Semiempirical PM3 calculations of pyridinium dichlorophosphinomethylides: Presence of negative hyperconjugation

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Semiempirical PM3 calculations have been carried out for the rotational and pyramidal inversion processes in the pyridinium dichlorophosphinomethylides. Geometry optimization of several representatives reveals a planar configuration at the ylidic carbon while pyramidal disposition is indicated at the phosphorus. There are two minima separated by a saddle point on the potential surface of the rotational curve of the pyridinium dichlorophosphinomethylide. The conformers represented by two minima have the lone pair of electrons on phosphorus oriented orthogonally to the p orbital of the ylidic carbon. Of these, the more stable conformer has the phosphorus lone pair antiperiplanar to the pyridinium ring. Existence of significant negative hyperconjugation between the ylidic charge and the \( \sigma^*_{P-Cl} \) bonds in the most stable conformer is revealed by the C-P and P-Cl bond lengths and also by the atomic charges. The pyramidal inversion barrier of the dichlorophosphinomethylides is influenced by the nature of the substituent group at the ylidic carbon. The disposition at phosphorus in the transition structure of the pyramidal inversion approaches planarity.

Ylides are the versatile intermediates in organic synthesis.1-3 Theoretical calculations pertaining to the conformations of the simplest ylides with hydrogen as the substituent have been carried out earlier.4-18 Existence of the negative hyperconjugation in several alkenylphosphines,19-21, diphenylphosphate and aminophosphate,22,23, carbanion adjacent to sulfoxide, sulfone and sulfonium centres2 and several related molecules has been well established by using spectroscopic techniques as well as theoretical analysis.

Recently synthesis and reactions of a variety of dihalophosphinyl ylides, viz. triphenylphosphonium dihalophosphinomethylides have been reported.24 Molecular structures of triphenylphosphoniumylidyldihalo25,26 and monohalophosphines27 as determined by X-ray crystallographic studies reveal the existence of negative hyperconjugation in these species. We prepared the analogous pyridinium dichlorophosphinomethylides28-30 and demonstrated the synthetic utility of these intermediates and their isoquinolinium analogues by obtaining 2-phosphaindolizines29,30 and 1,3-azaphosphol[5,1-\( \alpha \)]isoquinolines31, respectively through 1,5-electrocyclization32. These dihalophosphinyl ylides incorporate several interesting structural features namely, the presence of a carbanionic centre adjacent to the dihalophosphino group thus providing the possibility of negative hyperconjugation by donation of the ylidic charge into the \( \sigma^*_{P-X} \) orbitals, free rotation about the C-P bond and inversion at the phosphorus. The size of the molecules of these species being quite big, semiempirical PM3 calculations are more appropriate and practical to get approximate information about the molecular structures, relative energetics, conformational preferences and inversion barriers of a variety of the pyridinium dichlorophosphinomethylides having different substituent groups at the ylidic carbon to determine the presence of negative hyperconjugation in this category of ylides as well. The results are reported in this paper.

Computational Methods
The calculations were carried out using PM3 procedure33 incorporated in the MOPAC 6.0 package34. Geometries of methylidichlorophosphine 1, N-(dichlorophosphinomethyl)pyridinium ions 2 and pyridinium dichlorophosphinomethylides 3 were optimized at the SCF level of computation by minimizing the energy and gradient norm with respect to all geometrical variables.

\[
\begin{align*}
&\text{H}_3\text{C}\text{C=PCl}_2 \\
&\text{N}^+\text{C-PCl}_2 \\
&\text{N}^+\text{C-PCl}_2
\end{align*}
\]

1 \hspace{1cm} 2 \hspace{1cm} 3
In case of 3, two different orientations of the phosphorus lone pair of the PCI₂ group with respect to the pyridinium ring i.e. antiperiplanar and synperiplanar, resulting from rotation about the C_ylide-P bond, were used as input geometries in order to obtain two minima corresponding to rotamers A and B.

