A Study of the Bonding and Geometry in Phosphacumulene Ylides

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Phosphacumulene Ylides, Molecular Orbital Calculations

A series of ab initio molecular orbital calculations have been carried out on phosphacumulene ylides of the type H₃P=C= X where X = S, O, CNH, and (OH)₂. The variation in the P–C–C bond angle was examined and compared to the experimentally determined structures of analogs. The dominant factor in setting the P–C–C angle was found to be the relative π-acceptor capability of the C= X fragment in the plane of the bending motion. Quantitative PMO-arguments were constructed for the X = S, O and (OH)₂ cases along this line. It is also shown, that P–C σ* character mixes into the highest occupied molecular orbital. The magnitude of this effect is dictated by the amount of bending and this strongly influences the P–C nuclear spin coupling constants. Finally, the bonding in H₃P=C=PH₃ was also investigated in a similar manner.

Introduction

Over the past decade there have been many theoretical [1] and experimental [2] studies pertaining to the bonding in alkylidene phosphoranes. These have concentrated on the nature of the P=C bond and the conformation at the ylide carbon. The former question has often been directed towards the involvement of d orbitals at phosphorus. This has sometimes been reformulated in terms of a resonance hybrid of 1 and 2, the ylide and ylene forms.

This work is directed towards a beautiful series of phosphacumulene ylides, 3–6, prepared first by Birum and Matthews [3a], Bestmann and Saalfrank [3b] and synthetically used by Bestmann and coworkers [3c]. The ylides here and throughout the paper have been drawn in their ylene form for convenience only. The P–C–P bond angle in these compounds has been shown in the solid state to vary in the following fashion: 3 [4] –168.0°; 4 [5] –145.5°; 5 [6] –134.0°; 6 [7] –125.6°. We have studied the bending in these compounds and the related hexaphenylcarbodiphosphorane (7) by means of ab initio molecular orbital calculations. The solid state structure might well be somewhat different from those in the liquid or gas phases. For example, 7 must have a very low P–C–P bending force constant since in one crystal modification there are two molecular forms. In one molecule the P–C–P angle is 130.1° and 143.8° in the other [8]. An X-ray determination of another crystal modification [9] gave a P–C–P angle of 134.4° at room temperature and 131.7° at –160 °C. Finally, it was concluded from an electron diffraction study [10a] of hexamethyldibodiphosphorane that there was rapid inversion in the molecule giving an average linear structure, and a recent structure of (P₉Me₃)₂C has given an even smaller P–C–P angle of 121.8° [10b]. The situation is probably not too different for 3–6 and there is some NMR information [11] on 6 consistent with a low barrier of inversion at the ylide carbon. Nonetheless we feel that a diminution of the P–C–C bond angle on going from 3–6 correctly corresponds to the liquid and gas phases. The reasons behind this will be the focus of our study.

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Model compounds, 8–12, were chosen as suitable candidates for this work with geometrical details given in the Appendix. The *ab initio* molecular orbital calculations were of the STO-3G type [12]. An analysis of the wave functions in the molecules represented by 13 was carried out by means of a quantitative perturbational molecular orbital (PMO) method, developed by Whangbo and Wolfe [13]. Here the molecular orbitals of 13 are expressed by combinations of the orbitals from the $H_3P=C$ and $C=X$ fragments. We will build up the orbitals for the $H_3P=C$ fragment first and then interact them with those of the $C=X$ fragments. This will allow us to determine a relative sequence of P-C-C bending which depends only on the electronic differences in the C=X fragments.

**The $H_3P=C$ Fragment**

The orbitals of our $H_3P=C$ fragment can be derived qualitatively in a simple fashion. Figure 1 shows an orbital interaction diagram of the well-known orbitals of $PH_3$ [1c, d, e] with the atomic s and p levels of carbon. At low energy the carbon s orbital is stabilized by the lone pair, $n$, orbital of $PH_3$. At higher energy, $2a_1$ represents the bonding interaction of $n$ with carbon p$_z$, moderated by antibonding from carbons s. This is shown in 14. The degenerate $\sigma_n$ set [14] of $PH_3$ is stabilized somewhat by carbon p$_x$ and p$_y$. Finally, $2e$ is a largely nonbonding orbital on carbon. It is derived from a bonding interaction between $\sigma_n^*$ and carbon p$_x$, p$_y$ with $\sigma_n$ mixed in antibonding fashion, 15. In a sense

