

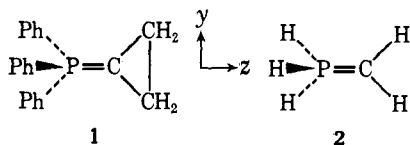
## Structural Effects of 3d Orbitals in Alkylidene Phosphoranes

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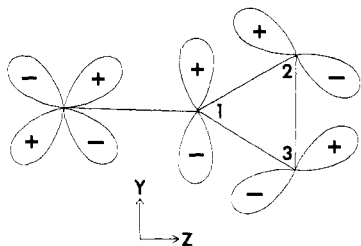
**Abstract:** In cyclopropylidene phosphorane there exists, in addition to the usual out-of-plane  $p_x$ - $d_{xy}$  bonding, a geometrically unique possibility for interaction between the Walsh orbitals of the cyclopropane ring and an in-plane P 3d orbital. A shortened PC bond, long PC-C bonds, and a short  $H_2C$ - $CH_2$  bond are predicted. The effect of the P 3d orbitals being occupied is also manifested in the barrier to rotation about the C-C bond in ethylidene phosphorane.

The synthesis and reactions of the interesting phosphonium ylide **1** have been reported by Bestmann and coworkers.<sup>1</sup> In a recent study of bonding in phosphonium ylides we found that in the model compound **2**



in addition to the primary  $d_{zz}$ - $p_x$   $\pi$  interaction there is a smaller but significant contribution from in-plane  $d_{yz}$ - $CH_2$  bonding.<sup>2</sup> The latter interaction could be described as hyperconjugative electron transfer from the methylene group to the phosphorus 3d<sub>yz</sub> orbital.

The cyclopropylidene phosphorane system offers a unique opportunity for enhancement of this in-plane effect. The highest occupied orbitals of the cyclopropane ring are the degenerate Walsh set,<sup>3</sup> one of which has the correct symmetry to interact with  $d_{yz}$  of phosphorus. The interaction of these orbitals which lie in the  $yz$  plane is shown below.



The net result of the interaction is expected to be (1) electron transfer from the cyclopropane ring to P, (2) increased P-C bonding, (3) weakened  $C_1$ - $C_2$  and  $C_1$ - $C_3$  and strengthened  $C_2$ - $C_3$  bonding.

These qualitative conclusions were tested by extended Hückel molecular orbital computations<sup>4</sup> on the

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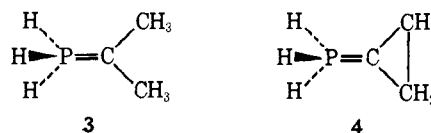
(1) H. J. Bestmann and T. Denzel, *Tetrahedron Lett.*, 3591 (1966); H. J. Bestmann, T. Denzel, and R. Kunstmann, *ibid.*, 2895 (1968); H. J. Bestmann and R. Kunstmann, *Chem. Ber.*, 102, 1816 (1969).

(2) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, 92, 3929 (1970).

(3) A. D. Walsh, *Trans. Faraday Soc.*, 45, 179 (1949).

(4) The parameters specified in ref 2 were used. The same P-C, P-H, and C-H distances were also used for compounds **3** and **4**. All C-C bond lengths were taken as 1.54 Å, all C-C-H bond angles were tetrahedral, C-P-H angles were 122.8°, and the C-C-C angles were 120° in **3** and 60° in **4**. The choice of exponent and valence state ionization potential for the five, component 3d Slater-type basis functions is described in ref 2. The expression given in ref 2 for off-diagonal Hamiltonian matrix elements was employed for all compounds of this study.

model compounds isopropylidene phosphorane (**3**) and cyclopropylidene phosphorane (**4**). Whereas the quan-



titative agreement of the extended Hückel results with (future) experimental findings may be questioned, we will see that the calculated structural properties of these compounds are distinctly and qualitatively different, depending on the contribution of the 3d orbitals to the bonding. The results discussed below invite experimental determination of the degree of this d-orbital contribution.

