# Semiempirical and nonempirical quantum-chemical methods applied to the structure of P-substitute phosphaalkenes

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# SEMIEMPIRICAL AND NONEMPIRICAL QUANTUM-CHEMICAL METHODS
# APPLIED TO THE STRUCTURE OF P-SUBSTITUTE PHOSPHAALKENES

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Quantum-chemical studies have been performed on the structures of the phospha-
alkenes $RP = CH_2$, in which the substituent R may have various electronic param-
eters; the nonempirical MO LCAO SCF method has been used with the OST-3G, OST-
3G*, 4-31G, 4-31G*, 4-31G**, and 4-31G(d) bases, as well as in the semiempiri-
cal MINDO approximation. The calculations with the 4-31G and 4-31G(d) bases
give satsifactory values for the geometrical parameters and energies of the
boundary MO. OST-3G is unsuitable for describing the energies of the MO, but
MINDO can be used. The HOMO are of π type, below which lie n-type MO. The
gap between them for any R other than an alkyl group is increased by compar-
ison with $HP + CH_2$. The P=C bond is appreciably polarized by R, particularly
if it is capable of π conjugation; the length varies little in this series
because the resonance and polarization effects balance. The relative reactiv-
ities of the P-substituted phosphaalkenes in 1,2-addition reactions are dis-
cussed.

This paper continues rsearch on phosphorus-carbon bonds, electronic effects from sub-
tituents, and reactivity in the phosphaalkenes [1-4]. Much evidence has accumulated on the
structures and properties of two-coordinate phosphorus compounds [5], but most of the data
relate to polyatomic compounds containing bulky substituents. Systematic measurements on
small molecules in that class are difficult because of their kinetic instability, and the
relevant studies are few. In particularly, only recently have photoelectron spectra been
recorded for four simple phosphaalkenes [6-8]. Consequently, a logical description can be
given for the structures and properties of those compounds beginning with simple ones only
by quantum-chemical methods, which provide reliable conclusions on the electronic structures
of $HP = CH_2$, $HP = NH$ and $HP = PH$ and on the strengths of the π bonds [5, 9] and also enable
one to interpret the photoelectron spectra for $HP = CH_2$, $HP = CHMe$ and $MeP = CH_2$ [7]. Non-
empirical methods applied to fluorinated phosphaalkenes [10, 11] have shown that some elec-
tronic effects from the fluorine are specific for the P=C π bonds. With more complicated
molecules, one is inevitably forced to use simplified quantum-chemical methods, so one
has to examine the reliability. We have found [3, 4] that semiempirical methods are sui-
table for qualitative characterization of the phosphaalkenes but do not always give good
quantitative descriptions because of various deficiencies in the parameterization.

A condition for constructing reactivity theory for the phosphaalkenes from quantum
studies is that one should have a correct description of the molecular geometry and the
positions of the boundary MO. Also, inadequate information on the lability bounds for
P=C bonds has stimulated theoretical studies on how groups affect the characterisitcs.
We have examined how the geometrical and electronic structures in the phosphaalkenes are
affected when there are various sustituents on the phosphorus atom, and we have also tested
and compared the most economical computational scHems in order to derive satisfactory ap-
proaches to two-coordinated phosphours compounds.

We examined the phosphaalkenes $RP = CH_2$ (I VIII; I R = F; II R = Cl; III R = Br; IV
R = I; V R = CN; VI R = $NH_2$; VII R = OH; VIII R = SH). The nonempirical calculations were

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TABLE 1. Bond Lengths ℓ and Bond Angles in the Phosphaalkenes I—IX $R\diagdown P{=}C\diagup^{H_Z}_{\diagdown H_E}$