![Interaction Diagram](image-url)
of d orbitals on the 2e set of Figure 1 would be to stabilize slightly this fragment orbital by mixing phosphorus $d_{xz}$ and $d_{yz}$ in-phase with respect to carbon $p_y$ and $p_z$—see 16. This, of course, is exactly the role played by $\sigma^*_n$ in Figure 1. The $d_{xz}$, $d_{yz}$—set and $\sigma^*_n$ both have the same symmetry and both function as $\pi$-acceptors, thus, which one is dominant cannot be determined experimentally [1c, e] and need not concern us since the $H_3P=C$ fragment remains constant throughout our analysis [15]. It will not affect the qualitative details along the series given by 13.

The $H_3P=C=C=X$ and $H_3P=C=PH_3$ molecules

Our ab initio calculations on 8–11 gave the following optimized P–C–C bond angles: 8 – 180°, 9 – 180°, 10 – 164°, 11 – 125°. Thus, our bond angles are all calculated to be too large with the exception of 11 compared to the experimental compounds 3–6. Increasing the size of the basis set was not considered worthwhile since we have already made rather drastic simplifications in the molecular skeleton and a rigorous geometric search varying the C–C–X angles and P–C, C–C, and C–X distances would have been prohibitively time-consuming. Furthermore, the bending potentials are all rather soft—a situation which is likely to be found in the parent molecules. The total energy rises much more slowly upon bending in 9 than in 8, therefore, the tendency towards linearity goes in the sequence 8 > 9 > 10 > 11 which qualitatively matches that for the series in 3–6. The total Mulliken overlap population between $C_1$ and $C_2$, shown in 17 when the P–C–C angle is set at 180°, also follows this pattern. If one assumes that the calculated overlap population is a rough guide for the strength of the $C_1$–$C_2$ bond, then 17 shows that as the $C_1$–$C_2$ bond becomes stronger, the tendency for the P–C–C angle to become linear is larger. This is turn can be traced to the amount of $\pi$-bonding between the $H_3P=C$ and $C=X$ units.
analogous to the situation we have seen before in \( \text{H}_3\text{P} = \text{C} \). In the HOMO, \( 2e \) is antibonding with respect to \( \pi \) and bonding with \( \pi^* \). This produces an orbital with little density on C2—depending on the extent of \( \pi \) and \( \pi^* \) mixing into \( 2e \). The crucial point of our argument concerning the bending in the \( \text{H}_3\text{P} = \text{C} = \text{C} = \text{X} \) series is that the relative extent of mixing \( \pi \) and \( \pi^* \) varies in a regular fashion.

For 8 and 9 (X = S, O) it will make essentially no difference whether the \( \text{P} = \text{C} = \text{C} = \text{X} \) unit is bent conserving a symmetry plane, 19, or perpendicular to it, 20. This is a consequence of the fact that in the linear, \( C_3V \), geometry the HOMO is an \( e \) set and the effects of bending to 19 on one member will be matched by those in the other upon going to 20. Put in another way, the rotational barrier about the P-C bond in the non-linear geometry is expected to be very small. This situation is also found for the parent alkylidene-phosphoranes [1a-f]. The experimental conformation of 3 was found [5] to be analogous to that in 19 while that in 4 [5] lies between that of 19 and 20. For visual convenience we shall examine the distortion maintaining \( C_3 \) symmetry as in 19. When this is done there is essentially no change in the energy of the antisymmetric member in the HOMO, 18b. However, the symmetric member does vary in the following way. The overlap between \( 2e_s \) (the symmetric member of \( 2e \) in \( \text{H}_3\text{P} = \text{C} \)) and \( \pi_s \) is diminished upon bending. This will stabilize that component of the molecular orbital, 21, since \( 2e_s \) and \( \pi_s \) are antibonding. In the same fashion bending causes a loss of bonding between \( 2e_s \) and \( \pi^*_s \), 22, and this tends to raise the energy of the symmetric member of the HOMO. Therefore, along our series of molecules as the \( \pi \)-donor character of \( \text{C} = \text{X} \) increases, the P-C-C bond angle decreases. Alternatively, as the \( \pi \)-acceptor character of \( \text{C} = \text{X} \) increases, the P-C-C bond tends more towards linearity. This argument has, of course, several counterparts in organic chemistry. Substitution of \( \pi \)-acceptors such as keto or cyano groups on amines makes them more planar while the substitution of \( \pi \)-donors has the opposite effect and raises the inversion barrier [17].

