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Experimental and theoretical examinations of n→σ* negative hyperconjugation in pyridinium dichlorophosphinomethylide

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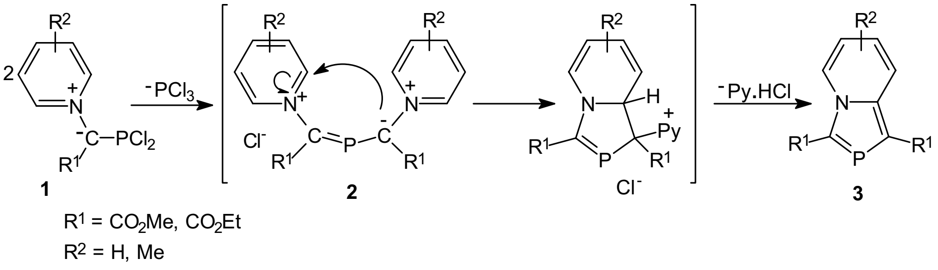
Dedicated to Professor Alfred Schmidpeter on his 75th birthday

Abstract—An X-ray crystal structure investigation as well as theoretical DFT (hybrid B3LYP/6-31G** level) calculations of 2-ethylpyridinium dichlorophosphino-ethoxycarbonylmethylide confirm the existence of significant n→σ* negative (anionic) hyperconjugation between the ylidic charge and the $\sigma*_{\text{P–Cl}}$ bond in the most stable conformer, which has the phosphorus lone pair oriented orthogonally to the ylidic p_z orbital, resulting in elongation of the P–Cl bond parallel to the p_z orbital but shortening of the C–P bond.

Recently we demonstrated that pyridinium dichlorophosphinomethylides **1** disproportionate to generate bis(pyridinium ylidyl)phosphenium chlorides **2**, which afforded 2-phosphaindolizines **3** via 1,5-electrocyclization (Scheme 1).[1] Similar behaviour was exhibited by isoquinolinium dichlorophosphinomethylides to give 1,3-azaphospholo[5,1-*a*]isoquinolines under these conditions.[2]

As regards to the reaction shown in Scheme 1, there are two significant observations: firstly, in contrast to triphenylphosphonium dichlorophosphinomethylides,[3] **1** disproportionate rapidly in solution to generate **2** and finally **3**; secondly, the P–Cl bond of the initially formed intermediate bis(pyridinium ylidyl)chlorophosphines expected from disproportionation of **1** dissociates spontaneously to produce **2**. The ionic nature of **2** is indicated



Scheme 1.

Keywords: Negative hyperconjugation; Pyridinium dichlorophosphinomethylides; X-ray structure; B3LYP calculations; Bis(pyridinium ylidyl)phosphenium chlorides.

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[†] X-ray crystal structure determination.

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by its insolubility in diethyl ether. It has been reported that bis(triphenylphosphonium ylidyl)halophosphines also change rapidly into ionic compounds.[4] These changes can be rationalized on the basis of negative hyperconjugation,[5] the existence of which has been established for a variety of ylides[3,6–8] and related species.[9–11] We have now investigated the existence of negative hyperconjugation in **1** by X-ray crystal structure determination and B3LYP/6-31G** calculations of 2-ethylpyridinium dichlorophosphino-ethoxycarbonylmethylide **4** and the results are reported herein.

The X-ray structure investigation[12] of **4**[13,14] revealed the presence of two independent molecules **4a** and **4b** (Fig. 1) in the unit cell whose relevant structural data are given in Table 1.

In order to study the presence of negative hyperconjugation theoretical B3LYP/6-31G** calculations[15] of **4** and also those of the *N*-(dichlorophosphino-ethoxycarbonylmethyl)-2-ethylpyridinium ion **5** (Fig. 2), in which negative hyperconjugation would be absent, have been carried out. Selected calculated bond lengths and angles of **4** and **5** are given in Table 1.

The calculated bond lengths and angles of **4** compare well to those obtained from the X-ray structure investigation, except that the calculations give slightly longer P–Cl bond lengths (deviation +4.88–5.41 pm). The most characteristic features of the molecular structure are a planar arrangement around the ylidic carbon atom, C1/C3 (the sum of the angles being ~360°) as observed in other pyridinium ylides,[16,17] and a pyramidal coordination of the phosphorus atom. The conformation adopted by the dichlorophosphino moiety with respect to the rest of the molecule indicates that the phosphorus lone pair is oriented orthogonally to the p_z orbital of the ylidic carbon atom thus making their interaction minimal.