In order to locate the transition structure on the potential surface of the rotational curve of 3, the reported procedure was followed. For this purpose, the dihedral angle N-C-P-Cl₁ was repeatedly changed and the energy of the resulting conformation was determined till the energy of the system passed a maximum on the reaction curve. The conformation with highest energy (TS_rot) was refined by minimizing the gradient. The transition nature of TS_rot was verified by the presence of only one imaginary frequency in the force constant calculations. The saddle point (TS_inv) in the process of inversion at phosphorus was obtained by converging together the geometries of the two minima (rotamers, A and B) till both geometries converged on the transition structure.

Results and Discussion
Rotation about C_ylide-P bond
In the series of hetero substituted alkene derivatives, H₂C=CHX (X = NH₂, OH, SH, PH₂) identification of the most stable conformer has been done by using different spectroscopic techniques as well as theoretical analysis of the internal rotation process. The theoretical calculations of the alkenylphosphines reveal that the most stable conformer has the lone pair on the phosphorus oriented orthogonally to the adjacent \( \tau \)-system which makes the interaction between them impossible. Furthermore, the P–H bond in vinylphosphine acts as electron acceptor (negative hyperconjugation) and the interactions, \( \pi_{C=C} \rightarrow \sigma^*_{P-H} \) and \( \pi^*_{C=C} \rightarrow \sigma_{P-H} \) play an important role in the stabilization of the most stable conformer.

In view of the structural similarity of the pyridinium dichlorophosphinomethylides with vinylphosphines, the analysis of the rotation process around the C_ylide-P bond in four representative ylides has been carried out to determine the most stable conformation(s) and also to locate the saddle point on the hypersurface representing the transition structure in the process of rotation. A particular rotamer is characterized by the characteristic dihedral angles \( \omega_i\) (N-C-P-Cl₁) and \( \omega_2\) (N-C-P-Cl₂). The calculations reveal the existence of two minima (structures A and B) separated by a saddle point (TS_rot) representing the transition structure. The relative energies of the three rotamers, A, B and TS_rot, are plotted as a function of the dihedral angle, \( \omega(N-C-P-Cl₁) \) (Figure 1). Alternatively, A can change into B through inversion at phosphorus and a saddle point (TS_inv) is located on the potential energy hypersurface resulting from the process of inversion (Figure 2). The transition state nature of TS_rot and TS_inv are confirmed by one imaginary frequency in each case. The geometric parameters of these four forms of each of the four pyridinium dichlorophosphinomethylides 3 along with those of the corresponding N-(dichlorophosphinomethyl)-pyridinium ions 2 are given in Table I.
The two minima (A and B) are separated by an energy barrier of 2.8-4.7 kcal mol\(^{-1}\) and, in conformity with the earlier results\(^{20,21}\), have the phosphorus lone pair orthogonal to the \(\pi\) orbital on the ylidy carbon making the interaction between the phosphorus lone pair and the ylidy charge impossible. In the more stable conformer A, the lone pair on phosphorus is anti-periplanar (oN-C-P-Cl = 49°) to the iminium nitrogen while in the comparatively less stable conformer B, it lies syneriplanar (oN-C-P-Cl = 128°) with the pyridinium ring. Repulsion between the phosphorus lone pair and \(\pi\)-orbitals of the pyridinium ring make the latter conformer less stable. In the TS\(_{\text{rot}}\), the phosphorus lone pair is almost parallel to the ylidy charge causing maximum repulsion.

The rotational barrier of 4.1-9.4 kcal mol\(^{-1}\) in the present case is much higher than the values found for ethenylphosphine and other related systems\(^{20,21}\). The increased rotational barrier in 3 is due to a stronger repulsion between the phosphorus lone pair and the ylidy charge in the TS\(_{\text{rot}}\) as compared to the n\(_{\text{p+}}\)(P-C)=C interaction in the vinylphosphines. The value of the rotational barrier in 3 is also influenced by the size of the substituent group at the ylidy carbon; it is highest for 3c having the bulkiest benzoyl group at the ylidy carbon.

**Negative Hyperconjugation**

The existence of negative hyperconjugation in a particular conformer is manifested not only by lowering of its potential energy but also by charge transfer and bond elongation\(^{36,37}\).