| Parameter | Method | I | II | III | IV | V | VI | VII | VIII | IX |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Compound | | | | | |
| $l$(P=C), pm | MINDO | 158,0 | 156,8[a] | 156,6 | 156,7 | 157,5 | 157,4[a] | 157,6 | 156,9 | 156,6[a] |
| | OST-3G | 161,5 | 161,6 | — | — | 162,3 | 161,5 | 161,4 | 161,6 | 161,7[b] |
| | 4-31G | 165,1 | 165,8 | 165,0 | — | 167,4 | 166,0 | 165,2 | 166,2 | 167,2[b] |
| | exp. [12] | 167,0 | 165,8 | — | — | 165,8 | — | — | — | 167,3 |
| | | 165,1[c] | | | | | | | | |
| $l$(P—R), pm | MINDO | 154,8 | 198,7[a] | 38,8 | 226,6 | 165,8 | 161,2[a] | 159,5 | 194,6 | 134,1[a] |
| | OST-3G | 163,5 | 211,5 | — | — | 179,7 | 169,4 | 169,1 | 210,1 | 138,9[b] |
| | 4-31G | 169,9 | 226,7 | — | — | 183,8 | 173,2 | 173,5 | 229,8 | 144,9[b] |
| | exp. [12] | 158,0 | 205,9 | 222,0 | — | 178,8 | — | — | — | 142,0 |
| ∠CPR, deg | MINDO | 107,8 | 108,2[a] | 108,5 | 110,9 | 106,7 | 108,8[a] | 106,4 | 107,4 | 102,8[a] |
| | OST-3G | 99,7 | 100,0 | — | — | 98,8 | 102,0 | 98,9 | 100,7 | 97,1[b] |
| | 4-31G | 99,8 | 100,0 | 104,0 | — | 99,8 | 104,6 | 99,7 | 99,9 | 98,5[b] |
| | exp. [12] | 104,0 | 103,0 | — | — | 101,4 | — | — | — | 97,4 |
| ∠PCH$_Z$, deg | MINDO | 128,6 | 128,5[a] | 128,4 | 128,5 | 128,7 | 128,5[a] | 128,0 | 128,0 | 127,1[a] |
| | OST-3G | 124,1 | 126,3 | — | — | 126,2 | 125,4 | 124,3 | 126,1 | 126,0[b] |
| | 4-31G | 124,0 | 125,3 | — | — | 125,3 | 125,5 | 122,9 | 125,5 | 125,3[b] |
| | exp. [12] | — | 124,6 | — | — | 124,8 | — | — | — | 124,4 |
| ∠PCH$_E$, deg | MINDO | 117,9 | 118,3[a] | 118,5 | 118,4 | 118,1 | 118,3[a] | 118,4 | 118,6 | 120,0[a] |
| | OST-3G | 120,8 | 119,1 | — | — | 119,8 | 120,0 | 121,1 | 120,4 | 121,1[b] |
| | 4-31G | 119,0 | 118,4 | — | — | 118,7 | 118,5 | 119,5 | 118,7 | 119,8[b] |
| | exp. [12] | — | 117,2 | — | — | 117,2 | — | — | — | 118,3 |

aData from [3]; bdata from [5] supplemented and revised in this study; cvalue corrected for the discrepancy between experiment and nonempirical calculation in the 6-31G* basis [10].

TABLE 2. Energies of Boundary MO in Phosphaalkenes (nonempirical calculations)

| Compound | Orbital | MO energy, eV | | | | | |
|---|---|---|---|---|---|---|---|
| | | OST-3G | OST-3G* | 4-31G | 4-31G(d) | 4-31G* | 4-31G** |
| I | π* | 6,593 | 6,829 | 1,981 | 2,226 | 2,281 | 2,269 |
| | π | —7,205 | —7,223 | —10,229 | —10,046 | —9,974 | —9,972 |
| | n | —8,554 | —8,853 | —11,885 | —11,924 | —11,690 | —11,683 |
| II | π* | 5,506 | 5,808 | 1,507 | 1,770 | 1,614 | 1,603 |
| | π | —8,104 | —7,859 | —10,297 | —10,097 | —10,240 | —10,237 |
| | n | —8,999 | —9,022 | —11,096 | —11,122 | —11,055 | —11,051 |
| V | π* | 5,178 | 5,256 | 1,125 | 1,250 | 1,220 | 1,211 |
| | π | —8,155 | —8,066 | —10,406 | —10,282 | —10,353 | —10,351 |
| | n | —9,325 | —9,486 | —11,640 | —11,742 | —11,562 | —11,557 |
| VI | π* | 7,319 | 7,676 | 3,101 | 3,386 | 3,239 | 3,223 |
| | π | —6,017 | —6,103 | —8,527 | —8,440 | —8,406 | —8,415 |
| | n | —8,514 | —8,540 | —10,725 | —10,719 | —10,645 | —10,629 |
| VII | π* | 6,896 | 7,141 | 2,572 | 2,805 | 2,793 | 2,783 |
| | π | —6,719 | —6,728 | —9,380 | —9,238 | —9,227 | —9,223 |
| | n | —8,110 | —8,387 | —10,869 | —10,931 | —10,773 | —10,760 |
| VIII | π* | 6,812 | 6,598 | 1,994 | 2,233 | 2,101 | 2,104 |
| | π | —6,112 | —6,275 | —9,208 | —9,023 | —9,157 | —9,133 |
| | n | —7,572 | —7,404 | —10,118 | —10,210 | —10,084 | —10,057 |
| IX | π* | 6,776 | 6,899 | 2,344 | 2,581 | 2,491 | 2,511 |
| | π | —7,377 | —7,300 | —9,689 | —9,502 | —9,615 | —9,577 |
| | n | —8,236 | —8,440 | —10,395 | —10,479 | —10,349 | —10,336 |

