Ab Initio LCAO–MO–SCF Study of Bonding in the Simplest Phosphorus Ylide

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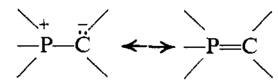
Abstract: *Ab initio* LCAO–MO–SCF calculations have been carried out for two conformations of the hypothetical phosphonium ylide, CH_2PH_3, using two uncontracted Gaussian basis sets, one with and the other without phosphorus d orbitals. An essentially zero barrier to C–P bond rotation was calculated in either basis set. The nature of the carbon–phosphorus bond has been investigated in detail, and it is seen that the energy change upon allowing d character to the phosphorus atom is commensurate with C–P p_π–d_π feedback. Three-dimensional electron density plots are presented and interpreted in terms of bond contributions.

The structure of phosphorus ylides is generally written[1] as a resonance hybrid



(1)

There has been controversy as to the extent of d-orbital participation in bonding in these compounds in order to give the double-bonded form shown on the right-hand side of eq 1. The ^{31}P nuclear magnetic resonance[2,3] chemical shifts of these compounds have been interpreted to indicate essentially no electronic feedback from the carbon to the phosphorus while chemical evidence, particularly the striking difference between the stabilities of the nitrogen and phosphorus ylides, supports the double-bonded formulation. Observations of an abnormally short P–C bond[4–6] as well as some infrared data[7,8] agree with this p_π–d_π interpretation of the chemical findings.

In the study reported here, we have investigated the electronic structure of the simplest phosphorus ylide, methylenephosphorane, CH_2PH_3, which has never been prepared. However, methylenetrimethylphosphorane, $CH_2P(CH_3)_3$, has been made and there is no *a priori* reason to believe that simple methylenephosphorane should not be a representative phosphorus ylide.

After completion of the basic SCF calculations the results of which are reported herein, two papers[9,10] dealing with extended Hückel calculations on methylenephosphorane and some other phosphorus ylides appeared in the literature. This is particularly fortuitous since it allows comparison between the results of a still somewhat questionable semiempirical approach, using Slater orbitals, to those obtained in an *ab initio* study based on a set of Gaussian orbitals which is about equal to the best atom-optimized Slater minimum basis set with respect to deviations from the Hartree–Fock limit for the constituent atoms.

Calculational Details

By comparison with the geometries of stable phosphorus ylides,[4–6] particularly $CH_2P(C_6H_5)_3$,[6] the following interatomic distances and angles have been chosen: P–C = 1.66 Å, C–H = 0.95 Å, P–H = 1.424 Å, ∠HCH = 125°, and ∠HCP = 93.5°, with the two hydrogens and the phosphorus surrounding the carbon all being in the same plane as the carbon. The two limiting conformations, which were studied, are the eclipsed form in which one of the P–H bonds lies in the same plane as the C–H bonds and the staggered form where this P–H bond has been rotated by 90° so that it lies in a plane which bisects the H–C–H angle.

Ab initio LCAO–MO–SCF calculations were carried out with an uncontracted Gaussian basis set using nine s-type and five p-type atom-optimized exponents (with and without an added d exponent) to describe the phosphorus, five s-type and two p-type to describe the carbon, and three s-type to describe each of the five hydrogen atoms. The computer programs employed (with the LCAO–MO–SCF calculations being done with program MOSES[11]), the Gaussian atomic exponents used, and other calculational details have been described previously.[12]

Results and Discussion

The overall calculated energies not corrected for electron correlations are presented in Table I for methylenephosphorane. Although both the staggered and eclipsed forms were evaluated, their energies are so close that only a single value need be shown to the precision of Table I. The binding energy given in this table corresponds to the sum of the total SCF energies of the constituent atoms minus that of the molecule. The differences between the various values presented for the (951/52/3) basis set[13] and the respective ones for the (95/53/3) basis set show the effect of allowing d

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[1] A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 7.

[2] See ref 1, pp 76–79.

[3] M. M. Crutchfield, C. L. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "P^{31} Nuclear Magnetic Resonance," Wiley-Interscience, New York, N. Y., 1967, pp 380–390.

[4] J. C. Bart, *J. Chem. Soc. B*, 350 (1969).

[5] P. J. Wheatley, *J. Chem. Soc. A*, 5785 (1965).

[6] T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, 18, 81 (1965).

[7] L. V. Senyavina, E. V. Dyatlovitskays, N. Y. Sheinker, and L. D. Bergelson, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1979 (1964).