Figure 1 shows the relevant parts of the population analysis for **3** and **4**. The qualitative argument offered above is substantiated. There is significant charge transfer for **4** in the  $yz$  plane, as evidenced by the charge distribution and even more clearly by Figure 2, an electron density difference map<sup>5</sup> in that plane. The electron density shift for **4** is substantially greater than for **3**, which lacks the propitiously oriented Walsh-orbital system. The evidence for this is in the relative charge distribution and the greater  $\pi$  bonding: the P-C overlap population is 1.53 for **4** and 1.43 for **3** when d orbitals are included, 0.92 for both without d orbitals. If a dipole moment is computed from point charges, then (with 3d orbitals) this moment is in the direction  $P^+-C^-$  for **3**, but for **4** it is reversed.

The in-plane interaction in **4**, and correspondingly **1**, is therefore highly enhanced.<sup>6</sup> We believe that the effect will manifest itself in the geometry of **1** and predict for this molecule a short P-C bond ( $\sim 1.63$  Å), long  $C_1$ - $C_2$  and  $C_1$ - $C_3$  bonds ( $\sim 1.56$  Å), and a short  $C_2$ - $C_3$  bond ( $\sim 1.50$  Å). We would also like to point out the close relation of this system to the norcaradiene-cycloheptatriene equilibrium problem<sup>7</sup> and the stabilization of the cyclopropylcarbinyl cation.<sup>8</sup> In each case we are seeing the conformationally sensitive conse-

(5) D. B. Boyd, *J. Chem. Phys.*, 52, 4846 (1970); *Theor. Chim. Acta*, 18, 184 (1970).

(6) A cyclopropenylidene phosphorane has been synthesized by S. V. Krivun, N. S. Semenov, S. N. Baranov, and V. I. Dulenko, *Zh. Obshch. Khim.*, 40, 1904 (1970).  $R_3P=C(CH_2)_2$  is an interesting system because the zwitterionic resonance structure would lead to an antiaromatic cyclopropenide anion, and hence this would be another situation in which the multiple-bonded nature of the PC linkage is enhanced.

(7) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

(8) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, 88, 2321 (1966), and references therein; R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964); *Tetrahedron Lett.*, 3819 (1965).

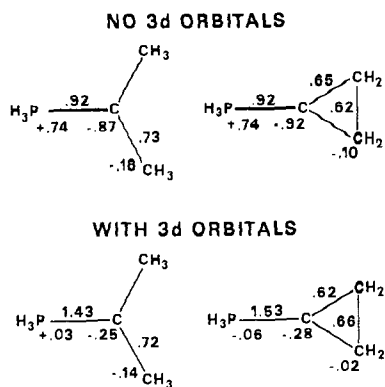
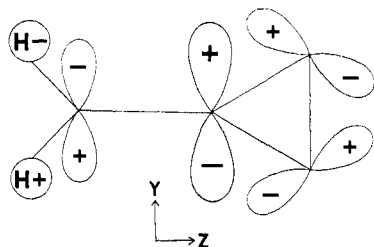


Figure 1. Mulliken population analyses of the extended Hückel numbers are net atomic charges of the nonhydrogenic atoms and unsigned numbers are overlap populations. The assumed conformation of the methyl groups in  $\text{H}_3\text{PC}(\text{CH}_3)_2$  is such that the molecule has  $C_2$  symmetry, one PCCH dihedral angle is  $90^\circ$  in each methyl group, and there are three hydrogens on one side of the carbon plane and six hydrogens on the other side. This rotamer is calculated (with or without d orbitals) to be more stable than one with one or both methyl groups rotated  $60^\circ$  about the CC bonds.

quences of the interaction of a Walsh orbital with an external  $\pi$ -electron acceptor—a low-lying unfilled orbital.

The recent structure determination of methylenecyclopropane<sup>9</sup> provides an interesting comparison with cyclopropylidene phosphorane. In the hydrocarbon there is no in-plane d orbital for  $\pi$  bonding between the ethylenic carbon and the cyclopropane Walsh orbitals. The structure observed has the  $\text{CH}_2-\text{CH}_2$  bond longer (1.54 Å), and hence weaker, than the other C-C ring bonds (1.46 Å). The extended Hückel calculations successfully indicate this relative order. The calculations also give the lowest empty MO  $\pi^*$  character and  $b_1$  symmetry with a nodal pattern to favor the  $\text{CH}_2-\text{CH}_2$  bond being shorter than the other ring bonds. The highest occupied MO is not the  $b_1$  C=C  $\pi$  orbital but a  $b_2$   $\sigma$  orbital. This  $b_2$  MO is made up of the same Walsh orbital that was stabilized by interaction with the high-lying  $d_{yz}$  orbital in **1** and **4**, but now it is destabilized by hyperconjugative interaction with an occupied  $\sigma$  orbital of the exocyclic methylene group. The highest occupied MO is  $\text{C}_1-\text{C}_2$  and  $\text{C}_1-\text{C}_3$  bonding and  $\text{C}_2-\text{C}_3$  antibonding, as indicated below by the interaction in the  $yz$  plane of the relevant atomic and hybrid orbitals.