*Observed ionization potentials: II—$I_1$ = 10.05 eV, $I_2$ = 10.75 eV [8]; IX = $I_1$ = 10.30 eV, $I_2$ = 10.70 eV [7].

performed with GAUSSIAN-76/79 and GAUSSIAN-80 programs with the OST-3G, OST-3G*, and 4-31G bases, and also with 4-31G extended in three ways: by the inclusion of the d functions for elements in the second period, with the inclusion of the p functions for the hydrogen atoms and the d functions for the second-period elements, and with the inclusion of the d functions for the phosphorus atom. Subsequently, those bases are denoted by 4-31G*, 4-31G**, and 4-31G(d). The semiempirical calculations were performed in the MINDO approximation, whose applicability here has been demostrated [3]. In all cases, the geometry was optimized completely. The errors in the calculated characteristics arising from geometry distortion were estimated from calculations based on the observed geometrical parameters if known. The results were compared with analogous data for HP-$CH_2$ (IX), which were taken from MINDO calculations in [3] and in the OST-3G basis from [5]; the other data for IX are our own.

Table 1 gives the bond lengths and angles for I-IX as well as the measured values [12]. The best agreement is obtained from the nonempirical calculation with 4-31G: standard deviation from experiment in the length 4 pm, and in the angles 2°. MINDO is the worst, with the corresponding deviations 7 pm and 5°, with the bond lengths underestimated and the bond angles too large. That feature of MINDO was observed in our previous phosphaalkene calculations.

Table 2 gives the boundary MO energies in I-II and V-IX from nonempirical methods, and Table 3 gives the compositions; Table 4 gives the corresponding characteristics for I-IX from MINDO. The filled MO sequence is the same no matter what the method: the HOMO is the π orbital for the three-center four-electron system R—P=C, and that following it is an n orbital, i.e., a combination of orbitals from the unshared electron pairs on the phosphorus and the atom in the R group, where in III and IV, the predominant contribution is from the unshared pair on the bromine (iodine), and in the other cases, from the phosphorus atom. Previous MINDO semiempirical calculations on IX and various of its derivatives [3] have shown that the same sequence of higher filled MO applies, which has been confirmed for IX and its methyl derivatives by photoelectron spectroscopy [7]. The [3] results and the present ones indicate that the HOMO in all known and most possible monosubstituted phosphaalkenes are of π type.

The first and second ionization potentials $I_1$ and $I_2$ for IX agree satisfactorily with the energies $\varepsilon_\pi$ and $\varepsilon_n$ for the filler π and n MO as calculated in the 4-31G(d) basis. When this paper had been sent to press, results were published on the photoelectron spectrum of II [8]; the results for $I_1$ and $I_2$ correspondingly were 10.05 and 10.75 eV and agree well with our calculated $\varepsilon_\pi$ and $\varepsilon_n$ in the 4-31G basis with d-function inclusion [8] and in the

TABLE 3. Boundary MO Compositions in Phosphaalkenes from Nonempirical Calculations in the 4-31G Basis with Optimal Geometrical Parameters

