichte zeigen, daß die Valenzorbitale von C_2H_4PH und C_2H_4S in enger Beziehung stehen und daß diese den entsprechenden Orbitalen des Cyclopropans ähnlich sind.

1. Introduction

As part of the study of the electronic structure of phosphorus compounds e.g. [1–4] which has been underway in our laboratory, it seemed desirable to investigate the strained-ring compound called phosphirane, C_2H_4PH, for which no prior quantum-mechanical study has been reported. For comparison purposes, we then calculated in the same basis sets wave functions for the related molecule (thiirane) in which a sulfur atom is substituted for the PH fragment, and for which several prior *ab initio* studies [5–8] have been reported. Our thiirane energy is lower than all except those from the contracted Gaussian basis calculations of Strausz, Gosavi, Denes, and Csizmadia [8] which appeared after our work was completed.

2. Calculational Details

The calculations on phosphirane, C_2H_4PH, were carried out using the following reported microwave C_s geometry [9]: $C{-}C = 1.502$ Å, $C{-}P = 1.867$ Å, $C{-}H_{cis} = 1.092$ Å, $C{-}H_{trans} = 1.093$ Å, and $P{-}H = 1.428$ Å; with $\angle CPC = 47.44°$, $\angle HPC = 95.22°$, $\angle CCH_{cis} = 118.00°$, and $\angle CCH_{trans} = 117.00°$. For thiirane, C_2H_4S, the calculations were carried out for a single atomic arrangement corresponding to the C_{2v} microwave structure [10]: $C{-}C = 1.492$ Å, $C{-}S = 1.819$ Å, and $C{-}H = 1.078$ Å, with $\angle CSC = 48.43°$, $\angle HCH = 116.00°$, and $\angle CCH = 117.82°$.

The LCAO-MO-SCF calculations were carried out with uncontracted (95/52/3) Gaussian basis sets containing a total of 58 *sp* functions for thiirane and 61 for phosphirane and uncontracted (951/52/3) sets containing 64 spd functions for thiirane and 67 for phosphirane, using the program MOSES. Atom-optimized exponents were employed for the *s* and *p* orbitals [4, 11], along with values of 0.435 for the sulfur and 0.360 for the phosphorus *d* orbitals. These *d*-orbital exponents were obtained from optimization on phosphine [12] and phosphine oxide [13] for the phosphorus and on hydrogen sulfide [11] and sulfoxylic acid tautomer [11] for sulfur. Further details of the calculational methods have been described elsewhere [4].

3. Results and Discussion

3.1. Molecular Results

The total energy and dipole moment obtained for thiirane in the various prior calculations are compared with our results in Table 1. Obviously the (52) description of sulfur by Clark [5] is inadequate and not in balance with that of the other atoms, since it led to both a poor total energy and dipole moment. It is interest to compare our single-determinant SCF results for thiirane with the group-function calculations on this molecule by Franchini and Zandomeneghi [7]. They used the group-function method with and without configuration interaction, but even their best CI energy of − 474.6465 a.u. is inferior to our single-determinant result of −474.8717 a.u. The SCF group-function method introduces correlation within each electron group [14]. The first-order correlation corrections to the SCF group function then involve only doubly excited states [15], and it is these states that Franchini and Zandomeneghi mixed into their CI function. One might have expected that this much configuration interaction would push the energy below the Hartree-Fock limit; this being the rationale of the group function approach. But the fact is, it does not. Expanding the basis set in a single-determinant SCF calculation is more worthwhile than configuration interaction with a limited basis. This might be surprising except that Allen and Karo [16] observed the same thing long ago in comparing minimal-Slater SCF calculations on hydrogen fluoride, with and without CI, to the Hartree-Fock limit. Strausz, Gosavi, Denes, and Csizmadia [8] have used a [641/41/1] Gaussian set contracted from (1291/116/3) in their very recently published work on thiirane. Their energy is 0.39 a.u. = 245 kcal/mole lower than our best, and is a strong demonstration of

Table 1. Values of total energy and of dipole moment calculated for the C_2H_4S molecule