[8] L. C. Thomas and R. A. Chittendden, *Spectrochim. Acta*, 21, 1905 (1965); L. Horner and H. Oediger, *Justus Liebigs Ann. Chem.*, 67, 142 (1959). For comparison, see T. E. Gier, *J. Amer. Chem. Soc.*, 83, 1769 (1961).

[9] R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *ibid.*, 92, 3929 (1970).

[10] D. B. Boyd and R. Hoffmann, *ibid.*, 93, 1064 (1971).

[11] L. M. Sachs and M. Geller, *Int. J. Quantum Chem.*, 1S, 445 (1967).

[12] J.-B. Robert, H. Marsmann, I. Absar, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 93, 3320 (1971).

[13] The notation (*abc*/*ef*/*g*) corresponds to the use of *a* (s-type), *b* (p-type), and *c* (d-type) exponents for the phosphorus, *e* (s-type) and *f* (p-type) for the carbon, and *g* (s-type) for each hydrogen, with all exponents except the d (which was molecularly optimized in another molecule) being atom optimized.

Table I. SCF Energies of Methylenephosphorane, CH_2PH_3

Energy term	Value
Nuclear (au)	64.7042
Electronic (au)	
(95/52/3)	−445.5205
(951/52/3)	−445.6233
Total[a] (au)	
(95/52/3)	−370.8163
(951/52/3)	−380.9191
Binding[a,b] (eV)	
(95/52/3)	9.92
(951/52/3)	12.72

[a] SCF values only, exclusive of correlation and other corrections. [b] Sum of atomic energies minus molecular energy, with the same optimized basis sets used for the atoms in the molecule and in the free state.

character. In these calculations, an additional 65 kcal/mol of stabilizing energy is given to the molecule CH_2PH_3 by the inclusion of d character; while for the isomeric monomethylphosphine,[14] CH_3PH_2, the stabilization ranges from 35 to 41 kcal in the same basis sets, depending on the particular rotational isomer.

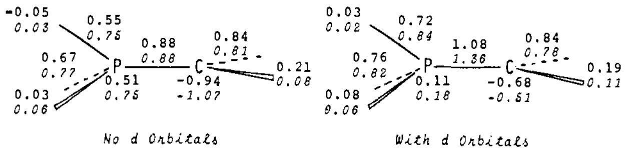
The barrier to internal rotation in methylenephosphorane is extremely small being calculated to be 0.003 kcal/mol with d orbitals included and 0.016 kcal/mol with no d character allowed, with the staggered rotamer being the more stable in both cases. As is usual,[14,15] allowing d character has only a small effect on the magnitude of the rotational barrier, whereas the total energy and the binding energy are changed by a much larger amount (see preceding paragraph). The rotational barrier for monomethylphosphine,[14] CH_3PH_2, was calculated in the same basis sets and was found to be 1.83 kcal/mol with d orbitals and 1.71 without, again with the same rotamer being the more stable in both cases. The experimentally measured rotational barrier[16] for this molecule is 1.96 kcal/mol. In view of the good match between the calculated and experimental values for monomethylphosphine, we can feel fairly certain that the calculated value of the barrier for methylenephosphorane is reasonably correct and that for all practical purposes there is no barrier to internal rotation in this ylide.

In the common electronic bond language of chemistry, the low barrier we have observed for internal rotation in methylenephosphorane indicates that there is no double bond character in the P–C bond. However, in this language, the bond could consist of a resonance between a single bond and a triple bond structure, with the latter (if present) being associated with concomitant P–H and C–H no-bond resonance contributions. Although twisting a double bond involves much energy, neither a single nor triple bond should in themselves exhibit any hindrance to rotation. It is interesting to note that, although the rotational barrier for methylenephosphorane is inappreciable, the relative energies of some of the orbitals are interchanged by rotation. Thus, for the staggered form, the ordering of the valence orbitals in order of increasing energy is 6a′, 7a′, 2a″, 8a′, 9a′, 3a″, and 10a′; whereas for the eclipsed form the ordering is 6a′, 7a′, 8a′, 2a″, 9a′, 10a′, and 3a″.

Mulliken net and overlap populations,[17] as well as the orbital energy, are shown for each of the valence orbitals of methylenephosphorane in Table II. Note that the second column of this table lists the major valence bond contributions to the respective orbital. These were obtained from inspection of the electron density plots of the orbitals (as will be seen in Figures 1 and 2) and were verified by reference to the electronic population data and the molecular wave function. In Table II, the values given on the first line for each orbital correspond to the (951/52/3) calculation for the eclipsed configuration. The value in italics and within parentheses on the next line shows the change induced by allowing d character to the molecule and the italicized value lying below this shows the effect of rotating from the staggered to the eclipsed form.