Hence, for  $\text{H}_2\text{C}=\text{C}(\text{CH}_2)_2$  the lowest energy  $\pi^* \leftarrow \sigma$  excitation should lead to an equalization of the C-C bond lengths in the ring (as well as a lengthening of the ethylenic bond and probable twisting<sup>10</sup>). One notes that this geometry change in the ring is analogous to

(9) V. W. Laurie and W. M. Stigliani, *J. Amer. Chem. Soc.*, **92**, 1485 (1970).

(10) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).

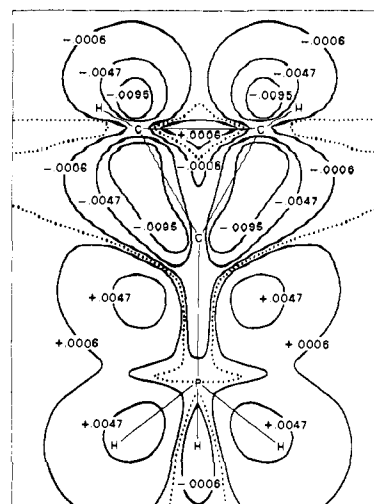


Figure 2. Electron density difference map of  $\text{H}_3\text{PC}(\text{CH}_2)_2$  showing the contours of electron density obtained by subtracting the total electron density computed without 3d orbitals from the density computed with their inclusion. Contours are in atomic units, and nodes are denoted by dotted lines. The map covers an area of  $4.5 \times 6.0$  Å in the plane of the phosphorus and carbon atoms. The projections of the C-H and P-H internuclear axes onto this plane are shown. Electron accumulations in the  $3d_{yz}$  orbital and in the  $\text{H}_2\text{C}-\text{CH}_2$   $\sigma$ -bonding region are evident.

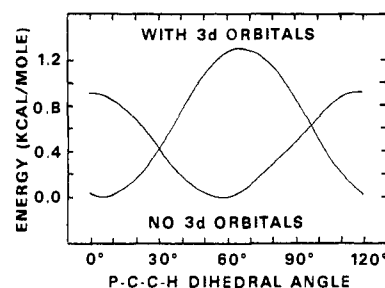
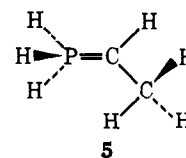


Figure 3. Energy curves for the rotation of the methyl group in  $\text{H}_3\text{PCHCH}_3$  computed from basis sets with and without d orbitals.  $0^\circ$  corresponds to one methyl hydrogen being cis to the P, and  $60^\circ$  to the trans rotamer. The energy is relative to that for the most stable rotamer in each basis set and is based on the sum over all electrons of the molecular eigenvalues as was done in ref 2.

what would happen when the d orbitals are allowed to interact with the ring in cyclopropylidene phosphorane. Thus, one could predict that the ring geometry of excited methylenecyclopropane is similar to that of ground-state  $\text{H}_3\text{PC}=\text{C}(\text{CH}_2)_2$ , if indeed d orbitals play a role in bonding in the latter compound.

A final interesting by-product of our study was the calculation of the barrier to internal rotation of the methyl group in ethylidene phosphorane (**5**). Figure 3 shows the energy of **5** as a function of rotation of

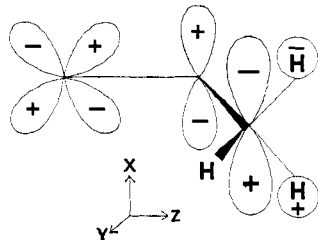


the methyl group. Without 3d orbitals the preferred geometry is staggered with respect to the PC bond. With 3d orbitals the eclipsed geometry is favored, just as it is in propylene.<sup>11,12</sup> We thus have still

(11) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

another indication of how the inclusion of 3d orbitals introduces the characteristic features of a  $\pi$  bond.