In the N-(dichlorophosphinomethyl)pyridinium ion 2 negative hyperconjugation will be absent. Thus a comparison of the charge densities and bond lengths in the two minima of the ylide 3 with those of the corresponding pyridinium ion 2 provides a measure of the extent of the negative hyperconjugation in the

<table>
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<th>1 MePCl(_2)</th>
<th>R = COOEt</th>
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<tr>
<td>2a (ion)</td>
<td>60.3</td>
</tr>
<tr>
<td>3a A</td>
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<td>3a B</td>
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<tr>
<td>3b B</td>
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<tr>
<td>3b TS(_{\text{rot}})</td>
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Table I—Dihedral angles \(\omega\) (°), bond lengths \(d\) (pm), electronic charges and conversion barriers (kcal mol\(^{-1}\)) of 1, 2 and 3.
former. In the most stable conformer A of the pyridinium dichlorophosphinomethylides 3, the two P–Cl bonds are equal in length but as compared to those in the corresponding pyridinium ion, they are longer by about 2.0-2.5 pm. As the optimized geometries (Figure 3) reveal, the two P–Cl bonds are symmetrically disposed ($\omega_1\text{N-C-P-Cl}_1 \approx \omega_2\text{N-C-P-Cl}_2$; Table 1) with respect to the plane of the ylidic carbon and in the conformer of minimum energy (A) they face the $p_z$ orbital on the ylidic carbon, thus providing the possibility of maximum $C_{ylic}\sigma_{p-C-Cl}$ interaction. In B representing the other minima, two P–Cl bonds are again equal in length, but increase in bond length in relation to the pyridinium ions is only of the order of 1.0–1.5 pm. In TSrot., representing the saddle point, two P–Cl bonds are not equal in length as they are no more symmetrically disposed with respect to the plane of the ylidic carbon (Figure 4): the P–Cl bonds being parallel to the $p_z$ orbital is longer by about 1.1–2.7 pm than the P–Cl bond which lies approximately in the plane of the ylidic carbon. Furthermore, in accordance with the hyperconjugation theory$^{29}$, the C–P bond (177.2–178.9 pm) in the ylide (structure A) is shorter than the corresponding pyridinium ion (196.5–199.7 pm). Lengthening of the P–Cl bonds in the ylide is accompanied by the enhancement of the negative charge on chlorine, this increase being maximum in A. The molecular parameters of MePCl$_2$ as determined by PM3 calculations (Table I) further confirm the existence of the negative hyperconjugation in the pyridinium dichlorophosphinomethylides.

Analysis of the Inversion Process

A can change into B through pyramidal inversion at phosphorus also. The optimized geometry of the saddle point (TSinv.) obtained by semiempirical PM3 calculations is shown in Figure 4 and the geometric parameters are given in Table I. The calculated value of the inversion barrier for the ylides 3, 17.7–48.6 kcal mol$^{-1}$ is quite close to that reported for alkynyl phosphines$^{21}$, PH$_2^{22}$ and P$\text{H}_2\text{NH}^{22}$. The inversion barrier is lowest for 3C having benzyol group at the ylidic carbon which has analogy with the difference in the inversion barrier in amine and amide, the latter having a lower value. It is known that the benzyol group participates effectively in the delocalization of the ylidic charge in the pyridinium ylides which results in lowering of the inversion barrier in 3C.

Conclusions

The pyridinium dichlorophosphinomethylides, like their phosphonium analogues are stabilized by nega-

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**Figure 3** — PM3 optimized geometries of conformers A and B in 3a.

**Figure 4** — PM3 optimized geometries of rotational and inversional transition structures in 3a.
tive hyperconjugation resulting from donation of the ylidic charge into $\sigma^{*}_{P-C}$. It is manifested by lengthening of the P–Cl bonds but shortening of the C–P bond. The two minima of the ylides represented by different orientations of the phosphorus lone pair with respect to the pyridinium ring are separated by the transition structure having the lone pair parallel to the ylidic charge. The inversion barrier at phosphorus is influenced by the size of the group at the ylidic carbon.

Acknowledgement
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References