Inspection of the electron density maps for the valence molecular orbitals in the staggered and eclipsed configurations shows that 8a′ and 10a′ orbitals of the eclipsed configuration interconvert into the 2a″ and 3a″, respectively, of the staggered. Since the CH_2PH_3 molecule exhibits two nodal planes at right angles to each other, the rotational transfer of a P–H hydrogen from the CH_2 plane for the eclipsed configuration to the plane at right angles to it for the staggered leads to a transposition of the single plane of symmetry from one nodal plane to the other and hence accounts for the large changes in the H′ net and P–H′ overlap populations in Table II.

By subtracting the total gross atomic populations from the respective atomic number, the formal quantity called "charge on the atom" is obtained. As noted elsewhere[18] this quantity, whether coming from an *ab initio* or semiempirical calculation, is sensitive to the choice of basis set and is a formal rather than a physical property.[19] The atomic charges and important overlap populations for the staggered form of methylenephosphorane are shown below as they were obtained from our calculations, with the respective values resulting from the extended Hückel treatment[9] being given in italics.



No d Orbitals *With d Orbitals*

The generally good agreement between these numbers is gratifying and indicates that, except for compensating errors, the approximations and assumptions used in this particular semiempirical computation[9] do not seem to lead to large distortions of this particular property, if we assume that the (951/52/3) Gaussian basis set exhibits about the same electronic balance[19] as does a minimum Slater basis set. Of course, a number of examples of other molecules would be needed to show

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(14) I. Absar and J. R. Van Wazer, *J. Chem. Phys.*, **56**, 1284 (1972); also *Chem. Commun.*, 611 (1971).

(15) J.-B. Robert, H. Marsmann, and J. R. Van Wazer, *ibid.*, 356 (1970); also see J.-B. Robert, I. Absar, H. Marsmann, and J. R. Van Wazer, *J. Chem. Soc.*, in press.

(16) T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem. Phys.*, **35**, 2139 (1961).

(17) R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

(18) R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *Inorg. Chem.*, **9**, 2469 (1970); see footnotes 18 and 19.

(19) R. A. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).

Table II. Electron Populations and Orbital Energies for the Valence-Shell Molecular Orbitals of Methylenephosphorane, CH_2PH_3