| Compound | Orbital | Squares of AO coefficients | | |
|---|---|---|---|---|
| | | P | C | R |
| I | $\pi^*$ | $0{,}623\ (p_z)$ | $0{,}487\ (p_z)$ | $0{,}026\ (p_z)$ |
| | $\pi$ | $0{,}242\ (p_z)$ | $0{,}262\ (p_z)$ | $0{,}054\ (p_z)$ |
| | $n$ | $0{,}467\ (s)$ <br> $0{,}230\ (p_x+p_y)$ | $0{,}103\ (p_x+p_y)$ | $0{,}110\ (p_x+p_y)$ |
| II | $\pi^*$ | $0{,}593\ (p_z)$ | $0{,}501\ (p_z)$ | $0{,}016\ (p_z)$ |
| | $\pi$ | $0{,}193\ (p_z)$ | $0{,}209\ (p_z)$ | $0{,}192\ (p_z)$ |
| | $n$ | $0{,}215\ (s)$ <br> $0{,}169\ (p_x+p_y)$ | $0{,}034\ (p_x+p_y)$ | $0{,}350\ (p_x+p_y)$ |
| V | $\pi^*$ | $0{,}460\ (p_z)$ | $0{,}479\ (p_z)$ | $0{,}085\ (p_zC+p_zN)$ |
| | $\pi$ | $0{,}250\ (p_z)$ | $0{,}224\ (p_z)$ | $0{,}075\ (p_zC+p_zN)$ |
| | $n$ | $0{,}397\ (s)$ <br> $0{,}226\ (p_x+p_y)$ | $0{,}062\ (p_x+p_y)$ | $0{,}065\ (p_x+p_yC)$ <br> $0{,}077\ (p_x+p_yN)$ |
| VI | $\pi^*$ | $0{,}712\ (p_z)$ | $0{,}434\ (p_z)$ | $0{,}052\ (p_z)$ |
| | $\pi$ | $0{,}142\ (p_z)$ | $0{,}288\ (p_z)$ | $0{,}208\ (p_z)$ |
| | $n$ | $0{,}430\ (s)$ <br> $0{,}298\ (p_x+p_y)$ | $0{,}060\ (p_x)$ | $0{,}054\ (p_y)$ |
| VII | $\pi^*$ | $0{,}673\ (p_z)$ | $0{,}438\ (p_z)$ | — |
| | $\pi$ | $0{,}206\ (p_z)$ | $0{,}269\ (p_z)$ | $0{,}095\ (p_z)$ |
| | $n$ | $0{,}325\ (s)$ <br> $0{,}265\ (p_x+p_y)$ | $0{,}055\ (p_x+p_y)$ | $0{,}178\ (p_x+p_y)$ |
| VIII | $\pi^*$ | $0{,}632\ (p_z)$ | $0{,}448\ (p_z)$ | — |
| | $\pi$ | $0{,}100\ (p_z)$ | $0{,}167\ (p_z)$ | $0{,}360\ (p_z)$ |
| | $n$ | $0{,}150\ (s)$ <br> $0{,}252\ (p_x+p_y)$ | — | $0{,}247\ (p_x+p_y)$ |
| IX | $\pi^*$ | $0{,}606\ (p_z)$ | $0{,}495\ (p_z)$ | — |
| | $\pi$ | $0{,}274\ (p_z)$ | $0{,}251\ (p_z)$ | — |
| | $n$ | $0{,}356\ (s)$ <br> $0{,}319\ (p_x+p_y)$ | $0{,}033\ (p_x+p_y)$ | $0{,}088\ (s)$ |

4-31G and 4-31G(d) bases (the $\varepsilon_\pi$ and $\varepsilon_n$ calculated in those bases differed by 0.02-0.20 eV). Then the calculated $\varepsilon_\pi$ and $\varepsilon_n$ for I and V-VIII with the 4-31G(d) basis may be considered as preliminary approximations for $I_1$ and $I_2$ for those compounds. When the OST-3G basis in used to reproduce the phosphaalkene ionization potentials, there is a considerable deterioration in the results: the discrepancies between $I_1$ and $I_2$ for II and IX [7, 8] and the calculated $-\varepsilon_\pi$ and $-\varepsilon_n$ (Table 2) are 2-3 eV. The OST-3G basis cannot be used to compare reactivities for phosphaalkenes on the basis of the boundary MO energies. Supplementing 4-31G with the polarization functions for the atoms in the first and second periods does not lead to subtantial changes in $\varepsilon_\pi$ and $\varepsilon_n$.

Satisfactory relative estimates for $I_1$ and $I_2$ for the phosphaalkenes can be made by MINDO. The measurements [6-8] and the MO energies calculated in [3] give a standard deviation in $\varepsilon_\pi$ relative to $I_1$ of 0.5 eV, and for $\varepsilon_n$ relative to $I_2$ of 0.8 eV. The geometrical distortions introduced by MINDO have little effect on the boundary MO energies for I-IX: they are altered by not more than 5% (0.5-0.6 eV).

