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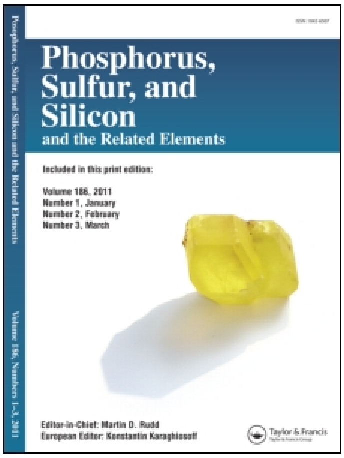

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Bonding in Cationic Phosphine Imines

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BONDING IN CATIONIC PHOSPHINE IMINES

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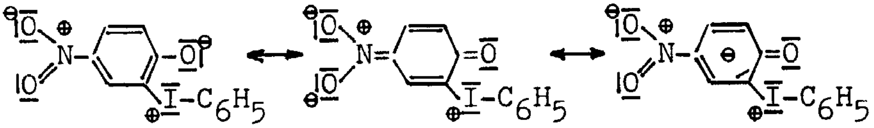
Abstract ^1H NMR spectra of pyridinium salts bearing a phosphine imine substituent in the 2-position reveal the formation of contact ion pairs. The high anion sensitivity of protons next to the pyridinium nitrogen and the phosphorus shows that these heteroatoms are both cationic centres. Hence, the classical all-octet formula A provides a better description of the cation than the alternative formulae B - D.

Chemists are used to describe their compounds by formulae (and corresponding names), preferentially one compound by one formula and one name. For mesomeric systems, more than one formula (and more than one name) is available, and the restriction to use only one of them necessitates a decision which to choose. Out of several, the formula (and name) ought to be selected which is the best model for the compound. This is not always done. For example, in the alkyloxonium/ alkoxycarbenium system ($R\text{-}\overset{\oplus}{\underline{O}}{=}CR_2 \longleftrightarrow R\text{-}\overline{\underline{O}}\text{-}\overset{\oplus}{C}R_2$), there can hardly be a doubt that, in a linear combination within a valence bond calculation, the all-octet oxonium formula contributes much more than the sextet carbenium formula. Nevertheless, it is quite customary to call such cations carbenium ions[1], e.g. 1,3-dioxolan-2-ylium cations[2]. For the phenolate anion of a 4-nitrophenol bearing a phenyliodonio substituent in 2-position, the certainly highly unimportant iodonium

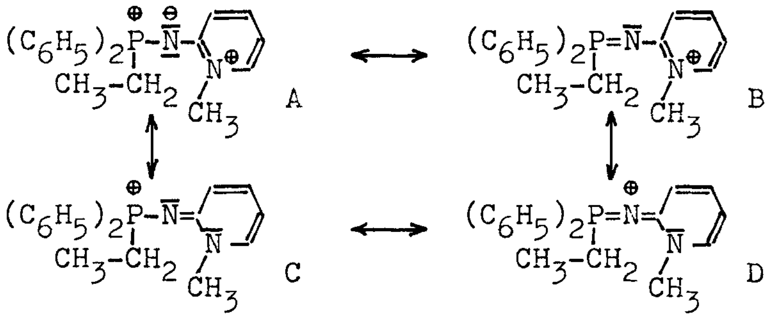


ylide formula was chosen in an attempt to make the readers believe that stable iodonium ylides exist[3]. For the bis-ylide of 1,1,3,3-tetraphenyl-2,4-bis(triphenylphosphonio)-1,3-diphosphetane, out of 14 mesomeric formulae, the two least satisfactory were chosen to construct the name 1,1,3,3-tetraphenyl-2,4-bis(triphenylphosphonio)-$1\lambda^5,3\lambda^5$-diphosphacyclobutadiene[4].

In order to do better, one is in need of a method which allows to judge which out of several mesomeric formulae is the dominating one. Since an adequate description of compounds is called for, this method should not be any sort of theoretical calculation, but direct measurement of properties with as little recourse to theory as possible. For charged species, we developed such a method.

Despite the large size of the ions, salts of organic cations and inorganic as well as organic anions form contact ion pairs in solvents of low polarity such as chloroform and methylene chloride. Due to Coulomb attraction, the charge centres approach each other as closely as possible, and the ^{1}H NMR spectra of the cations depend on the nature of the anions. In onium tetraphenylborates, the close approach of the boron to the onium centre causes protons in its vicinity to come into a position above one of the phenyl rings of the anions, and particularly great signal displacements to higher field are observed. This effect decreases quickly with increasing distance of the protons from the onium centre so that protons in an α-position can easily be reckognized. A large body of data shows that the anion associates always with the centre of positive charge, even in those cases in which the cation contains a neutral, but highly electronegative substituent[5]. This behaviour, then, allows to decide which atom within a cation carries the positive charge and, hence, which is the "best" formula for a mesomeric (or allegedly mesomeric) system.

For neutral species such as phosphine imines, the method is not directly applicable. However, an auxiliary positive charge removes the shortcoming. As an example of this extension of our method, we investigated a phosphine imine substituted pyridinium cation:



For this, four mesomeric formulae (A - D) come into immediate consideration. Formula D has its counterpart in the common name bis(triphenylphosphine)immonium cation[6] (hence, the formula $(C_6H_5)_3P=\overset{\oplus}{N}=P(C_6H_5)_3$) for the cationic species $\langle[(C_6H_5)_3P]_2N\rangle^{\oplus}$.

In $CDCl_3$, the following anion effects have been measured: $N-CH_3$: $\delta = 4.18$ ($I^{\ominus}$), 4.09 ($I_3^{\ominus}$), 3.26 ppm ($B(C_6H_5)_4^{\ominus}$); $P-CH_2$: $\delta = 2.91$ ($I^{\ominus}$), 2.80 ($I_3^{\ominus}$), 2.19 ppm ($B(C_6H_5)_4^{\ominus}$); $P-CH_2-C\underline{H}_3$: $\delta = 1.17$ ($I^{\ominus}$), 1.24 ($I_3^{\ominus}$), 0.94 ppm ($B(C_6H_5)_4^{\ominus}$). They are in complete agreement with formula A. The $B(C_6H_5)_4^{\ominus}$ anion causes an upfield shift of the $P-CH_2$ and $N-CH_3$ signals whose magnitude is incompatible with formula D. It has about half the magnitude observed for simple P-ethyl phosphonium and

N-alkyl pyridinium salts and is, hence, in accord with the anion spending half of its time close to P and the other half at the pyridinium N. The upfield shift of the P-CH_2 and N-CH_3 signals and the downfield shift for the P-CH_2-$C\underline{H}_3$ signal caused by $I_3^{\ominus}$ are typical for protons in an α/β position with respect to the onium centre and thus corroborate the conclusion that both P and pyridinium N are centres of positive charge. Comparative data of dialkylamino-pyridinium salts[7] disfavour a predominating mesomerism of formulae B and C (as an alternative model for the two onium centres). Formula A, therefore, represents the only satisfactory description of the cation for which, then, any $p_\pi d_\pi$ double bond formulae with and without aromatic pyridinium ring should be avoided. Per analogy, this result has consequences for neutral phosphine imines and related species.

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