		Net population[b]					Overlap population[b]				
Orbital	Major contribution[a]	P	C	$\frac{1}{2}(H_a + H_b)$	H′	H″	P–C	$\frac{1}{2}$(C–H_a + C–H_b)	P–H′	P–H″	Orbital energy,[c] eV
6a′	P–C σ	0.511[d]	0.487	0.029	0.021	0.184	0.381	0.113	0.066	0.060	−26.97
		(−0.124)[e]	*(0.059)*	*(0.009)*	*(−0.003)*	*(−0.001)*	*(0.011)*	*(0.030)*	*(−0.015)*	*(−0.011)*	(0.64)
		0.000[f]	*0.000*	*0.000*	*0.003*	*−0.002*	*0.000*	*0.000*	*0.007*	*−0.004*	*0.00*
7a′	C–H σ	0.569	0.365	0.059	0.054	0.049	−0.003	0.167	0.155	0.144	−22.44
	Some P–H σ	*(0.019)*	*(−0.102)*	*(−0.007)*	*(0.011)*	*(0.013)*	*(0.029)*	*(−0.030)*	*(0.023)*	*(0.026)*	*(0.45)*
		0.000	*0.000*	*0.000*	*0.007*	*−0.004*	*0.000*	*0.000*	*0.014*	*−0.007*	*0.00*
8a′	C–H σ	0.182	0.496	0.185	0.076	0.018	0.121	0.285	0.108	0.028	−16.36
	P–C π	*(0.066)*	*(0.076)*	*(0.031)*	*(−0.047)*	*(−0.012)*	*(−0.025)*	*(0.047)*	*(−0.036)*	*(−0.011)*	*(0.16)*
	Some P–H σ	*0.000*	*0.000*	*0.000*	*0.076*	*−0.038*	*−0.000*	*0.000*	*0.108*	*−0.054*	*0.00*
2a″	P–H	0.643	0.041	0.000	0.000	0.300	0.059	0.000	0.000	0.372	−14.67
	Some P–C π	*(0.013)*	*(−0.001)*	*(0.000)*	*(0.000)*	*(−0.035)*	*(−0.014)*	*(0.000)*	*(0.000)*	*(0.033)*	*(0.32)*
		−0.002	*−0.006*	*−0.002*	*−0.365*	*0.187*	*0.005*	*−0.003*	*−0.463*	*0.237*	*0.01*
9a′	P–C σ	0.830	0.370	0.097	0.056	0.019	0.278	0.158	0.065	0.023	−14.39
	Some C–H σ	*(0.135)*	*(−0.063)*	*(0.003)*	*(−0.002)*	*(0.002)*	*(−0.044)*	*(0.001)*	*(0.002)*	*(−0.001)*	*(0.06)*
		−0.004	*0.004*	*0.002*	*−0.008*	*0.002*	*0.001*	*0.004*	*−0.013*	*0.003*	*−0.01*
10a′	P–C π*	0.460	0.193	0.088	0.365	0.109	−0.082	0.122	0.390	0.124	−14.07
	P–H σ	*(0.095)*	*(−0.161)*	*(−0.002)*	*(−0.035)*	*(−0.013)*	*(−0.085)*	*(−0.043)*	*(0.089)*	*(0.020)*	*(0.02)*
	C–H σ	*0.006*	*0.002*	*−0.004*	*0.365*	*−0.185*	*0.004*	*0.000*	*0.390*	*−0.198*	*0.00*
3a″	C lp	0.133	1.370	0.000	0.000	0.168	0.334	0.000	0.000	−0.020	−7.20
	P–C π	*(0.061)*	*(−0.198)*	*(0.000)*	*(0.000)*	*(−0.153)*	*(0.164)*	*(0.000)*	*(0.000)*	*(0.096)*	*(−0.44)*
	Some P–H σ*	*0.000*	*0.000*	*0.000*	*−0.221*	*0.111*	*−0.000*	*0.000*	*0.023*	*−0.011*	*0.00*
Total		13.337	5.336	0.458	0.572	0.681	1.077	0.842	0.782	0.736	−12,125.58
		(0.145)	*(−0.384)*	*(0.034)*	*(−0.094)*	*(−0.199)*	*(0.197)*	*(0.001)*	*(0.060)*	*(0.149)*	(−2.97)
		0.000	*0.000*	*0.000*	*−0.144*	*0.072*	*0.000*	*0.000*	*0.066*	*−0.023*	*0.00*

[a] Dominant valence bond contributions to the molecular orbital. [b] Hydrogen atoms H_a and H_b are bonded to the carbon, whereas one hydrogen of the type H′ and two of type H″ are bonded to the phosphorus. [c] Note that for energy 1 au = 27.211 eV = 627.6 kcal/mol, according to E. R. Cohen and J. W. DuMond, *Rev. Mod. Phys.*, **37**, 537 (1965). [d] Values for the eclipsed rotamer in the (951/52/3) basis set. [e] The value calculated from the (951/52/3) basis set minus that calculated for the (95/52/3) basis set. [f] The value calculated for the eclipsed configuration minus that for the staggered configuration in the (951/52/3) basis set. The values given for orbitals 8a′ and 2a″ correspond to $(8a')_{eclip}$–$(2a'')_{stag}$ and $(2a'')_{eclip}$–$(8a'')_{stag}$, respectively. Likewise for orbitals 10a′ and 3a″, the respective values are $(10a')_{eclip}$–$(3a'')_{stag}$ and $(3a'')_{eclip}$–$(10a')_{stag}$. (See text for explanation.)

that the good agreement seen here is not simply fortuitous.

It is clear from the atomic charge values given in the above drawing that a physically reasonable apportionment of atomic orbitals in the LCAO approximation should lead to a charge distribution in which the phosphorus atom is positive and the carbon atom negative, with the introduction of d orbitals reducing but not eliminating these charges. For the isomeric monomethylphosphine in the same basis sets, the charge on the phosphorus is calculated to be −0.03 e and on the carbon −0.57, using d orbitals; whereas, the charges are respectively +0.22 and −0.70, with d orbitals disallowed. Since for the same basis sets, the change in the calculated charge on either carbon or phosphorus upon allowing d character is about twice as great for methylenephosphorane as for monomethylphosphine, we have some indirect evidence here for electronic feedback from the carbon to the phosphorus. Similar evidence is found in the fact that the P–C overlap population is increased by 0.20 e for the methylenephosphorane as compared to only 0.08 e for the monomethylphosphine upon allowing d character.