On going from \( \text{C} = \text{S} \) to \( \text{C} = \text{O} \) \( \pi \) goes down in energy. This is a result of the 3p orbitals of sulfur.
being more diffuse than 2p on oxygen coupled with the longer bond length in the C=S fragment compared to that in C=O. Both factors increase the π overlap in C=O so that while π is lowered in energy, π* also goes up. The relative energies of the C=X and H₃P=C π-type orbitals are shown in Figure 3. A quantitative consideration of the relative π-donor and π-acceptor capabilities of C=X in these ylides can be obtained by the PMO procedure of Whangbo and Wolfe [13]. The energies of the bonding and antibonding interactions of 2e with π and π* are solved by means of the secular determinant shown below:

$$\begin{vmatrix} \epsilon_1^* - E & A_{ij} - ES_{ij} \\ A_{ij} - ES_{ij} & \epsilon_1^* - E \end{vmatrix} = 0$$

Here \(\epsilon_1^*\) and \(\epsilon_2^*\) are the orbital energies of the fragments. \(S_{ij}\) and \(A_{ij}\) are the overlap and off-diagonal Fock matrix elements, respectively, between the relative fragment orbitals [13]. The matrix elements and orbital energies after interaction are listed in Table I. \(A E^{(2)}_{2e_{π}, π_n}\) represents the two electron stabilizing interaction between \(2e_{π}\) and \(π_n^*\) in eV. \(A E^{(4)}_{2e_{π}, π_n}\) is the four electron repulsion between the filled \(2e_{π}\) and \(π_n\). Finally \(A E_{TOT}\) is a sum of these two terms. In this manner we have partitioned 18a into the relative contributions of 21 and 22. As \(A E_{TOT}\) becomes more negative the tendency to remain linear becomes greater.

For C=O and C=S one can see that the overlap and Fock matrix terms are nearly twice as large for the interaction between \(2e_π\) and \(π_n^*\) than that for \(2e_π\) with \(π_n\). This is primarily due to the polarization in the π and π* orbitals. Although the π-donor interaction \((π_n\) with \(2e_π\)) is larger for C=O because of the smaller energy gap, the π-acceptor interaction \((π_n^*\) with \(2e_π\)) is also larger for the same reason. Our calculations give that latter effect as being more important – see Table I. Therefore, 8 should tend more towards linearity than 9. The PMO calculations for 10 will not be reported here. There is substantial mixing between the π and π* orbitals of the C=N=H fragment with σ and σ* orbitals. However, in qualitative terms since nitrogen is less electronegative than oxygen, the energy of π and π* is raised. Furthermore, π and π* will be less polarized then previously shown for CO and CS. This makes the C=NH group a worse π-acceptor and a better π-donor. Therefore, the P-C-C bond angle in 5 should be less than that in 3 or 4. Our calculations reflect this. There is again little difference in bending to 19 or 20 (19 is slightly favored). The C(OH)₂ group is somewhat different compared to the other C=X fragments. The relevant orbitals are presented in Figure 3. There are now three π-type orbitals perpendicular to the C(OH)₂ plane of the molecule. The two lowest in energy, labeled π and π*, are filled. The latter finds no symmetry match in the H₃P=C fragment in the linear geometry. A high-lying empty orbital, π*, the LUMO of a bent dihydroxy carbene, serves as the π acceptor level.

There is a relatively high-lying filled orbital, \(σ_n\), which interacts with \(2e_α\). It is destabilized by the appropriate symmetry combinations of in-plane lone-pair orbitals on oxygen and σ OH levels. The unfilled counterpart, 23 – not shown in Figure 3 – lies at very high energy since it is C-O σ-antibonding. Energetically 23 is essentially inaccessible as a π-acceptor while \(σ_n\) is a relatively good π-donor (see Table I). Therefore, the molecule bends strongly in the mirror plane (as in 19) rather than perpendicular to it (20).