Calculation	E_{tot}(a.u.)	$\mu(D)$
(52/52/2) GTO [5]	−456.0016	5.17
Min. basis STO, no *d* [6]	−474.4759	1.56
Min. basis STO, with *d* [6]	−474.5159	0.84
Group-function (GF), geminals, min. STO with *d* [7]	−474.6197	0.56
CI–GF, geminals, min. STO with *d* [7]	−474.6465	—
(95/52/3) GTO (our work)	−474.8387	1.24
(951/52/3) GTO (our work)	−474.8717	0.97
[641/42/1] GTO [8]	−475.2622	—
Experimental value	−477.74	1.84 [10]

Table 2. Atomic charges from a Mulliken population analysis of C_2H_4S

	S	C	H
(52/52/2) GTO [5]	+1.072	−0.908	+0.186
Min. STO, no *d* [6]	+0.066	−0.435	+0.201
Min. STO, with *d* [6]	+0.070	−0.425	+0.195
(95/52/3) GTO	+0.123	−0.470	+0.204
(951/52/3) GTO	−0.036	−0.362	+0.190

the power of such contracted bases. These authors present a thorough study of the orbital and total energy relations between thiirane and its isomers; but, although they compute the oscillator strength of several thiirane transitions, they do not give a computed dipole moment for the ground state.

The so-called "atomic charges" obtained by subtracting the Mulliken gross population [17] from the atomic number are shown in Table 2 for various calculations on thiirane. These data are unfortunately not available for the low-energy wave function of Strausz, Gosavi, Denes, and Csizmadia. If one assumes that a minimum-basis set of Slater orbitals epitomizes a balanced basis set in the Mulliken sense [18], the charges given in Table 2 indicate that the (95/52/3) Gaussian set is a reasonably well balanced one; whereas the (52/52/3) set of Gaussian orbitals [5] is horribly unbalanced, with the sulfur being starved for atomic orbitals. Note that adding a set of *d* orbitals to the minimum Slater basis set has very little effect on the atomic charges, whereas the effect is quite pronounced when going from our (95/52/3) to (951/52/3) Gaussian basis set. We attribute this difference to the choice of too large a radius for the *d* orbital in the Slater calculations [6]. Instead of using a Slater exponent of 1.7 for the *d* orbital, a value around 2.7 would have been more appropriate [19]. The *d* orbital corresponding to the 1.7 exponent obviously exhibited too large a radius to give the proper bonding contributions to the thiirane molecule, although it undoubtedly contributed to the desired polarization of the *s* and *p* orbitals [20]. As shown in Table 1, the fact that the change in total energy when allowing *d* orbitals to the Slater minimum-basis set and to the (95/52/3) Gaussian set was about the same is attributable to the fact that the absolute change in inner-orbital energies upon allowing *d* character is considerably greater than that for the outer orbitals for either basis set.

The "experimental" value for the thiirane energy was obtained by subtracting the sum of the atomic ionization potentials [21] (+476.74401 a.u.) and the standard heat of formation of the atoms [22] at 0 °K (+0.9762 a.u.) from the heat of formation of thiirane [22] at 0 °K (+0.0360 a.u.) and the zero-point vibration corrections (−0.0530 a.u.) obtained from an analysis of the IR spectrum [23]. The resulting energy of −477.737 a.u. is 68 kcal/mole above that given by Bonaccorsi, Scrocco, and Tomasi [6] for the same quantity. It seems most likely that the difference is due to our use of revised atomic ionization potentials! Both values are sufficiently far below all calculated thiirane energies so that the difference is not yet significant. But as calculations become more exact, the problem of obtaining accurate experimental energies promises to become a serious one.

The fundamental vibrational frequencies for phosphirane are available [24, 25], but thermochemical data are not. Nevertheless, the heat of formation of phosphirane from atoms at 298 °K can be estimated from the corresponding quantity for thiirane and Cottrell's [26] empirical bond energies.

