Abstract: In cyclopropylidenephosphorane there exists, in addition to the usual out-of-plane $p_d$-$d_p$ bonding, a geometrically unique possibility for interaction between the Walsh orbitals of the cyclopropane ring and an in-plane $P d_3$ orbital. A shortened PC bond, long PC-C bonds, and a short $H_2C-CH_2$ bond are predicted. The effect of the $P d_3$ orbitals being occupied is also manifested in the barrier to rotation about the $C-C$ bond in ethylidenephosphorane.

The synthesis and reactions of the interesting phosphonium ylide 1 have been reported by Bestmann and coworkers. In a recent study of bonding in phosphonium ylides we found that in the model compound isopropylidenephosporane (3) and cyclopropylidenephosphorane (4) whereas the quantitative 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 of 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. We believe that the effect will manifest itself in the geometry of 1 and predict for this molecule a short $P-C$ bond ($\sim 1.63 \text{ \AA}$), long $C_1-C_2$ and $C_2-C_3$ bonds ($\sim 1.56 \text{ \AA}$), and a short $C_1-C_3$ bond ($\sim 1.50 \text{ \AA}$). We would also like to point out the close relation of this system to the norcaradiene-cycloheptatriene equilibrium problem and the stabilization of the cyclopropylcarbinyl cation. In each case we are seeing the conformationally sensitive conse-

* Address correspondence to this author at The Lilly Research Laboratories.


(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 A, 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.


(6) A cyclopropyldienephosphorane has been synthesized by S. V. Krivun, N. S. Semenov, N. S. Baranov, and V. I. Dulento, Zh. Obsch. Khim., 40, 1904 (1970). $R_3P=C(CH_3)$ is an interesting system because the zwitieronic resonance structure would lead to an antiaromatic cyclopropenedi anion, and hence this would be another situation in which the multiple-bonded nature of the PC linkage is enhanced.


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 H₃PC(CH₂)₃ is such that the molecule has C₃v symmetry, one PCCH dihedral angle is 90° 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° about the CC bonds.

sequences of the interaction of a Walsh orbital with an external π-electron acceptor—a low-lying unfilled orbital.

The recent structure determination of methylene-cyclopropane⁹ provides an interesting comparison with cyclopropylidenephosphorane. In the hydrocarbon there is no in-plane d orbital for π bonding between the ethylenic carbon and the cyclopropane Walsh orbitals. The structure observed has the CH₂=CH₂ 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 π* character and b₁ symmetry with a nodal pattern to favor the CH₂=CH₂ bond being shorter than the other ring bonds. The highest occupied MO is not the b₁ C=C π orbital but a b₂ σ orbital. This b₂ MO is made up of the same Walsh orbital that was stabilized by interaction with the high-lying dₓᵧ orbital in 1 and 4, but now it is destabilized by hyperconjugative interaction with an occupied σ orbital of the exocyclic methylene group. The highest occupied MO is C₁–C₂ and C₁–C₃ bonding and C₂–C₃ antibonding, as indicated below by the interaction in the yz plane of the relevant atomic and hybrid orbitals.

Hence, for H₂C=C(CH₂)₃ the lowest energy π* ← σ 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 twisting¹⁰). One notes that this geometry change in the ring is analogous to what would happen when the d orbitals are allowed to interact with the ring in cyclopropylidenephosphorane. Thus, one could predict that the ring geometry of excited methylenecyclopropane is similar to that of ground-state H₂PC=CH(CH₂)₃, 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 ethylidenephosphorane (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.¹¹,¹² We thus have still

Figure 2. Electron density difference map of H₃PC(CH₂)₃ 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 × 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 3dₘ orbital and in the H₂C–CH₂ σ-bonding region are evident.

Figure 3. Energy curves for the rotation of the methyl group in H₃PC(CH₂)₃ computed from basis sets with and without d orbitals. 0° corresponds to one methyl hydrogen being cis to the P, and 60° 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.

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

Michael Barfield

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, $\mathcal{J}_{HH}$, have been reported. The physical situation which gives rise to this type of coupling is complex and existing theoretical studies have not been completely successful in correlating the experimental data.

In unsaturated molecules the π-electron mechanism is often the most important factor for coupling over four bonds. However, in saturated molecules and in certain conformations of unsaturated molecules the σ-electron mechanism is dominant. 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 of long-range H–H coupling constants over four bonds have been based on molecular fragments, the assumption that the σ- and π-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 are unresolved. There have been no previous systematic theoretical investigations of substituent effects on $\mathcal{J}_{HH}$, but some crude, qualitative MO descriptions 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 in the semiempirical INDO (intermediate neglect of differential overlap) approximation 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.

(4) M. Barfield, ibid., 41, 3625 (1964).
(5) M. Barfield, ibid., 48, 4458, 4463 (1968).


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