We see that the dominant factor in determining the relative amounts of bending in these molecules is a π effect – so the fragmentation procedure in 13 is the most useful way of viewing this. An alternative approach would use the fragmentation indicated in 24 and would analyze the effects of bending the H₃P unit off the axis as in 25 which, of course, is equivalent to 19. The analysis then focuses on the

Table I. The matrix elements and interaction energies between the in-plane π fragment orbitals.

<table>
<thead>
<tr>
<th></th>
<th>C=S</th>
<th>C=O</th>
<th>C(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{2e_π, π_n})</td>
<td>0.242</td>
<td>0.245</td>
<td>0.1701</td>
</tr>
<tr>
<td>(S_{2e_π, π_n^*})</td>
<td>0.130</td>
<td>0.140</td>
<td>0.087</td>
</tr>
<tr>
<td>(A_{2e_π, π_n})</td>
<td>−7.529</td>
<td>−7.374</td>
<td>−3.907</td>
</tr>
<tr>
<td>(A_{2e_π, π_n^*})</td>
<td>−3.628</td>
<td>−3.513</td>
<td>−2.322</td>
</tr>
<tr>
<td>(A E^{(2)}_{2e_π, π_n})</td>
<td>−6.709</td>
<td>−5.992</td>
<td>−0.064</td>
</tr>
<tr>
<td>(A E^{(4)}_{2e_π, π_n})</td>
<td>1.547</td>
<td>1.313</td>
<td>0.583</td>
</tr>
<tr>
<td>(A E_{TOT})</td>
<td>−5.162</td>
<td>−4.679</td>
<td>0.519</td>
</tr>
</tbody>
</table>
relative energies of the HOMO in the C=C=X unit, 26, and the magnitude of interaction with $\sigma_{n^*}$ in H$_3$P. The results are analogous to those presented before. The bending in 25 does, however, point out in a clearer fashion that mixing of antibonding $\sigma$ levels into the $\pi$-type HOMO of the molecule also occurs. The major perturbation arises from the mixing of a predominately P-C $\sigma^*$ orbital, 27, into

the HOMO, in a way exactly analogous to the pyramidal inversion problem of AH$_3$ molecules [17]. This stabilizes the HOMO strongly in a second order Jahn-Teller sense increasing the s-character for this level at the a-carbon. The magnitude of the mixing coefficient, $\lambda$ in 27, also determines the degree of bending. Arguments along this line of reasoning have been given by Glidewell [18]. Notice that the phosphorus 3s and carbon 2s atomic orbitals enter into 27 in an antibonding way. As the ylide bends, more of 27 is mixed in, consequently the P$_{3s}$-C$_{2s}$ bond order becomes smaller. This bond order squared varies in a linear fashion with $1/r_{p-c}$. Thus, as the P-C-C bond angle in 3-6 decreases, so should $1/J_{p-c}$. Experimentally [19] this is the case and is shown in 29. We have also carried out calculations of $1/J_{p-c}$ with the finite perturbation method at the CNDO/2 level [1 d]. The results shown in 29 are those for 8-10 at the experimental geometries of their analogs. Unfortunately the calculations on 11 did not come to a satisfactory level of convergence. While a quantitative comparison of the experimental and calculated couplings is not particularly good, the trend in both sets of numbers reinforces our notion that the bond angle does decrease in the order given and are not set solely by crystal packing effects. Recently Bestmann and coworkers reported the synthesis of the first cyclic phosphacumulene ylide 30 [11a], in which a small P-C-C angle is set by the five membered ring structure. Experimental information [19] indicates $1/J_{p-c}$ to be less than 3 Hz in this system, again in accord with our interpretation.