The effect on several calculated properties of adding an appropriate set of phosphorus d orbitals to the chosen (sp) basis set is shown in Table III for *ab initio* LCAO–MO–SCF computations on a series of phosphorus compounds. The orbital energy of the phosphorus "2p" inner-shell electron was chosen for inclusion in this table since both theoretical and experimental studies[18,20] related to inner-orbital photoelectron spectroscopy have shown that the orbital energy of any inner-shell electron decreases as electrons are withdrawn from its atom. Note in Table III that the results obtained for PH_3 in two different basis sets are about the same, indicating that, if the basis set gives at least a minimally acceptable description of the constituent atoms and is reasonably well balanced,[19] the change in the chosen properties upon adding d character is quite constant for a given molecule.

Table III. Effect of Adding Phosphorus d Character in *Ab Initio* SCF Calculations on Various Phosphorus-Based Molecules

		Change[a] upon adding d orbitals		
Molecule	Gaussian basis set	In total energy, au	In P "2p" orbital energy, eV	In charge on P, e
PH_3[b]	(95/3)	−0.06	+0.6	+0.22
PH_3[b]	(73/2)	−0.07	+0.3	+0.23
H_2PPH_2[c]	(73/2)	−0.16	+0.3	+0.17
OPH_3[d]	(73/52/2)	−0.20	+1.3	+0.50
OPF_3[e]	(84/52/52)	−0.57	+3.6	+0.99
HCP[f]	(73/52/2)	−0.08	+0.8	+0.18
CH_3PH_2[g,h]	(95/52/3)	−0.06	+0.6	+0.25
CH_2PH_3[g]	(95/52/3)	−0.10	+1.2	+0.40

[a] The value for the basis set with addition of an appropriate d exponent on the phosphorus minus the value for the basis set as listed. [b] J.-B. Robert, H. Marsmann, L. J. Schaad, and J. R. Van Wazer, *Phosphorus*, in press. [c] Gauche configuration. See ref 15. [d] H. Marsmann, L. C. D. Groenweghe, L. J. Schaad, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **92**, 6107 (1970). [e] I. Absar and J. R. Van Wazer, *J. Phys. Chem.*, **75**, 1360 (1971). [f] See ref 12. [g] Staggered configuration. [h] See ref 14.

Upon substituting the unshared pair of electrons of PH_3 by an oxygen atom to get OPH_3 [in a basis set

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(20) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsal.*, [4] 20 (1967).

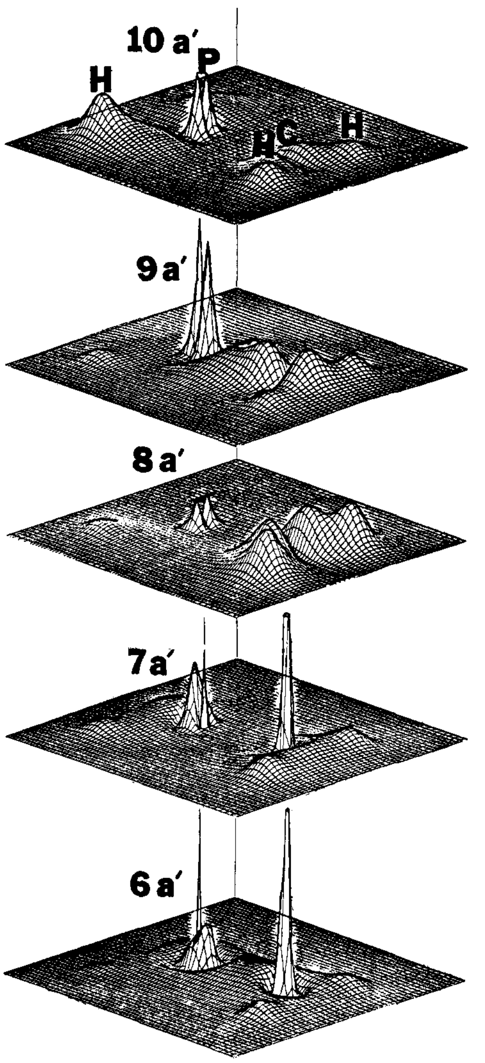

Figure 1. Electron density maps of the valence-shell orbitals of the eclipsed form of methylenephosphorane, as observed in the plane containing one of the hydrogens bonded to the phosphorus, the phosphorus and the carbon, and the two hydrogens bonded to the carbon. The molecular geometry is shown on the basal plane with the electron density perpendicular to it.