The LUMO for I-II and V-IX are antibonding $\pi^*$ MO, no matter what the calculation method. MINDO calculations for III and IV show that the orbital is of $\sigma^*$ type and is localized on the P-Br or P—I bond, although that result, which differs form all other calculations on phosphaalkenes [2-4, 7-11] is probably due to parameterization deficiencies for Br and I in the MINDO scheme.

These results indicate the electron effects from R attached to the phosphorus in the phosphaalkenes. The highest occupied $\pi$ MO in each compound has a composition showing that R participates in conjugation with the P=C $\pi$ system. A distinctive feature of that conjugation for the halogens is that the perturbation in the $\pi$ MO energy is slight, so there is only a slight effect on $I_1$, which consequently differ little in the I-IV and IX series. The change in MO energy is not directly related to the intramolecular mesomeric effect; neverthe-

TABLE 4.   Boundary MO Energies and Compositions in Phosphaal-
kenes from MINDO Calculations with Optimal Geometrical Param-
eters

| Com-<br>pound | Orbital | Energy, eV | Squares of AO coefficients | | |
| --- | --- | --- | --- | --- | --- |
| | | | P | C | R |
| I | $\pi^*$ | −0,719 | 0,456 $(p_z)$ | 0,520 $(p_z)$ | 0,024 $(p_z)$ |
| | $\pi$ | −10,399 | 0,433 $(p_z)$ | 0,469 $(p_z)$ | 0,098 $(p_z)$ |
| | $n$ | −11,879 | 0,238 (s)<br>0,333 $(p_x+p_y)$ | 0,099 $(p_x+p_y)$ | 0,171 $(p_x+p_y)$ |
| II[a] | $\pi^*$ | −0,945 | 0,448 $(p_z)$ | 0,536 $(p_z)$ | 0,016 $(p_z)$ |
| | $\pi$ | −10,615 | 0,397 $(p_z)$ | 0,420 $(p_z)$ | 0,183 $(p_z)$ |
| | $n$ | −11,650 | 0,196 (s)<br>0,265 $(p_x+p_y)$ | 0,116 $(p_x+p_y)$ | 0,366 $(p_x+p_y)$ |
| III | $\sigma^*$ | −1,024 | 0,552 $(p_y)$ | — | 0,319 $(p_y)$ |
| | $\pi$ | −10,533 | 0,335 $(p_z)$ | 0,370 $(p_z)$ | 0,295 $(p_z)$ |
| | $n$ | −11,263 | 0,141 (s)<br>0,204 $(p_x+p_y)$ | 0,078 $(p_x+p_y)$ | 0,536 $(p_x+p_y)$ |
| IV | $\sigma^*$ | −1,282 | 0,474 $(p_y)$ | — | 0,443 $(p_x+p_y)$ |
| | $\pi$ | −10,342 | 0,202 $(p_z)$ | 0,243 $(p_z)$ | 0,555 $(p_z)$ |
| | $n$ | −10,609 | 0,087 (s)<br>0,176 $(p_x+p_y)$ | — | 0,673 $(p_x+p_y)$ |
| V | $\pi^*$ | −1,166 | 0,386 $(p_z)$ | 0,545 $(p_z)$ | 0,069 $(p_zC+p_zN)$ |
| | $\pi$ | −10,815 | 0,463 $(p_z)$ | 0,416 $(p_z)$ | 0,121 $(p_zC+p_zN)$ |
| | $n$ | −11,827 | 0,238 (s)<br>0,337 $(p_x+p_y)$ | 0,111 $(p_y)$ | 0,078 $(p_xC)$<br>0,131 $(p_yN)$ |
| VI[a] | $\pi^*$ | 0,137 | 0,483 $(p_z)$ | 0,454 $(p_z)$ | 0,063 $(p_z)$ |
| | $\pi$ | −8,925 | 0,194 $(p_z)$ | 0,454 $(p_z)$ | 0,352 $(p_z)$ |
| | $n$ | −11,338 | 0,242 (s)<br>0,403 $(p_x+p_y)$ | 0,131 $(p_x+p_y)$ | 0,070 $(p_y)$ |
| VII | $\pi^*$ | −0,273 | 0,451 $(p_z)$ | 0,514 $(p_z)$ | 0,035 $(p_z)$ |
| | $\pi$ | −9,766 | 0,354 $(p_z)$ | 0,452 $(p_z)$ | 0,194 $(p_z)$ |
| | $n$ | −11,206 | 0,204 (s)<br>0,316 $(p_x+p_y)$ | 0,115 $(p_y)$ | 0,219 $(p_x+p_y)$ |
| VIII | $\pi^*$ | −0,710 | 0,433 $(p_z)$ | 0,543 $(p_z)$ | 0,024 $(p_z)$ |
| | $\pi$ | −9,863 | 0,216 $(p_z)$ | 0,313 $(p_z)$ | 0,471 $(p_z)$ |
| | $n$ | −11,164 | 0,177 (s)<br>0,378 $(p_x+p_y)$ | 0,070 $(p_x+p_y)$ | 0,270 $(p_y)$ |
| IX[a] | $\pi^*$ | −0,429 | 0,451 $(p_z)$ | 0,549 $(p_z)$ | — |
| | $\pi$ | −10,582 | 0,549 $(p_z)$ | 0,451 $(p_z)$ | — |
| | $n$ | −11,222 | 0,235 (s)<br>0,442 $(p_x+p_y)$ | 0,066 $(p_y)$ | 0,154 (s) |