$$\Delta H^\circ_{298}(\text{phosphirane}) \approx \Delta H^\circ_{298}(\text{thiirane}) + 2\,E_{PC} - 2\,E_{SC} + E_{PH}$$
$$= -597.988 - 126 + 130 - 77 = -671 \text{ kcal}$$

where E_{PC} is Cottrell's energy of a phosphorus-carbon bond, and E_{SC} and E_{PH} are defined similarly. Using the heat of formation of cyclopropane instead of that of thiirane gives instead an estimate of -654 kcal for phosphirane. The two estimates differ by only 0.027 a.u. so either is probably accurate enough to give a useful estimate of the total energy of phosphirane relative to separated particles. Since P and S are more nearly alike than are P and C, we choose the -671 value. Then

$$\begin{aligned}\Delta E^\circ_{298} &= \Delta H^\circ_{298} + 7RT = -666.7 \text{ kcal}\\ &= \Delta E_{\text{variational}} + \Delta(\text{trans}) + \Delta(\text{rot}) + \Delta(\text{zero-point})\\ &= \Delta E_{\text{variational}} - \tfrac{21}{2} RT + \tfrac{3}{2} RT + 0.0613 \text{ a.u.}\end{aligned}$$

This gives a $\Delta E_{\text{variational}}$, the phosphirane energy relative to separated atoms, of -1.1152 a.u. Including the atomic ionization potentials [21] gives $(-1.1152 - 420.1555) = -421.27$ a.u. as the experimental energy of the phosphirane potential minimum relative to separated electrons and nuclei.

In all of these calculations, the most recent values of the fundamental constants [27] were used, corresponding to

$$1 \text{ a.u.} = 27.2117 \text{ eV} = 627.52 \text{ kcal/mole} = 219475 \text{ cm}^{-1}.$$

The total energy, dipole moment, and atomic charges from a Mulliken population analysis are shown in Table 3 for the phosphirane molecule, which has not been studied previously. Note that the percentage difference between the SCF value of the total energy and the experimental value is about the same for thiirane as for phosphirane in the same basis set. Likewise, the increase in total energy upon allowing *d* orbitals is also similar (0.033 a.u. for C_2H_4S and 0.050 a.u. for C_2H_4PH). However, the atomic charge on the phosphorus is appreciably

Table 3. Calculated values for the C_2H_4PH molecule

Basis set	(95/52/3)	(951/52/3)
Total energy (a.u.)[a]	−418.6923	−418.7422
Dipole mom. (*D*)[b]	0.921	0.647
Atomic charges (*e*)		
P	+ 0.53	+ 0.30
C	− 0.49	− 0.35
H_c	+ 0.21	+ 0.20
H_p	+ 0.01	+ 0.09

[a] Experimental value: −421.27 a.u.

[b] Experimental value [9]: $\mu = 1.12\,D$.

higher than that on the sulfur whether or not *d* orbitals are allowed, and this is also true for the change in charge upon allowing *d* orbitals to the molecule.

3.2. Orbital Results

The Mulliken population analyses for the valence orbitals of phosphirane and thiirane are compared in Table 4 from which it can be seen that there is great similarity between the valence orbitals of these two molecules. This similarity extends to the valence-orbital energies which are reported in Table 5. The close correspondence between the P–C overlap of an orbital of phosphirane and the S–C overlap of the related orbital of thiirane should be particularly noted in Table 4, along with the similarities in the other overlap populations as well as in the gross populations of the carbon atoms and their attached hydrogens. Interestingly enough, the phosphorus gross population varies from orbital to orbital in about the same way as does the sulfur gross population between the related orbitals.

It also seemed desirable to find out whether or not the valence orbitals of cyclopropane in a comparable basis set would also be closely related to those of phosphirane and thiirane. Accordingly a calculation was carried out on cyclopropane using a (52/2) uncontracted Gaussian basis [28]. In order to carry out a proper comparison, it seemed appropriate to select sets of orbitals of *e* symmetry corresponding to the linear combination which would be directly comparable to molecules of C_{2v} symmetry. This was achieved by a 2′ diminution in the HCH angle at only one of the carbon atoms of cyclopropane, which resulted in a transformation of the D_{3h} symmetry of cyclopropane into C_{2v} without appreciable distortion of the wave function. As can be seen in Table 4, the resulting gross and overlap populations for cyclopropane agree quite well orbital-by-orbital with those of phosphirane and thiirane. Note, however, that the difference in the number of the valence-shell electrons of carbon (4), phosphorus (5), and sulfur (6) shows up predominantly in the molecular orbitals $3e'$ and $1e''$ for C_3H_6 and $11a'$ for C_2H_4PH.