The $R_3P=C=RP_3$ Molecules

The situation for carbodiphosphorane, (12), is very similar. At the linear geometry 2e in H$_3P=C$ interacts with $\sigma_{n^*}$ and $\sigma_n$ of PH$_3$ — see 31. The resultant, nonbonding HOMO, (32), has an obvious similarity to 18. Our ab initio calculations on 12 gave

a minimum at a P-C-P angle of 113°. While this is much smaller than that reported for 7 [8, 9] (but only 8° smaller than the value reported for CH$_3$(C$_6$H$_5$)$_2$P=C=P(C$_6$H$_5$)$_2$CH$_3$!), the R$_3$P group is not expected to be as good a $\pi$-acceptor as C=O or C=S. Therefore, we would expect a smaller angle than that for 3 or 4. Our calculations show that it costs only 5.3 kcal/mole to open the bond angle to 140°. INDO calculations [1j] have given a much stronger bending potential for this molecule. The isoelectronic Ph$_3$P$=\tilde{N}=PPh$_3$ cation has been used many times as a counterion in structural determinations of reactive or unstable anions. The available structures [20] show a varia-
tion in the P–N–P angle from 134.6°–180°! Clearly the bond angle is set here by differential intermolecular packing forces. There must be a very soft distortion surface. The Me₃Si–N–SiMe₃ anion is probably similar. In one structure [21] the Si–N–Si angle was found to be 125.6°. A discussion [18] of the bending in compounds of this type and CNDO/2 calculations [22] have been given elsewhere.

Conclusions and Extensions to Other Classes of Compounds

We have shown that the ordering of the P–C–C bond angles in 3–6 is primarily dependent on the π-acceptor strength of the C=X fragment. It is interesting to note that extensive theoretical and experimental work [23] on transition metal complexes of the type LₙM–C=X has also shown this trend, namely, the π-acceptor ordering is C=S > C=O > C=N–R. Perhaps the most quantitative theoretical work has been carried out on LₙNi(CO)₃ complexes where L=CS, CO, CN–Me, by Rauk and Ziegler [24]. This also follows the above pattern. Experimental evidence from transition metal chemistry also indicates that the CSe group in selenocarbonyl transition metal complexes LₙM–CSe is an even better π-acceptor than CS [23d]. The synthesis and structural characterization of a R₃P=C=C=Se molecule would therefore be an interesting test of our theoretical analysis. There have also been a number of structures [25] on compounds of the type R–N=C=S and R–N=C=O. In every instance, within a given R, the former compounds have a larger R–N–C angle than the latter ones. The similarity to the problem we have discussed is rather obvious. The isothiocyanates and isocyanates could be partitioned into R–N and C=X fragments. The important interaction would then be between the two sets of lone pairs on nitrogen (33) and the π, π* sets of the C=X groups. An imine of the type R–N=CR₂ would then be analogous to 6 and, of course, is strongly bent. The structures of many of these isothiocyanates and isocyanates have been determined in the gas phase by electron diffraction and microwave spectroscopy. This reinforces our belief that the P–C–C angle in 3 is greater than that of 4 in the gas phase as well. While we have concentrated on the effects of the π levels upon bending, there are also rather profound mixings with σ* levels and π levels of the same symmetry. It is in this context that the marked variations of Jₚ-c couplings occur. Perhaps more rigorous calculations of Jₚ-c could be used to predict the P–C–C angles in solution with some confidence.

Appendix

The geometrical parameters choosen for 8–12 were adapted from the structures of their analogs [5–9] with some exceptions. All P–H distances and H–P–C angles were set at 1.42 Å and 109.47°, respectively. In 10 the N–H distance and C–N–H angle was fixed at 1.0 Å and 120.0°. In 11 the C–O and O–H bond lengths were taken to be 1.35 and 0.97 Å. The C–C–0 angles were idealized at 120.0° and 110.0°, respectively. The P–C distance in 12 was set at 1.63 Å.

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[14] σn represents in a delocalized manner two of the three P–H σ bonds. The π symmetry of this set is evident from the drawing in Figure 1.

[15] The most extensive ab initio calculations on methylene phosphorane [2a, b] have shown little d orbital involvement. The highest occupied molecular orbital in this molecule was found to be basically a lone pair on carbon with smaller contributions on the PH3 hydrogens. Its shape is analogous to that of one member in 15 and can be derived by the intersection of σn and σn* of PH3 with the p orbital of a methylene fragment in the same way.


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