employing seven s and three p (with and without a d) exponents on the phosphorus], it is seen that the absolute values of the changes given in Table III all increase. Analysis[21] of the computations on OPH$_3$ show clearly that there is considerable p_π–d_π feedback of electrons from the oxygen to the phosphorus and that this is associated with a single molecular orbital. Even greater overall p_π–d_π feedback to the phosphorus has been computed[21] for the molecule OPF$_3$, which is seen to exhibit the largest absolute values for changes in all three of the properties listed in Table III. Thus, one might infer from this table that there is an appreciable amount of p_π–d_π feedback to the phosphorus in methylenephosphorane.

Three-dimensional electron density maps for the valence-shell molecular orbitals[22] for the eclipsed form of methylenephosphorane are shown in Figure 1, in which the molecular geometry is plotted on the basal plane and the electron density perpendicular to it. Although a full set of electron density maps was made for both the eclipsed and staggered forms, those for the eclipsed form are presented here because this rotamer exhibits five atoms in the same plane. These maps correspond to a slice through the molecule in this plane, containing the carbon and the two hydrogens bonded to it (right-hand front) as well as the phosphorus and one of the two hydrogens bonded to it (the latter appearing near the left-hand corner). The other two hydrogens bonded to the phosphorus are above and below the chosen plane. Of the seven valence-shell molecular orbitals, two (2a'' and 3a'') exhibit nodes in this plane and so they have been plotted in another plane at right angles to this one, passing through the P–C bond axis. The resulting electron density maps for orbitals 2a'' and 3a'' are shown in Figure 2. Comparison of all of these molecular orbital plots with similar ones[23] calculated for the atomic orbitals of the three constituent atoms shows that the antinodes and nodes (maxima and minima in the plots) of a given atomic orbital carry through to the molecule, wherein they may be distorted but remain basically unchanged.

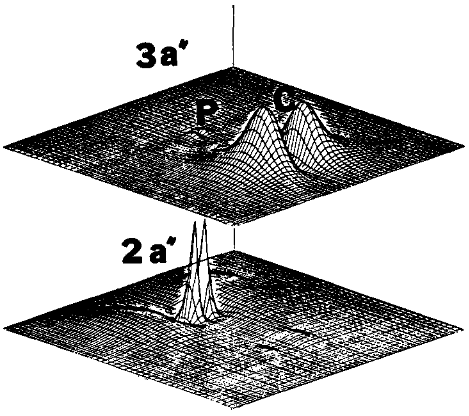

Figure 2. Electron density maps of the valence-shell orbitals of the eclipsed form of methylenephosphorane, as observed in a plane passing through the P–C bond axis perpendicular to the plane of the methylene group. This figure is to the same scale as Figure 1 but corresponds to a cut through the molecule at right angles to the cut of Figure 1.

We have found it convenient to define σ- and π-type bonding contributions with respect to a given pair of nuclei in a molecular orbital. Thus, any molecular orbital containing one nodal plane in which a certain internuclear axis lies can be called π-type with respect to the bonding between these two atoms, regardless of the presence of other nodal planes which might be situated elsewhere in the molecular orbital. Likewise, if nodal planes are either completely absent or do not

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(21) See Table III, footnotes *d* and *e*.

(22) In a recent unpublished study in our laboratory of *ab initio* wave functions, three-dimensional electron density maps were made for the four valence-shell molecular orbitals of water as described in a variety of Slater and Gaussian basis sets. It was found that the differences between a minimum Slater basis, an extended Slater description (larger than a double ζ set), a (52/2), a (73/3), and a (1052/41) Gaussian basis were very small with respect to the plot of any given molecular orbital, so that to the casual observer the choice of basis set was immaterial. Similar results have also been obtained for electron density maps of the ten valence-shell molecular orbitals of methylene fluoride as described in a smaller range of basis sets. We therefore conclude that the maps shown in Figures 1 and 2 of this paper are suitable representations of the respective molecular orbitals and that they exhibit practically the same shape as would similar plots obtained from use of an infinitely sized, balanced basis set (*i.e.*, the Hartree–Fock limit, corresponding to complete filling of Hilbert space). Following this argument, we also judge that Figures 3 and 4 are creditable.

(23) *E.g.*, see W. T. Bordass and J. W. Linnett, *J. Chem. Educ.*, 47, 672 (1970).