Since a population analysis results from integrations over space thus producing numbers which do not reflect electronic spatial distributions, appropriate electron-density plots should be much more suitable for showing the details of interrelations between wave functions of different molecules. For intercomparing the orbitals of phosphirane with those of thiirane and cyclopropane, three-dimensional plots are shown in Fig. 1 for those orbitals exhibiting electron densities in the ring plane. In these plots the magnitude of the electron-density in the plane of the ring is plotted perpendicular to this plane. Figure 1 shows that the intermolecular-orbital correlations made between these three molecules on the basis of the population analysis of Table 4 are clearly recognizable in the electron-density plots. Of particular interest is the good comparison between the two $2e'$ orbitals of cyclopropane and the respective orbitals of phosphirane ($3a''$ and $7a'$) and thiirane ($3b_2$ and $6a_1$), all of which are dominated by *s*-type atomic orbitals. The suitable choice of the pair of $3e'$ orbitals is also demonstrated by their correspondence to the related orbitals of phosphirane ($10a'$ and $5a''$) and thiirane ($8a_1$ and $4b_2$), all of which are based on *p*-type atomic orbitals.

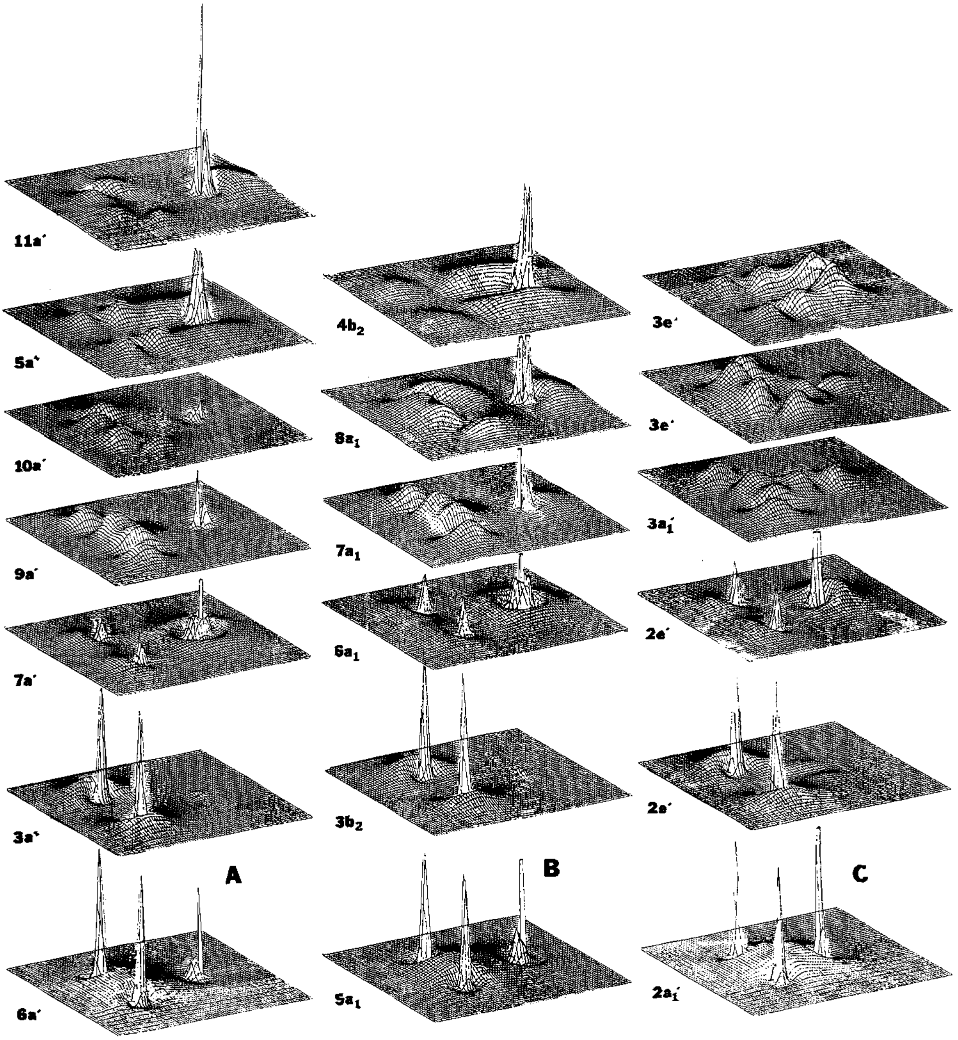

Fig. 1. Three-dimensional plots of the electron-densities in the ring plane (electron density shown on the vertical axis) for the valence molecular orbitals of (*A*) phosphirane, (*B*) thiirane, and (*C*) cyclopropane