*Data from [3].

less, it can be suggested that this effect is relatively small in I-IV.   Table 5 shows that
the $\pi$ charges on the R groups (R halogen) are low, so the electron-density transfer is
slight.   The charges on the carbon atoms vary in parallel with the halogen $\sigma_C^0$ [13].   The
charges on the phosphorus atoms vary in the opposite sense to $\sigma_C^0$, and are evidently determin-
ed by several characteristics of the R groups, including the electron affinities.   On the
whole, the changes in electron density in the R–P=C system, where R is a halogen, should be
considered as polarization of the F > Cl > Br > I bond, which decreases in the sequence P=C,
while the index of the P=C bond increases in the same order.   In VI-VII, where substituents
with strong electron-donor behavior participate in conjugation with the P=C bond, there are
more destabilizations of the $\pi$ MO and more transfer of $\pi$-electron density from the central
atom in the R group to the phosphorus, and more reduction in the $\pi$ index of the P=C bond than
is the case in I-IV.   In V, the CN group stabilizes the $\pi$ MO, while the electron density on
the carbon atom is reduced by comparison with I-IV; the two effects agree with electron-
acceptor behavior by CN [13].

The 4-31G atomic charges are much higher than the MINDO ones and are reduced somewhat
when the phosphorus d AO are incorporated into the basic set; in both cases, one finds the
same trends with R as observed in the semiempirical calculations (Table 6).   It is best to
consider the P=C polarization from the nonempirical data.   To establish the significance of

TABLE 5. Changes on Atoms and Groups P=C Bond Indices, and $\pi$ Components in Phosphaalkenes Calculated in the MINDO* Approximation

| Molecule | $q_P$ | $q_P^\pi$ | $q_C$ | $q_C^\pi$ | $q_R$ | $q_R^\pi$ | $W_{PC}$ | $W_{PC}^\pi$ |
|---|---|---|---|---|---|---|---|---|
| I | +0,488 | —0,088 | —0,281 | +0,039 | —0,341 | +0,049 | 1,886 | 0,948 |
| II** | +0,354 | —0,104 | —0,233 | +0,073 | —0,264 | +0,031 | 1,928 | 0,961 |
| III | +0,264 | —0,119 | —0,203 | +0,090 | —0,202 | +0,029 | 1,934 | 0,961 |
| IV | +0,032 | —0,163 | —0,123 | +0,139 | —0,039 | +0,024 | 1,934 | 0,954 |
| V | +0,345 | —0,112 | —0,165 | +0,118 | —0,307 | +0,006 | 1,907 | 0,950 |
| VI** | +0,416 | —0,035 | —0,341 | —0,091 | —0,183 | +0,126 | 1,842 | 0,877 |
| VII | +0,315 | —0,098 | —0,232 | +0,028 | —0,201 | +0,070 | 1,889 | 0,928 |
| VIII | +0,145 | —0,134 | —0,168 | +0,086 | —0,103 | +0,048 | 1,918 | 0,940 |
| IX | +0,145 | —0,097 | —0,163 | +0,097 | —0,080 | — | 1,964 | 0,991 |

*$q_A$ charge on atom A, $q_A^\pi$ $\pi$ component, $q_R$ charge on groups R, $W_{PC}$ P=C bond under, $W_{PC}^\pi$ $\pi$ component, **Data from [3].