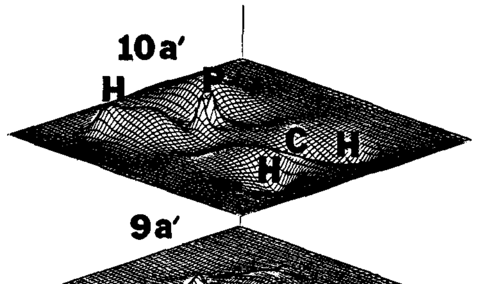

Figure 3. Electron density difference plots for the eclipsed form of methylenephosphorane in the same geometry as Figure 1. The electron density scale of this figure is magnified five times that of Figure 1.

contain the chosen internuclear axis, the molecular orbital may be referred to as having σ character with respect to the particular bond. According to these conventions, we see that with respect to the P–C bond in the eclipsed configuration molecular orbital 6a′ may be described as $(s_\sigma{-}s_\sigma)$, 7a′ as $(s_\sigma{-}s_\sigma)^*$, 8a′ and 2a′′ as $(p_\pi{-}p_\pi)$, 9a′ as $(p_\sigma{-}p_\sigma)$, 10a′ as $(p_\pi{-}p_\pi)$, and 3a′′ as $(p_\pi{-}p_\pi)^*$. Note that orbital 3a′′ clearly depicts the lone-pair electrons on the carbon as well as showing P–C π bonding. This conclusion is in accord with the exceptionally large value of the net electronic population on carbon and the relatively large P–C overlap population given for orbital 3a′′ in Table II. Although there may be small carbon lone-pair contributions from orbitals 8a′ and 10a′, both the appearance of these orbitals in Figure 1 and the population analysis of Table II indicate that this cannot be large. Therefore, we see that the carbon lone pair occurs in p-like lobes above and below the CH_2 plane and is essentially confined to the least energetic of the orbitals, 3a′′ in the eclipsed configuration and its rotational equivalent 10a′ in the staggered form.

Since addition or deletion of phosphorus d character to the wave function causes only small, hardly noticeable changes in the electron density maps, with no gross alteration in their individual shapes, the descriptions given above for the valence-shell molecular orbitals with respect to P–C bonding are independent of the contributions afforded by the d orbitals. However, it should be noted from Table II that the largest change in the P–C overlap population on adding d character is found for orbital 3a′′ with the next largest for orbital 10a′. Also the largest change in orbital energy upon allowing d character is observed for orbital 6a′ with the next larger for 7a′ and 3a′′.

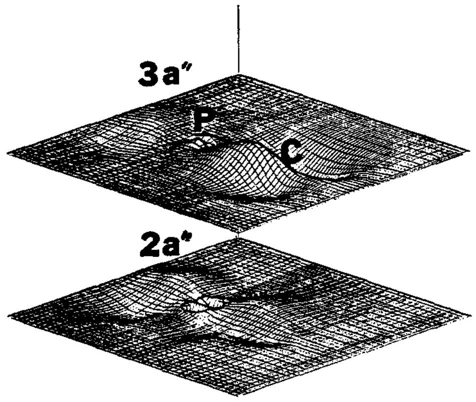

Figure 4. Electron density difference plots for the eclipsed form of methylenephosphorane in the same geometry as Figure 2. The electron density scale of this figure is magnified five times that of Figure 2 and is the same as that of Figure 3.

Electron density difference plots demonstrating the effect of adding d character to all of the valence orbitals (as depicted in Figures 1 and 2) are shown in Figures 3 and 4. Note that the humps and valleys indicating the electron density are magnified five times in Figures 3 and 4 as compared to Figures 1 and 2. Figures 3 and 4 demonstrate the complicated nature of the changes induced in the valence orbitals by supplying d character to the phosphorus. As can be seen from orbitals 6a′, 10a′, and particularly 8a′, the density of the electrons on the hydrogen atoms bonded to the methylene carbon is strongly affected by the presence or absence of d orbitals on the phosphorus atom to which they are not directly bonded. Indeed, allowing d character to the phosphorus has a generally more pronounced local effect on the electron density of the CH_2 group than on that of the PH_3 group of the CH_2PH_3 molecule.