The electron-density plots show that the main difference between orbital $6a'$ of phosphirane, $5a_1$ of thiirane, and $2a'$ of cyclopropane lies in the fact that the third carbon of cyclopropane bonds through its second (and hence outermost) *s*-orbital antinode; whereas for phosphorus and sulfur, the bonding is through overlap of the third *s*-orbital antinode. This acts to push the concentration of electrons in the bonding region away from the region of the phosphorus or sulfur nuclei. Similarly, the *p*-type orbitals of phosphirane and thiirane ($9a'$, $10a'$, $5a''$, $11a'$ of C_2H_4PH; $7a_1$, $8a_1$, and $4b_2$ of C_2H_4S) exhibit bonding through the outermost of the two *p*-orbital antinodes of the phosphorus and sulfur thereby leading to the observed differences in electron-density distribution between these orbitals

Table 4. Electronic population analysis[a] for the valence orbitals of C_2H_4X molecules

X	Orbs.	Gross population					Overlap population				
		M[b]	C	H_M	H_C[c]	H'_C	M–C	C–C	M–H	$C–H_C$	$C–H'_C$
P(H)	$6a'$	0.435	0.789	0.014	0.048	0.048	0.271	0.372	0.001	0.049	0.049
S	$5a_1$	0.524	0.670	—	0.034		0.217	0.326	—	0.038	
$C(H_2)$	$2a'_1$	0.614	0.614	0.027	0.027		0.276	0.277	0.029	0.029	
P(H)	$3a''$	0.108	0.665	0.000	0.163	0.162	0.069	−0.150	0.000	0.193	0.193
S	$3b_2$	0.068	0.655	—	0.155		0.036	−0.151	—	0.192	
$C(H_2)$	$2e'$	0.101	0.646	0.000	0.152		0.054	−0.147	0.000	0.181	
P(H)	$7a'$	0.954	0.217	0.197	0.027	0.044	−0.086	0.072	0.221	0.048	0.063
S	$6a_1$	1.157	0.315	—	0.053		−0.063	0.119	—	0.065	
$C(H_2)$	$2e'$	0.827	0.283	0.202	0.051		−0.079	0.121	0.240	0.060	
P(H)	$8a'$	0.182	0.593	0.045	0.221	0.123	0.091	0.139	0.017	0.193	0.095
S	$2b_1$	0.095	0.603	—	0.175		0.040	0.153	—	0.154	
$C(H_2)$	$1a''_2$	0.448	0.449	0.109	0.109		0.101	0.102	0.095	0.095	
P(H)	$9a'$	0.338	0.529	0.131	0.043	0.157	0.009	0.232	0.147	0.032	0.132
S	$7a_1$	0.451	0.587	—	0.094		0.170	0.271	—	0.077	
$C(H_2)$	$3a'_1$	0.475	0.470	0.099	0.097		0.093	0.093	0.104	0.103	
P(H)	$4a''$	0.007	0.514	0.000	0.245	0.241	0.005	−0.198	0.000	0.236	0.232
S	$1a_2$	0.002	0.520	—	0.240		0.001	−0.203	—	0.236	
$C(H_2)$	$1e''$	0.000	0.523	0.000	0.239		0.000	−0.199	0.000	0.227	
P(H)	$10a'$	0.507	0.371	0.434	0.039	−0.003	−0.148	0.239	0.210	0.031	0.003
S	$8a_1$	0.773	0.604	—	0.005		0.016	0.269	—	0.005	
$C(H_2)$	$3e'$	0.298	0.773	0.052	0.013		−0.092	0.461	0.033	0.008	
P(H)	$5a''$	1.070	0.485	0.000	0.016	0.021	0.374	−0.212	0.000	0.015	0.019
S	$4b_2$	1.094	0.397	—	0.028		0.255	−0.193	—	0.017	
$C(H_2)$	$3e'$	0.927	0.458	0.000	0.039		0.278	−0.275	0.000	0.025	
P(H)	$11a'$	1.109	0.184	0.090	0.002	0.007	−0.193	0.111	−0.177	0.003	0.014
S	$3b_1$	1.874	0.009	—	0.027		−0.036	0.004	—	0.014	
$C(H_2)$	$1e''$	0.697	0.174	0.318	0.080		−0.132	0.066	0.302	0.075	
P(H)	total	14.702	6.346	0.911	0.803	0.799	0.380	0.598	0.426	0.798	0.799
S	total	16.036	6.362	—	0.810		0.480	0.587	—	0.794	
$C(H_2)$	total	6.389	6.389	0.805	0.806	0.494	0.492	0.800	0.800		