(12) The character of the highest occupied MO of **5** is similar to that of butadiene. The conformational preference of **5**



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(with 3d orbitals) can be understood in terms of the pseudo- $\pi$  orbital of the methyl group preferring a position of minimum overlap with the  $P=C$   $\pi$  orbital. Similar rationalizations have been applied to the conformational preferences of polyenes; see R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966). J. P. Lowe, *ibid.*, **92**, 3799 (1970), has applied similar hyperconjugative arguments to the structural properties of ethane and propylene with apparent success [see, however, I. R. Epstein and W. N. Lipscomb, *ibid.*, **92**, 6094 (1970)].

## Conformation and Substituent Dependence of Long-Range H-H Coupling over Four Bonds

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**Abstract:** A theoretical study of the conformation and substituent dependence of long-range coupling constants between protons separated by four bonds is presented in terms of self-consistent perturbation theory in the semiempirical INDO (intermediate neglect of differential overlap) approximation of molecular orbital theory. Calculated results are reported for propane and propene and their monosubstituted fluoro and cyano derivatives, which are taken as representative of inductive and hyperconjugative substituents, respectively. It is predicted that the long-range coupling constants for the monosubstituted derivatives of propane should be more positive than the propane value. Hyperconjugative substituents at the terminal carbons would be an exception, as negative shifts are noted in these cases. Similar trends in the long-range coupling constants for the various monosubstituted derivatives of propene are consistent with the experimental data. The calculated results also show that the orientation of the coupled protons with respect to the substituent is an important factor.

A large number of experimental values of long-range coupling constants between protons separated by four bonds,  ${}^4J_{HH'}$ , have been reported.<sup>1,2</sup> The physical situation which gives rise to this type of coupling is complex and existing theoretical studies<sup>3-7</sup> have not been completely successful in correlating the experimental data.

In unsaturated molecules the  $\pi$ -electron mechanism is often the most important factor for coupling over four bonds.<sup>3,5-7</sup> However, in saturated molecules and in certain conformations of unsaturated molecules the  $\sigma$ -electron mechanism is dominant.<sup>2,4</sup> Coupling constants between nuclei separated by four bonds are strongly conformation and substituent dependent and can be either positive or negative in sign. Because of the unavailability of experimental data for unstrained and unsubstituted hydrocarbons, the problem of elucidating the conformational dependencies are inextricably associated with uncertainties in the nature of substituent effects.

Existing theoretical descriptions<sup>3-7</sup> of long-range H-H coupling constants over four bonds have been

based on molecular fragments, the assumption that the  $\sigma$ - and  $\pi$ -electron systems can be treated independently, and neglect of substituent effects. Because integral parameters were determined semiempirically, questions of the importance of direct *vs.* indirect mechanisms<sup>8</sup> are unresolved. There have been no previous systematic theoretical investigations of substituent effects on  ${}^4J_{HH'}$ , but some crude, qualitative MO descriptions<sup>2,9</sup> appeared to be reasonably consistent with the experimental results.

In the present study some of the difficulties mentioned above are overcome by means of calculations based on self-consistent perturbation theory<sup>10</sup> in the semiempirical INDO (intermediate neglect of differential overlap) approximation<sup>11</sup> of self-consistent-field molecular orbital (SCF-MO) theory. This method permits all valence-electron calculations on hydrocarbons of variable geometry with substituents in the second row of the periodic table.

### I. Theoretical Formulation

Calculations of H-H coupling constants are based on approximate molecular orbital wave functions<sup>10</sup>

- (1) S. Sternhell, *Pure Appl. Chem.*, **14**, 15 (1964).
- (2) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).
- (3) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).
- (4) M. Barfield, *ibid.*, **41**, 3825 (1964).
- (5) M. Barfield, *ibid.*, **48**, 4458, 4463 (1968).
- (6) R. Ditchfield and J. N. Murrell, *Mol. Phys.*, **15**, 533 (1968).
- (7) M. Barfield and J. J. Reed, *J. Chem. Phys.*, **51**, 3039 (1969).

- (8) M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).
- (9) D. J. Sardella, *J. Mol. Spectrosc.*, **31**, 70 (1969).
- (10) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).
- (11) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).