The difference plots for orbitals 2a′′ and 3a′′ in one plane plus 8a′ and 10a′ in the other, in which $p_\pi{-}d_\pi$ feedback from C to P should be observable, are seen (in Figures 3 and 4) not to exhibit individually a hump on either side of the P–C bond axis, as would be expected if $p_\pi{-}d_\pi$ bonding could be assigned to an individual molecular orbital as was the case with phosphine oxide (see Table III, footnote *d*). Instead, however, orbitals 3a′′ and 2a′′ each exhibit a hump on one side of the bond axis and a valley on the other, as can be seen in Figure 4, with the increase in electron density for one orbital lying on the opposite side of that for the other. The situation is similar but even more complex for orbitals 8a′ and 10a′ in Figure 3.

Although Figures 3 and 4 indicate that there is no simple $p_\pi{-}d_\pi$ feedback to the phosphorus of methylenephosphorane in the sense that it shows up in any given molecular orbital, it can be seen from Table II that the molecular orbitals which are π-like with respect to the P–C bond contribute essentially all of the increase in P–C overlap population upon allowing d character to the phosphorus. Thus, the sum of the values in parentheses for the P–C overlap in Table II add up to −0.004 for the σ-like orbitals (6a′, 7a′, and 9a′) while the corresponding sum for the π-like orbitals (8a′, 2a′′, 10a′, and 3a′′) is +0.210, with +0.164 being contributed to the latter from orbital 3a′′. These conclusions are borne out by a set of electron density difference maps (not shown) similar to Figures 3 and 4 representing the sum of the molecular orbitals which are π-like and the sum of those which are σ-like with respect to the P–C bond.

To summarize our work, methylenephosphorane and other phosphorus molecules which might be expected to exhibit the p_π–d_π bonding of classical electronic theory are found to have π-like orbitals even when d character is disallowed; but, when d character is included, the bonding in these molecular orbitals taken as a group is particularly enhanced. However, the electronic feedback upon allowing d character is often dominated by polarization effects,[24] which occur in all molecules without exception, when atomic orbitals of higher symmetry than those needed for the most simple description are included in the LCAO approximation.

Acknowledgment. We wish to thank the National Science Foundation for partial support of this work.

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Extremely High Polarizability of Hydrogen Bonds

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Received June 7, 1971

Abstract: SCF–MO–LCGO calculations are performed for $H_5O_2^+$ as a model illustrating the properties of a symmetrical hydrogen bond with a double-minimum potential well. The potential curves for the proton in the hydrogen bond with and without electrical fields for various O–O distances are calculated, along with the dipole moments, polarizabilities, hyperpolarizabilities, and transition moments of the OH stretching vibrations in the hydrogen bond. The total dipole moment is almost twice as large as the contribution of the proton alone for displacements which are not too large. The relation between the dipole moment and the displacement cannot be approximated linearly. Thus hyperpolarizabilities are of importance. The most important result obtained is that the polarizability is about two orders of magnitude larger than usual polarizabilities. The polarizability of unsymmetric hydrogen bonds may also be considerably larger. The large polarizability causes three interaction effects: an interaction between symmetrical hydrogen bonds *via* proton dispersion forces, an induced-dipole interaction of the hydrogen bonds with the anions and the dipole fields of the solvation molecules, and an interaction between the transitions in the hydrogen bond and other, especially the intermolecular, vibrations. These interactions cause the strong continuous absorption which is observed in the ir spectra with liquid systems containing such hydrogen bonds. The smaller polarizability of unsymmetrical hydrogen bonds causes band broadening.

A continuous absorption was observed in the infrared spectrum on investigating acid and base solutions in the range of the fundamental vibrations[2] and in the range of the overtones,[3,4] as well as with acidic and basic polyelectrolytes.[5–8] This is caused in the acid solutions by $H_5O_2^+$ groupings and with bases by $H_3O_2^-$ groupings.[8] The continuum is not only observed in the presence of these bonds between water molecules but also in the case of many other liquid systems in which hydrogen bonds of type $BH^+\cdots B$ or $(AH\cdots A)^-$ are present.[9,10] It was possible to show that this continuum is caused by the special properties of these symmetrical hydrogen bonds with a double-minimum potential well in which the proton tunnels. Such hydrogen bonds are extremely polarizable.[11] This polarizability can be made plausible considering the distances between the energy levels and the symmetry of the wave functions in Figure 1. The wave function of the ground state E_{0+} of the tunneling proton is symmetric, that of the excited state, E_{0-}, is antisymmetric. If the first excited state is mixed with the ground state, an asymmetric charge distribution results. The first excited level of a tunneling proton is separated only slightly from the ground level. Thus, an extremely

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