[a] These values are calculated from a (951/52/3) basis set for the phosphirane and thiirane molecules and a (52/2) basis set for cyclopropane.

[b] The M stands for P of X = P(H), or C of X = $C(H_2)$.

[c] For the C_2H_4PH molecule, the H_C corresponds to the hydrogen which is *cis* to the H_M hydrogen and H'_C to that which is *trans*.

and the respective cyclopropane molecular orbitals ($3a'$, $3e'$, and $3e'$) which are also dominated by *p*-type atomic orbitals. The most pronounced case of this pushing of bonding electrons away from the region of the phosphorus or sulfur nuclei is found for orbitals $9a'$ of C_2H_4PH and $7a_1$ of C_2H_4S, as can be seen in Fig. 1.

The figure clearly shows that the most stable valence-shell molecular orbital of each molecule (bottom plots) is strongly bonding and involves the *s* atomic orbitals of all three of the ring atoms. The next two valence-shell molecular orbitals are also based on the *s* atomic orbitals of the three ring atoms but exhibit

Table 5. Orbital energies calculated for C_2H_4PH and C_2H_4S, with *d* orbitals allowed

C_2H_4PH		C_2H_4S	
Orbital	Energy (eV)	Orbital	Energy (eV)
$1a'$ P "1*s*"	−2176.2	$1a_1$ S "1*s*"	−2502.2
$2a'$ C "1*s*"	− 308.4	$2a_2$ C "1*s*"	− 308.9
$1a''$ C "1*s*"	− 308.4	$1b_2$ C "1*s*"	− 308.9
$3a'$ P "2*s*"	− 204.6	$3a_1$ S "2*s*"	− 243.9
$4a'$ P "2*p*"	− 147.0	$4a_1$ S "2*p*"	− 180.5
$5a'$ P "2*p*"	− 146.9	$2b_2$ S "2*p*"	− 180.5
$2a''$ P "2*p*"	− 146.9	$1b_1$ S "2*p*"	− 180.4
$6a'$	− 29.7	$5a_1$	− 30.8
$3a''$	− 22.4	$3b_2$	− 22.8
$7a'$	− 20.7	$6a_1$	− 22.4
$8a'$	− 17.3	$2b_1$	− 17.6
$9a'$	− 15.4	$7a_1$	− 15.7
$4a''$	− 13.7	$1a_2$	− 14.1
$10a'$	− 12.0	$8a_1$	− 11.3
$5a''$	− 9.7[a]	$4b_2$	− 10.5
$11a'$	− 9.7	$3b_1$	− 8.0

[a] When given with more accuracy, the $5a''$ molecular orbital of phosphirane is found to be higher in energy than orbital $11a'$.

either no-bonding or antibonding characteristics within the ring. The remaining orbitals which contribute to bonding of the ring atoms all involve the *p* atomic orbitals of these atoms, with the two more stable of these molecular orbitals being $(\overline{p_\sigma - p_\sigma - p_\sigma})$. With respect to the interactions of the ring atoms, the phosphorus or sulfur (or alternatively the third carbon of cyclopropane) is strongly π-bonded to the C_2H_4 group by atomic *p* orbitals with nodal planes perpendicular to the ring plane ($5a''$, $4b_2$, $3e'$); whereas similar π antibonding is achieved for the case where the nodal plane of the *p* atomic orbitals lies in the ring plane. By looking at plots similar to those given in Fig. 1 corresponding to the planes passing through each of the ring atoms and the center of the ring, the same kind of information concerning the bonds to the hydrogen atoms is obtained as is given by Fig. 1 for the bonding within the ring plane.