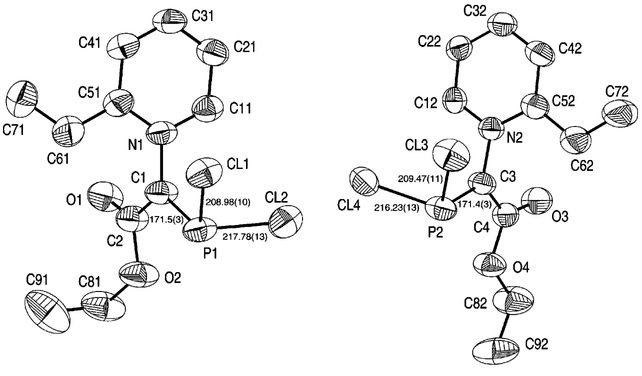
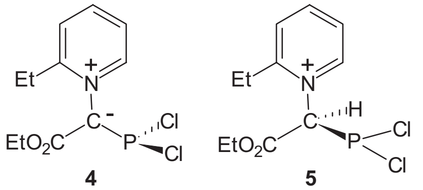


Figure 1. ORTEP view of the two independent molecules (**4a** and **4b**) of the ylide **4** in the crystal. Displacement ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity. P, C and P, Cl bond lengths in pm.



4 **5**

Figure 2.

The existence of negative hyperconjugation in a particular conformer is manifested not only by the lowering of its potential energy relative to other conformers, but also by charge transfer and bond elongation.[4–6] Thus, both P1–Cl1 (P2–Cl3) and P1–Cl2 (P2–Cl4) in **4** are longer than in the ion **5**, although elongation of P1–Cl2 (P2–Cl4) is much more pronounced as the bond stands roughly perpendicular to the plane of the ylidic carbon (dihedral angles 101.2(3)° in **4a** and −109.5(2)° in **4b**) and hence is almost parallel to its p_z orbital thereby allowing transfer of the ylidic charge to the $\sigma^*_{\text{P–Cl2}}$ orbital more effectively. The shorter P–Cl bond involves the chlorine atom lying almost in the plane of the ylidic carbon atom. In the structure there are no intermolecular distances shorter than the sum of the van der Waals radii. The observed conformation of the PCl_2 group as well as the presence of two different P–Cl bond lengths are therefore to be attributed mainly to hyperconjugation effects. Furthermore, as a consequence of the transfer of the ylidic charge to the $\sigma^*_{\text{P–Cl2}}$ orbital, the C–P bond in **4** becomes shorter than in the pyridinium ion **5**. The negative charges on Cl1 (−0.275) and Cl2 (−0.328) in **4** are larger than in **5** (−0.138 and −0.116, respectively), confirming the transfer of the ylidic charge into the $\sigma^*_{\text{P–Cl}}$ orbitals of the former.

In covalent bis(pyridinium ylidyl)chlorophosphines, transfer of the negative charge from two ylidyl moieties into the lone $\sigma^*_{\text{P–Cl}}$ orbital is sufficient to eliminate Cl^- generating ionic **2**. Thus, preferential disproportionation of **1** and subsequent ionization of the resulting bis(pyridinium ylidyl)chlorophosphines can be rationalized by invoking n→σ* negative hyperconjugation in these species.

Table 1. Selected bond lengths and angles in **4** and **5**

	Bond lengths (pm)			Bond angles (°)			Torsion angles (°)	
	P1–Cl1 P2–Cl3	P1–Cl2 P2–Cl4	P1–C1 P2–C3	P1–C1–N1 P2–C3–N2	P1–C1–C2 P2–C3–C4	C2–C1–N1 C4–C3–N2	Cl1–P1–C1–C2 Cl3–P2–C3–C4	Cl2–P1–C1–C2 Cl4–P2–C3–C4
4a X-ray	208.98(10)	217.78(13)	171.5(3)	123.05(19)	121.3(2)	115.3(2)	−159.6(3)	101.2(3)
4b X-ray	209.47(11)	216.23(13)	171.4(3)	123.31(19)	121.8(2)	114.6(2)	153.3(2)	−109.5(2)
4a B3LYP/6-31G**	213.86	223.19	175.0	124.40	120.08	115.08	−157.36	102.56
5 B3LYP/6-31G**	206.79	208.37	194.0	108.21	116.82	110.86	78.73	−26.65

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