TABLE 6. Charges on p and C Atoms in Phosphaalkenes Calculated in the 4-31G(d) Basis and Products of them

| Molecule | $q_P$ | $q_C$ | $q_P q_C$ | Molecule | $q_P$ | $q_C$ | $q_P q_C$ |
|---|---|---|---|---|---|---|---|
| I | +0,635 | —0,529 | —0,3359 | VII | +0,528 | —0,517 | —0,2730 |
| II | +0,388 | —0,481 | —0,1866 | VIII | +0,260 | —0,496 | —0,1290 |
| V | +0,344 | —0,451 | —0,1551 | IX | +0,174 | —0,514 | —0,0894 |
| VI | +0,497 | —0,570 | —0,2832 | | | | |

the polar component in the P=C bond, one can compare the products of the charges on the phosphorus and carbon atoms [10]. Table 6 shows that all these quantitites are negative, so in I-IX there is electrostatic attraction between those centers, which is minimal for R = H and maximal for R = F, $NH_2$, or OH, which groups show the largest resonant effects [13].

This explains why the changes in phosphorus-carbon bond length $\ell_{PC}$ are slight in I-IX in spite of the obvious differences in R participation in the $\pi$ conjugation; the length is governed by two effects: increase associated with electron-density displacement from the unshared pairs in R and reduction by electrostatic attraction between the phosphorus and carbon. In I-IX, the two effects increase together (Table 6) and they almost completely balance out. Our calculations indicate that is reduced when R is an electron donor, which indicates that electrostatic attraction predominates over $\pi$ conjugation. In I and II, the shortening in P=C by comparison with IX has been measured (Table 1) but is reproduced only in the nonempirical calculations and for I it has been assumed also in calculations in the 6-31G* [10] and 3-21G* [11] bases.

The level of the n MO in the P-substituted phosphaalkenes is stabilized when the electron density on R increases, which agrees with the linear relation between $\varepsilon_n$ and $q_R^*$. In MINDO, that trend is related only to the reduction in electron density on the phosphorus $\sigma$ orbitals on account of the substituent inductive effect, as is evident form the linear relation between $\varepsilon_n$ and the inductive constants $\sigma_I$ for the R groups [13], and although the $\varepsilon_n$ for III and IV deviate from that trend. However, it is most likely that this simple trend is due to inadequate reproduction of detailed electron-electron interaction effects in the MINDO calculations, particularly as regards the phosphorus unshared pair. On the whole, the effects of R on $\varepsilon_n$ for I-IX are more marked than on $\varepsilon_\pi$. Consequently, the gap between the $\pi$ and n MO alters appreciably when R is varied. Our calculations and the [7] measurements and calculations indicate that the gap increases in the following R sequence: Me < H < Cl < SH < CN < OH < F < $NH_2$. The same sequence appears to apply for the preference in forming $\pi$ complexes between these phosphaalkenes and metal ions by comparison with the correponding n complexes. That series is also analogous to the sequence of increasing electrostatic interaction between the phosphorus and carbon. The 4-31G and extended-basis calculations related to it indicate that the LUMO in RP = $CH_2$ is stabilized in the following

*An illustration of this type of linear relationship will be published in the next issue of the journal.

series: $NH_2 <$ H $<$ SH $\simeq$ F $<$ Cl $<$ CN (Table 2).  Therefore, the P-chloro and P-cyano phospha-alkenes should be the most effective dienophils in reactions involving 4 + 2-cycloaddition. Previously, the formation of 4 + 2 cycloadducts has been demonstrated in the reactions of $ClP = C(SiMe_3)_2$ with dienes [5], which is readily explained, since the effects from the silyl groups on the carbon atom additionally stabilize the LUMO in the phosphaalknes [3].

Nonempirical 4-31G calculations, including ones with the basis extended with the phosphorus d functions, lead to satisfactory geometrical parameters and boundary MO energies for P-substituted phosphaalkenes.  The OST-3G basis is unsuitable for describing the MO energies for these compounds, but semiempirical MINDO can be used, and the results obtained with the optimized and the observed geometrical parameters differ little.  In the $RP = CH_2$ phospha-alkenes, the HOMO is of $\pi$ types, and below it lies an occupied MO of n type. The gap between them for any R other than an alkyl group is increased by comparison with $HP = CH_2$, so the complexing of such phosphaalkenes and addition to them should occur mainly at the phosphorus-carbon $\pi$ bond.

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