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References

1. Absar, I., Robert, J. B., Van Wazer, J. R.: J. chem. Soc. Faraday transactions II **68**, 1055 (1972).
2. Absar, I., Van Wazer, J. R.: J. Amer. chem. Soc. **94**, 2382 (1972).
3. Absar, I., Van Wazer, J. R.: J. chem. Physics **56**, 1284 (1972).
4. Robert, J. B., Marsmann, H., Absar, I., Van Wazer, J. R.: J. Amer. chem. Soc. **93**, 3320 (1971).
5. Clark, D. T.: Theoret. chim. Acta (Berl.) **15**, 225 (1969).
6. Bonaccorsi, R., Scrocco, E., Tomasi, J.: J. chem. Physics **52**, 5270 (1970).
7. Franchini, P. F., Zandomeneghi, M.: Theoret. chim. Acta (Berl.) **21**, 90 (1971).
8. Strausz, O. P., Gosavi, R. K., Denes, A. S., Csizmadia, I. G.: Theoret. chim. Acta (Berl.) **26**, 367 (1972).
9. Bowers, M. T., Beaudet, R. A., Goldwhite, H., Tang, R.: J. Amer. chem. Soc. **91**, 17 (1969).

10. Cunningham, G. L., Jr., Boyd, A. W., Myers, R. J., Gwinn, W. D.: J. chem. Physics **19**, 676 (1951); Shoemaker, R. L., Flygare, W. H.: J. Amer. chem. Soc. **90**, 6263 (1968).
11. Van Wazer, J. R., Absar, I.: In: Sulfar research trends. Advances in chemistry series, Vol. 110, p. 20. American Chemical Society 1972.
12. Robert, J. B., Marsmann, H., Schaad, L. J., Van Wazer, J. R.: Phosphorus **2**, 11 (1972).
13. Marsmann, H., Groenweghe, L. C. D., Schaad, L. J., Van Wazer, J. R.: J. Amer. chem. Soc. **92**, 6107 (1970).
14. Franchini, P. F., Vergani, C.: Theoret. chim. Acta (Berl.) **13**, 46 (1969).
15. McWeeny, R.: Rev. mod. Physics **32**, 335 (1960).
16. Allen, L. C., Karo, A. M.: Rev. mod. Physics **32**, 275 Fig. 1 (1960).
17. Mulliken, R. S.: J. chem. Physics **23**, 1833, 1841, 2338, 2343 (1955).
18. Mulliken, R.S.: J. chem. Physics **36**, 3428 (1962).
19. Absar, I., Van Wazer, J. R.: Chem. Physics Letters **11**, 310 (1971).
20. Coulson, C. A.: Nature **221**, 1106 (1969).
21. Moore, C. E.: Ionization potentials and ionization limits derived from the analysis of optical spectra, NSRDS-NBS 34. Washington: U.S. Government printing office 1970.
22. Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H.: Selected values of chemical thermodynamic properties, NBS technical note 270-3. Washington: U.S. Government printing office 1968.
23. Guthrie, G. B., Jr., Scott, D. W., Waddington, G.: J. Amer. chem. Soc. **74**, 2795 (1952).
24. Mitchell, R. W., Kuzma, L. J., Pirkle, R. J., Merritt, J. A.: Spectrochim. Acta A**25**, 819 (1969).
25. Chan, S., Goldwhite, H., Keyzer, H., Tang, R.: Spectrochim. Acta A**26**, 249 (1970).
26. Cottrell, T. L.: The strengths of chemical bonds, 2nd edition. London: Butterworth's 1958.
27. Taylor, B. N., Parker, W. H., Langenberg, R. N.: Rev. mod. Physics **41**, 375 (1969).
28. Marsmann, H., Robert, J.-B., Van Wazer, J. R.: Tetrahedron **27**, 4377 (1971).

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